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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION

COMMISSION ON PHYSICAL ORGANIC CHEMISTRY*

GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY

(Recommendations 1982)

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*Membership of the Commission during the period (1976-1982) in which this Glossary was prepared was as follows:

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LIST OF GENERAL SYMBOLS

A	pre-exponential factor in Arrhenius equation (see *energy of activation*).
a	parameter in empirical expression for rate constant (see *enthalpy of activation*)
α	order of reaction with respect to reactant A (see *order of reaction*).
b	parameter in empirical expression for rate constant (see *enthalpy of activation*).
β	order of reaction with respect to reactant B (see *order of reaction*).
C_p	heat capacity (at constant pressure).
c	parameter in empirical expression for rate constant (see *enthalpy of activation*.
d	parameter in empirical expression for rate constant (see *enthalpy of activation*).
e	base of natural logarithms (e = 2.718).
E_a	energy of activation (see *energy of activation*).
G	Gibbs energy.
H	enthalpy.
h	Planck constant.
K	Kelvin (unit of temperature).
K	equilibrium constant.
k	rate constant (see *order of reaction*).
$\boldsymbol{k}$	Boltzmann constant.
lg	decadic logarithm.
ln	natural logarithm.
λ	wavelength.
ν	frequency.
$\ominus$	(superscript) relating to thermodynamic standard state.
p	pressure.
R	gas constant.
S	entropy.
s	second (unit of time).
Σ	summation.
T	temperature.
t	time.
v	rate of reaction (see *rate of reaction*).
$\ddagger$	(superscript) relating to transition state).
$\longleftrightarrow$	See *delocalization*.
[X]	concentration of X.

INTRODUCTION TO 1982 REVISION

At its first set of meetings, in September 1976, the recently constituted IUPAC Commission III.2 (Physical Organic Chemistry) initiated a project on the definition of terms used in Physical Organic Chemistry. It was noted that the formulation of novel scientific concepts was often arbitrary and unclear, and that scientific communication between physical organic chemists had been hampered by disagreement on the meaning of important terms. It was agreed that the progress of the subject could be helped by the compilation of a Glossary of terms with the co-operation of active research workers, authors, and teachers of the subject. The provisional version of the Glossary was published in 1979, and a historical account of procedure and progress up to that stage was outlined in the provisional publication, IUPAC PHYSICAL ORGANIC GLOSSARY (1979).

The present revision incorporates modifications agreed by the Commission at its meetings during the period 1979-1982, partly in response to comments received since the provisional publication.

Many people have generously helped, either by the formulation of draft definitions or by constructive criticism. In addition to the contributors mentioned in the provisional publication (many of whom have given further assistance) the following have contributed to this Revision:

Ng. T. Anh
J. A. Berson
J. H. Callomon
A. C. Day
I. Fleming
R. Hoffmann
P. Laszlo
M. P. Melrose
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O. Weissbach

However, inclusion in this list should not be taken as an individual's endorsement of the Glossary or resposibility for its remaining flaws. Apologies are offered in advance for any inadvertent omission of the names of contributors. My most sincere thanks also go to Miss Kathleen Harris who typed most of the text and especially to Miss Lesley Dinsdale without whose competent and dedicated help the production of this Report in its final form could not have been completed.

The following criteria were adopted for the inclusion of a term, but it is inevitable that their application may be found to be somewhat subjective:

1. A term must be in current use by several independent authors or have been in such use until recently.

2. It must have a meaning in Physical Organic Chemistry that is either not given in non-scientific dictionaries or in standard text-books of Chemistry or which significantly differs from the definition given in such reference works. Alternatively, there must be some ambiguity or uncertainty in its usage by physical organic chemists or fairly widespread ignorance of its meaning. The terms included here are generally treated inadequately in terminology reports of other IUPAC commissions. The most relevant of these reports are cited in the bibliography at the end of the Glossary; their contents are intended to be complemented (and not repeated) by the present Glossary. Attention is particulary drawn to IUPAC MANUAL APPENDIX V (1981), the preparation of which overlapped the later stages of work on the present Glossary: the definitions in the two documents are intended to be mutually

consistent. More recently, Commission III.3 (Organic Photochemistry) has begun work on the definition of terms used in photochemistry. Stereochemical terminology is currently under consideration by a working party jointly set up by Commissions III.2 and III.1.

The aim of the Glossary is to provide guidance on physical-organic chemical terminology with a view to achieving a far-reaching consensus on the definition of useful terms and the abandonment of unsatisfactory ones. The Commission is anxious to emphasize that it cannot (and would not wish to) impose rules or restrictions, which might hinder rather than help the precise formulation of new ideas.

As a matter of policy, named reactions (such as Diels-Alder) and symbolic representations of mechanisms (S_N1, etc.) have been excluded. These topics are currently under consideration by other working parties of the Commission.

Generally speaking, operational definitions were preferred to definitions couched in terms of theoretical models. We have tried to avoid taking sides on issues of scientific, as distinct from semantic, disagreement. Similarly, we hope not to have incorrectly attributed named equations. With this kind of danger in mind, we have only sparingly inserted references to individual authors, either to indicate the origin of a term or to direct attention to a helpful, more elaborate discussion of a concept. It was felt justifiable to exclude named equations and effects that, at the time of compilation of this edition of the Glossary, would not normally be found in the literature without a source reference.

A cross (+) against the title of an entry implies that we recommend discontinuation of its use.

The arrangement of entries is simply alphabetical. *Italicized* words in the body of a definition, as well as those cited at the end, point to relevant cross-references; *underlining* implies that the cross-reference is of special importance to the entry in which it occurs. The appearance of a term in quotation marks in the body of a definition indicates that no further information will be found under that heading. A list of symbols used in the Glossary (and not explicitly defined each time they occur) is provided.

In accordance with general practice Kekulé structures are normally used in this Glossary to represent the formulae of aromatic compounds. A single hexagon with a full circle inside is used in cases where delocalization is emphasized.

With a progressively evolving subject it is, of course, impossible to produce a set of definitions of indefinitely lasting validity. The revision of this Glossary of terms is therefore expected to remain a continuing responsibility of the Commission.

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May 1983

ABSTRACTION REACTION

A chemical reaction, the main feature of which is the *bimolecular* removal of an atom (neutral or charged) from a *molecular entity*. For example,

$CH_3COCH_3 + CH_3CO_2^- \longrightarrow (CH_2COCH_3)^- + CH_3CO_2H$

(proton abstraction from acetone)

$CH_4 + Cl\cdot \longrightarrow H_3C\cdot + HCl$

(hydrogen abstraction from methane)

ACID

See *Brønsted acid, Lewis acid, hard acid.*

ACIDITY

(1) Of a compound:

For *Brønsted acids* it means the tendency of the compound to act as a proton donor. It can be quantitatively expressed by the acid dissociation constant of the compound in water or in some other specified medium. For *Lewis acids* it relates to the dissociation constants of *Lewis adducts.*

(2) Of a medium:

The use of the term is mainly restricted to *Brønsted acids*, when it means the tendency of the medium to protonate a specified reference base. It is quantitatively expressed by the appropriate *acidity function.*

ACIDITY FUNCTION

Any quantitative scale that measures the thermodynamic proton-donating or -accepting ability of a solvent system or a closely related thermodynamic property, such as the tendency of the *lyate ion* of the solvent system to form *Lewis adducts.* (The term "basicity function" is not in common use in connection with basic solutions.) Acidity functions are not unique properties of the solvent system alone but depend on the solute (or family of closely related solutes) with respect to which the thermodynamic tendency is measured.

Commonly used acidity functions refer to concentrated acidic or basic solutions. Acidity functions are usually established over a range of compositions of such a system by spectrophotometric or nmr measurements of the degree of protonation (or Lewis adduct formation) for the members of a series of structurally similar indicator bases (or acids) of different strengths: the best known of these functions is the Hammett acidity function H_0 (for uncharged indicator bases that are primary aromatic amines). For detailed information on other acidity functions, on the evaluation of acidity functions, and on the limitations of the concept, see ROCHESTER (1970).

HAMMETT (1940,1970).

ACTIVATED COMPLEX

See *transition state*.

ACTIVATION ENERGY

See *energy of activation*.

ADDITION

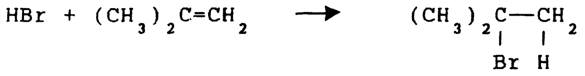
(1) Short for *addition reaction.*

(2) Loosely, the formation of an *adduct.* (For an example, see *Lewis acid.)*

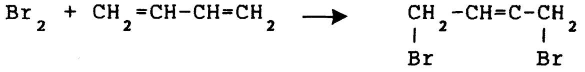
(3) Loosely, any *association* or *attachment.*

ADDITION REACTION

A *chemical reaction* resulting in only a single reaction product from two or three reacting *molecular entities*, with formation of two chemical *bonds* and a net reduction in bond multiplicity in one of the reactants. The reverse process is called an "elimination reaction". For example:

(a)  (1,2-addition)

$$HBr + (CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_2\underset{Br}{C}{-}\underset{H}{CH_2}$$

(b)  (1,4-addition)

$$Br_2 + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \underset{Br}{CH_2}{-}CH{=}C{-}\underset{Br}{CH_2}$$

See also *addition*, *α-addition*, *cheletropic*, *cycloaddition*.

ADDITIVITY PRINCIPLE

The hypothesis that each of several structural features of a *molecular entity* makes a separate and additive contribution to a property of the substance concerned. More specifically, it is the hypothesis that each of several *substituent groups* in a parent molecule makes a separate and additive contribution to the standard Gibbs energy change (or *Gibbs energy of activation*) corresponding to a particular equilibrium (or reaction rate). For further information and examples see BENSON (1976).

ADDUCT

A new *chemical species* AB, each *molecular entity* of which is formed by direct combination of two separate molecular entities A and B in such a way that there is no change in *connectivity* of atoms within the moieties A and B. Stoichiometries other than 1:1 are also possible. An "intramolecular adduct" can be formed when A and B are *groups* contained within the same molecular entity.

This is a general term which, whenever appropriate, should be used in preference to the less explicit term *complex*. For examples see *Lewis adduct*, *Meisenheimer adduct*, *π-adduct*.

A-FACTOR

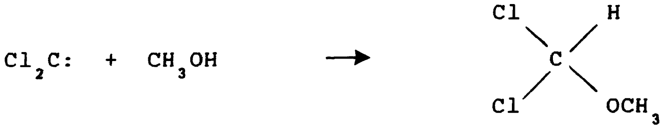
See *energy of activation*.

ALCOHOLYSIS

See *solvolysis*.

α-ADDITION *(alpha-Addition)*

A *chemical reaction* resulting in a single reaction product from two or three reacting *chemical species*, with formation of two new chemical *bonds* to the same atom in one of the reactant *molecular entities*. For example:



(This particular example can also be viewed as an *insertion reaction*.) In inorganic chemistry such α-addition reactions, generally to a metallic central atom, are known as "oxidative additions".

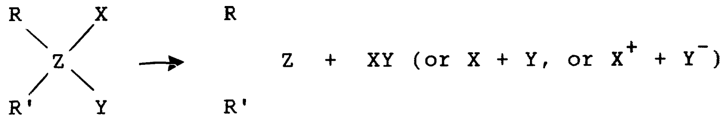
α-Addition is the reverse of *α-elimination*.

α-EFFECT *(alpha-Effect)*

The enhancement of *nucleophilicity* that may be found when the atom adjacent to a *nucleophilic* site bears a lone pair of electrons. For example, in some situations HO_2^- is more nucleophilic than HO^-

α-ELIMINATION (alpha-Elimination)

A reaction of the general type



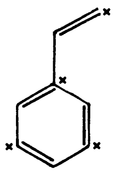
$$R(R')Z(X)(Y) \longrightarrow R(R')Z + XY \text{ (or } X + Y\text{, or } X^+ + Y^-\text{)}$$

where the central atom Z is most commonly carbon. The reverse reaction is called *α-addition.*

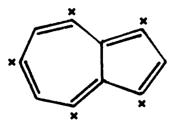
ALTERNANT

A *conjugated system* is termed alternant if its atoms can be divided into two sets such that no atom of one set is directly linked to any other atom of the same set.

Example of alternant system:



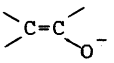
Example of non-alternant system:



(Two atoms of the unstarred set are directly linked.)

AMBIDENT

A description applied to a *chemical species* whose *molecular entities* each possess two alternative and strongly interacting distinguishable reactive centres to either of which a *bond* may be made in a reaction: the centres must be connected in such a way that reaction at either site stops or greatly retards subsequent attack at the second site. The term is most commonly applied to *conjugated nucleophiles*, for example the enolate ion



$$>C=C(-)O^-$$

(which may react with *electrophiles* either at the β-carbon atom or at oxygen) or γ-pyridones, and also to the vicinally ambident cyanide ion, nitrite ion, and unsymmetrical hydrazines.

Molecular entities containing two non-interacting (or feebly interacting) reactive centres, such as the dianions of dicarboxylic acids, are not generally considered to be ambident and are better described as "bifunctional".

The Latin root of the word implies two reactive centres, but the term has in the past also incorrectly been applied to chemical species with more than two reactive centres. For such species the existing term "polydent" (or, better, "multident") is more appropriate.

See GOMPPER (1964); SMITH and DeWALL (1977).

AMPHIPROTIC (SOLVENT)

Both *protogenic* and *protophilic*; for example, H_2O and CH_3OH.

ANCHIMERIC ASSISTANCE

See *neighbouring-group participation.*

ANIONOTROPIC REARRANGEMENT (or Anionotropy)

See *tautomerism.*

ANION RADICAL

See *radical ion.*

ANTARAFACIAL, SUPRAFACIAL

When a part of a molecule ("molecular fragment") undergoes two changes in bonding (*bond*-making or bond-breaking), either to a common centre or to two separate centres, external to itself, these bonding changes may be related in one of two spatially distinct ways. These are designated as "antarafacial" if opposite faces of the molecular fragment are involved, and "suprafacial" if both changes occur at the same face. The concept of "face" is clear from the diagrams in the cases of planar (or approximately planar) frameworks with isolated or interacting p-orbitals (Figs. a and b on the next page). The terms antarafacial and suprafacial are, however, also employed in cases in which the essential part of the molecular fragment undergoing changes in bonding comprises two atoms linked only by a σ-bond. In these cases it is convenient to refer to the phases of the local σ-bonding orbital: occurrence of the two bonding changes at sites of like orbital phase is regarded as suprafacial, whereas that at two sites of opposite phase is antarafacial. The possibilities are shown for C-C and C-H σ-bonds in Figs. c and d. There may be two distinct and alternative *stereochemical* outcomes of a suprafacial process involving a σ-bond between saturated carbon atoms, i.e. either retention or inversion at both centres. The antarafacial process results in inversion at one centre and retention at the second.

For examples of the use of these terms see *cycloaddition, sigmatropic reaction.*

See also *anti, sigma,pi.*

ANTI

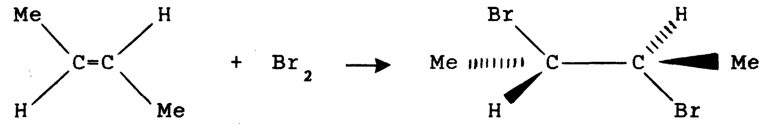
In the representation of *stereochemical* relationships "anti" means "on opposite sides" of a reference plane, in contrast to "syn" which means "on the same side", as in the following examples.

(1) Two substituents attached to atoms joined by a single *bond* are anti if the torsion angle (dihedral angle) between the bonds to the substituents is greater than 90°, or syn if it is less than 90°. (A further distinction is made between antiperiplanar, synperiplanar, anticlinal and synclinal.)

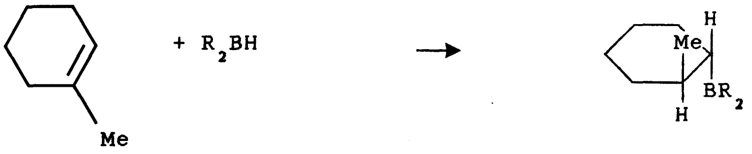
KLYNE and PRELOG (1960); IUPAC ORGANIC RULES (1979).

(2) Addition to a carbon-carbon double bond:

anti:

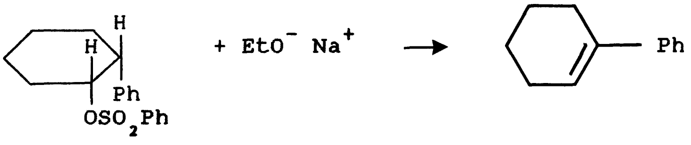


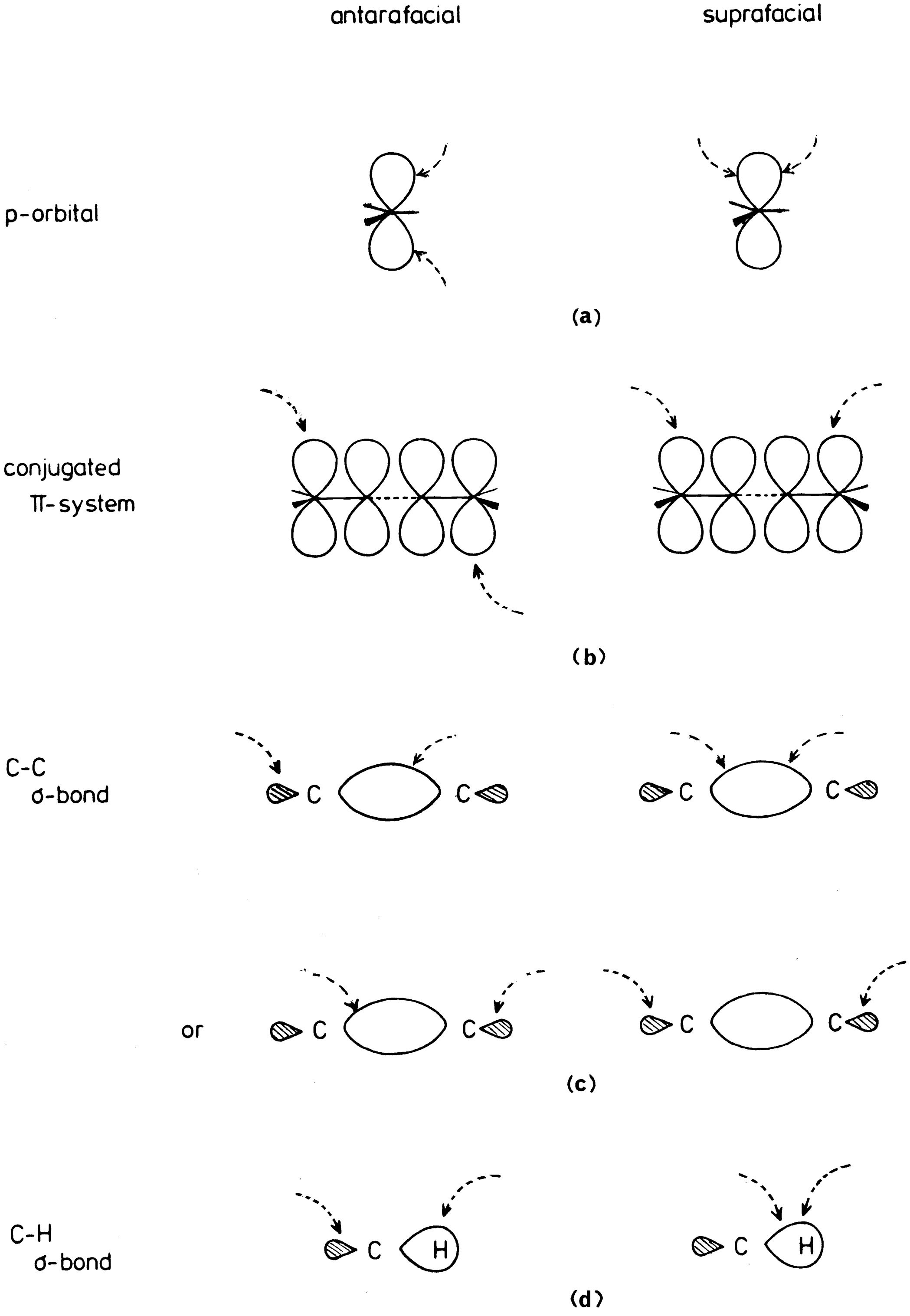
syn:



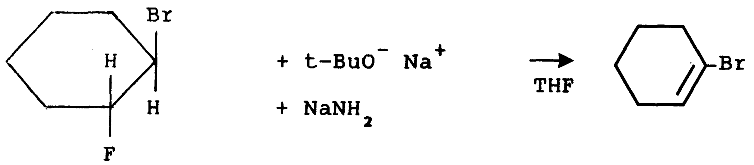
(3) Olefin-forming elimination:

anti:




antarafacial
suprafacial
p-orbital
(a)
conjugated π-system
(b)
C-C σ-bond
C
C
or
(c)
C-H σ-bond
C
H
(d)

syn:



+(4) In the older literature the terms anti and syn were used to designate stereoisomers of oximes and related compounds. That usage was superseded by the terms "trans" and "cis" or (*E*) and (*Z*), respectively.

IUPAC ORGANIC RULES (1979)

In the examples described under (2) and (3) anti processes are always *antarafacial* and syn processes are suprafacial.

ANTIAROMATIC

See *aromatic.*

ANTI-MARKOVNIKOV ADDITION

See *Markovnikov rule.*

APROTIC (SOLVENT)

Neither *protogenic* nor *protophilic* (in a given situation). (With extremely strong *Brønsted acids* or bases, solvents that are normally aprotic may accept or lose a proton. For example, acetonitrile is in most instances an aprotic solvent, but it is protophilic in the presence of concentrated sulphuric acid and protogenic in the presence of potassium tert-butoxide. Similar considerations apply to benzene, trichloromethane, etc.).

See also *dipolar aprotic solvent.*

AQUATION

The incorporation of one or more integral molecules of water into another species with or without displacement of one or more other atoms or *groups*. For example, the substitution of water into the inner *ligand* sphere of an inorganic *complex* is an aquation reaction.

See also *hydration.*

AROMATIC

(1) In the traditional sense, "having a chemistry typified by benzene".

(2) A cyclically *conjugated molecular entity* with a stability (due to *delocalization*) significantly greater than that of a hypothetical classical structure (e.g. a *Kekulé structure*) is said to possess aromatic character. If the structure is of higher energy (less stable) than such a hypothetical classical structure, the molecular entity is "antiaromatic".

See also *Hückel (4n + 2)rule*, *Möbius aromaticity.* See ATKINS (1974).

(3) The terms aromatic and antiaromatic have been extended to describe the stabilization or destabilizaton of *transition states* of *pericyclic reactions*. The hypothetical reference structure is here less clearly identified, and use of the terms is based on application of the *Hückel (4n + 2) rule* and on consideration of the topology of orbital overlap in the transition state. Reactions involving antiaromatic transition states proceed much less easily (if at all) than those involving aromatic transition states.

DEWAR (1971); ZIMMERMAN (1971).

ARRHENIUS ENERGY OF ACTIVATION

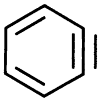
See *energy of activation.*

ARRHENIUS EQUATION

See *energy of activation.*

ARYNE

A (usually *transient*) *chemical species* characterized by the grouping (of carbon atoms):



This simplest aryne is called "benzyne" (C_6H_4).

ASSOCIATION

The assembling of separate *molecular entities* into any aggregate, especially of oppositely charged free ions into *ion pairs* or larger and not necessarily well-defined clusters of ions held together by electrostatic attraction. The term signifies the reverse of *dissociation*, but is not commonly used for the formation of definite *adducts* by *colligation* or *co-ordination.*

ASYMMETRIC INDUCTION

The formation of a reaction product with a new chiral centre (and containing unequal amounts of the consequently generated stereoisomeric forms of the product) from a single precursor in which that centre was prochiral. Such a step requires the use of an optically active material (reagent, solvent, *catalyst*, enzyme, etc.) or an optically active precursor (in which case the chiral forms that are produced in unequal amounts are diastereoisomers).

Asymmetric induction in combination with separation processes may constitute an "asymmetric synthesis".

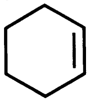
For the definition of the terms "chiral", "diastereoisomer", "enantiomer", "prochiral", "stereoisomeric", see IUPAC ORGANIC STEREOCHEMISTRY RULES (1974).

ATTACHMENT

A *transformation* by which one *molecular entity* (the *substrate*) is converted into another by the formation of one (and only one) two-centre *bond* between the substrate and another molecular entity and which involves no other changes in *connectivity* in the substrate. For example, the formation of an acyl cation by attachment of carbon monoxide to a *carbenium ion* (R^+):

$$R^+ + CO \longrightarrow (RCO)^+$$

The product of an attachment may also be the *adduct* of the two reactants, but not all adducts can be represented as the products of an attachment. (For example, the Diels-Alder *cycloaddition*

$CH_2{=}CH{-}CH{=}CH_2 + H_2C{=}CH_2 \longrightarrow$ 

results in an adduct of 1,4-butadiene and ethene, but the reaction cannot be described as an attachment since bonds are formed between more than two centres).

See also *electron attachment.*

AUTOCATALYTIC REACTION

A *chemical reaction* in which a product (or a *reaction intermediate*) also functions as a *catalyst.* In such a reaction the observed *rate of reaction* is often found to increase with time from its initial value.

See *order of reaction.*

AUTOPROTOLYSIS

A *proton transfer* reaction between two identical molecules (usually a solvent), one acting as a *Brønsted acid* and the other as a *Brønsted base*. For example:

$$2H_2O \longrightarrow H_3O^+ + OH^-$$

AUTOPROTOLYSIS CONSTANT

The product of the activities (or, more approximately, concentrations) of the species produced as the result of *autoprotolysis*. For solvents in which no other ionization processes are significant the term is synonymous with "ionic product" or "self-dissociation constant". The autoprotolysis constant for water, K_w, is equal to the product of activities

$$(H_3O^+)(OH^-) = 1.0 \times 10^{-14}\ \mathrm{mol}^2\ \mathrm{dm}^{-6} \text{ at } 25°\mathrm{C}.$$

+ AZACARBENE

See *nitrene*.

+ AZENE

See *nitrene*.

+ AZYLENE

See *nitrene*.

BASE

See *Brønsted base, hard base, Lewis base.*

BASICITY FUNCTION

See *acidity function.*

BATHOCHROMIC

The term refers to any effect on a *molecular entity* (by a *substituent group,* solvent, etc.) that causes its electronic absorption or emission spectrum to be shifted to longer wave-lengths. The associated spectral shift is often referred to as a "bathochromic shift" or, somewhat misleadingly, as a "red-shift".

The opposite effect is called "hypsochromic" and the corresponding spectral shift to shorter wavelengths ("hypsochromic shift") is, again somewhat misleadingly, widely known as a "blue-shift".

BENZYNE

See *aryne*.

BIFUNCTIONAL CATALYSIS

Catalysis by a bifunctional *chemical species* involving a *mechanism* in which both functional groups are implicated in the *rate-limiting step*, so that the corresponding *catalytic coefficient* is larger than that expected for catalysis by chemical species containing only one of these functional groups.

The term should not be used to describe the *concerted* action of two different catalysts ("concerted catalysis").

BIMOLECULAR

See *molecularity.*

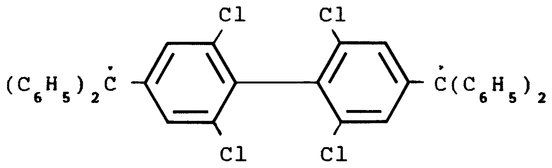
BINDING SITE

A specific region (or atom) in a *molecular entity* that is capable of entering into a stabilizing interaction with another molecular entity. An example of such an interaction is that of an active site in an enzyme with its *substrate*. Typical forms of interaction are by *hydrogen bonding, co-ordination,* and *ion pair* formation.

Two binding sites in different molecular entities are said to be complementary if their interaction is stabilizing.

BIRADICAL

A *molecular entity* in an electronic state described by a formula or by a combination of *contributing structures*) containing two unpaired electrons in atomic orbitals on different atoms. (The term embraces both singlet and triplet species.) For example:



This term is synonymous with "diradical".

See also *carbene*.

BODENSTEIN APPROXIMATION

See *steady state*.

BOND (COVALENT BOND)

A region of relatively high electron density between atoms which arises at least partly from sharing of electrons and gives rise to an attractive force and characteristic internuclear distance between the atoms. For example: the C-H bond in hydrocarbons. The term "bond" should be avoided in describing the coulombic attraction between ions of opposite charge, as in crystals, or in describing *van der Waals forces* or *hydrophobic interactions*.

See also *co-ordination, dipolar bond, hydrogen bond, multi-centre bond*.

BOND DISSOCIATION

See *heterolysis, homolysis*.

(In ordinary usage the term refers to homolysis only.)

BOND DISSOCIATION ENERGY, D

The enthalpy (per mole) required to break a given *bond* of some specific *molecular entity* by *homolysis*, e.g. for $CH_4 \rightarrow H_3C\cdot + H\cdot$, symbolized as $D(CH_3\text{-}H)$; (cf. *heterolytic bond dissociation energy*.)

See also *bond energy*.

BOND ENERGY (Mean bond energy)

The average value of the gas-phase *bond dissociation energies* (usually at a temperature of 298K) for all *bonds* of the same type within the same *molecular entity*. The mean C-H bond energy for methane, for example, is one-fourth the enthalpy of reaction for $CH_4(g) \rightarrow C(g) + 4H(g)$.

Tabulated bond energies are generally values of mean bond energies averaged over a number of selected typical *chemical species* containing that type of bond.

BOND MIGRATION

See *migration*.

BOND NUMBER

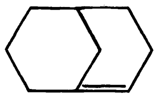
The number of electron-pair *bonds* between two nuclei in any given *Lewis formula*. For example, the bond number between the carbon atoms in ethylene (ethene) is two and between the carbon and hydrogen atoms it is one.

BOND ORDER

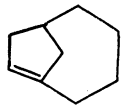
A theoretical index of the degree of bonding between two atoms relative to that for a normal single bond, i.e., the bond provided by one localized electron pair. (In the valence bond theory it is a weighted average of the *bond numbers* between the respective atoms in the *contributing structures*. In molecular-orbital theory it is calculated from the weights of the atomic orbitals in each of the occupied *molecular orbitals*). For example, in valence-bond theory the bond order between adjacent carbon atoms in benzene is 1.5; in molecular-orbital theory it is 1.67.

BREDT'S RULE

A double bond cannot be placed with one terminus at the bridgehead of a bridged ring system unless the rings are large enough to accommodate the double bond without excessive strain. This qualitative rule, originally formulated by J. Bredt, has been quantified by the proposal that the sum of the numbers of atoms (*S*-number) in the three bridges between the two bridgeheads of a bicyclic system determines whether that system can accommodate a bridgehead double bond. Compounds with *S*>7 with a double bond at the bridgehead of a bicyclic system have been isolated: e.g.



Bicyclo[3.3.1.]non-1-ene
(*S*=7)

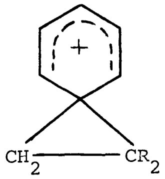


Bicyclo[4.2.1]non-1(8)-ene
(*S*=7)

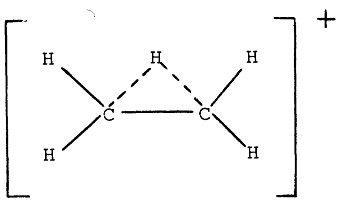
BREDT, THOUET and SCHMITZ (1924); see also FAWCETT (1950), WISEMAN (1967).

BRIDGED CARBOCATION

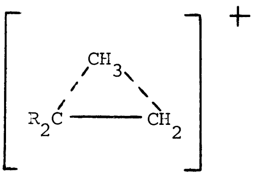
A carbocation (real or hypothetical) in which there are two (or more) carbon atoms that could in alternative *Lewis formulae* be designated as *carbenium centres* but which is instead represented by a structure in which a *group* (a hydrogen atom or a hydrocarbon residue, possibly with substituents in non-involved positions) bridges these potential carbenium centres. The bridging group thereby delocalizes the cationic charge. One may distinguish "electron-sufficient bridged carbocations" and "electron-deficient bridged carbocations". Examples of the former are phenyl-bridged ions (for which the trivial name "phenonium ion" has been used), such as (A). These ions are straightforwardly classified as *carbenium ions*. The latter type of ions necessarily involves three-centre bonding. Structures (C) and (D) contain five-co-ordinate carbon atoms. The "hydrogen-bridged carbocation" (B) contains a two-co-ordinate hydrogen atom. (The formulae are intended for purposes of definition only. Their inclusion has no bearing on the question whether or not they correspond to real *chemical species*).



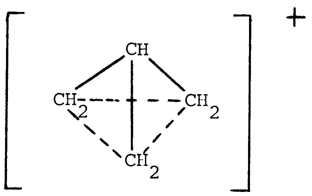
(A)



(B)



(C)



(D)

See also *carbonium ion, multi-centre bonding, neighbouring-group participation.*

BRØNSTED ACID (Brönsted acid)

A *molecular entity* capable of donating a proton to a base, (i.e. a "proton donor") or the corresponding *chemical species*. For example: H_2O, H_3O^+, CH_3CO_2H, H_2SO_4, HSO_4^-.

See also *conjugate acid-base pair.*

BRØNSTED BASE (Brönsted base)

A *molecular entity* capable of accepting a proton from an acid (i.e. a "proton acceptor") or the corresponding *chemical species*. For example: OH^-, H_2O, $CH_3CO_2^-$, HSO_4^-, SO_4^{2-}.

See also *conjugate acid-base pair.*

BRØNSTED CATALYSIS LAW (Brönsted catalysis law)

See *Brønsted relation.*

BRØNSTED EXPONENT (Brönsted exponent)

See *Brønsted relation.*

BRØNSTED RELATION (Brönsted relation)

The name applies to either of the equations

$$k_{HA}/p = G(K_{HA}q/p)^{\alpha}$$

and

$$k_{A}/q = G(K_{HA}q/p)^{-\beta}$$

where α, β and G are constant for a given reaction series, (α and β are called Brønsted exponents), k_{HA} and k_A are *catalytic coefficients* (or rate coefficients of reactions whose rates depend on the concentrations of HA and/or of A^-), K_{HA} is the acid dissociation constant of the acid HA, p is the number of equivalent acidic protons in the acid HA, and q is the number of equivalent basic sites in its conjugate base A^-. The chosen values of p and q should always be specified. (The charge designations on HA and A^- are only illustrative.)

The Brønsted relation is often termed the "Brønsted *catalysis* law" (or the "Catalysis Law"). Although justifiable on historical grounds, this name is not recommended, since Brønsted relations are now known to apply to many uncatalysed reactions (such as simple *proton transfer reactions*).

See also *linear Gibbs energy relation*.

CAGE

An aggregate of molecules, generally in the condensed phase, that surrounds the fragments formed by thermal or photochemical dissociation of a precursor species. Because the cage hinders the separation of the fragments by diffusion, they may preferentially react with one another ("cage effect") but not necessarily to re-form the precursor species. For example,

$$\text{R-N=N-R} \xrightarrow{\Delta} [\text{R}\cdot + \text{N}\equiv\text{N} + \text{R}\cdot]_{\text{cage}} \longrightarrow \text{R-R} + \text{N}_2$$

See also *geminate recombination.*

CAGE COMPOUND

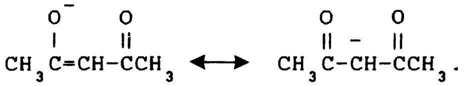
See *inclusion compound.*

CANONICAL FORM

See *contributing structure*.

CARBANION

Generic name for anions containing an even number of electrons and which have an unshared pair of electrons on a tervalent carbon atom (e.g. Cl_3C^- or $HC\equiv C^-$) or - if the ion is mesomeric (see *mesomerism*) - which have at least one *contributing structure* with an unshared pair of electrons on a tervalent carbon atom, for example,



$$CH_3\overset{O^-}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}CH_3 \longleftrightarrow CH_3\overset{O}{\overset{\|}{C}}-\overset{-}{C}H-\overset{O}{\overset{\|}{C}}CH_3.$$

See also *radical ion*.

CARBENE

Generic name for the species H_2C: and substitution derivatives thereof, containing an electrically neutral bivalent carbon atom with two nonbonding electrons. The nonbonding electrons may have antiparallel spins (singlet state) or parallel spins (triplet state).

(It is a generic term which is preferred to the alternative "methylene".)

See also *biradical*.

CARBENIUM CENTRE

The three-coordinate carbon atom in a *carbenium ion* on which the excess positive charge of the ion (other than that located on heteroatoms) may be considered to be largely concentrated i.e. which has the vacant p-orbital. (N.B.: It is not always possible to identify such an atom.)

CARBENIUM ION

A generic name for *carbocations*, real or hypothetical, that have at least one important *contributing structure* containing a tervalent carbon atom with a vacant p-orbital. (The name implies a protonated carbene or a substitution derivative thereof.)

The term was proposed as a replacement for the traditional usage of the name *carbonium ion*.

To avoid ambiguity, the name should not be used as the root for the systematic nomenclature of carbocations. The corresponding difficulty confused carbonium ion nomenclature for many years. For example, the term "ethyl carbonium ion" has at times been used to refer either (incorrectly) to $CH_3CH_2^+$ or (correctly according to older rules) to $CH_3CH_2CH_2^+$.

CARBOCATION

A cation containing an even number of electrons in which a significant portion of the excess positive charge is located on one or more carbon atoms. This is a general term embracing *carbenium ions*, all types of *carbonium ions*, *vinyl cations*, etc. Carbocations may be named by adding the word "cation" to the name of the corresponding *radical* [IUPAC ORGANIC RULES (1969), Rule C-83.1, alternative (*a*)]. Such names do not imply structure (e.g., whether three-co-ordinated or five-co-ordinated carbon atoms are present).

See also *bridged carbocation, radical ion.*

CARBONIUM ION

The term should for the present be avoided or at least used with great care since several incompatible usages are current. It is not acceptable as the root for the systematic nomenclature of *carbocations*.

1. In most of the existing literature the term is used in its traditional sense for what is here defined as *carbenium ion*.

2. A carbocation, real or hypothetical, that contains at least one five-co-ordinate carbon atom.

3. A carbocation, real or hypothetical, whose stucture cannot adequately be described by two-electron two-centre *bonds* only. (The structure may involve carbon atoms with a co-ordination number greater than five.)

CARBYNE

Generic name for the species $H\dot{C}:$ and substitution derivatives thereof (such as $EtO_2C-\dot{C}:$), containing an electrically neutral univalent carbon atom with three non-bonding electrons. Use of the alternative name "methylidyne" as a generic term is not recommended.

CATALYSIS

The action of a *catalyst*.

CATALYSIS LAW

See *Brønsted relation*.

CATALYST

A substance that participates in a particular *chemical reaction* and thereby increases its rate but without a net change in the amount of that substance in the system. At the molecular level, the catalyst is used and regenerated during each set of *microscopic chemical events* leading from a *molecular entity* of reactant to a molecular entity of product.

See also *autocatalytic reaction, bifunctional catalysis, catalytic coefficient, general acid catalysis, general base catalysis, intramolecular catalysis, micellar catalysis, Michaelis-Menten kinetics, phase-transfer catalysis, pseudo-catalysis, rate of reaction, specific catalysis.*

CATALYTIC COEFFICIENT

If the *rate of reaction* (v) of a reaction is expressible in the form

$$v = (k_0 + \sum k_i[C_i]^{n_i})\ [A]^{\alpha}[B]^{\beta}.....$$

where A, B,.... are reactants and C_i represents one of a set of *catalysts*, then the proportionality factor k_i is the catalytic coefficient of the particular catalyst C_i. Normally the partial *order of reaction* n_i with respect to a catalyst will be unity, so that k_i is an $(\alpha+\beta+...+1)$th order rate coefficient. The proportionality factor k_0 is the $(\alpha+\beta+...)$th order rate coefficient of the uncatalysed component of the total reaction.

CATIONOTROPIC REARRANGEMENT *(Cationotropy)*

See *tautomerism.*

CATION RADICAL

See *radical cation.*

CHAIN REACTION

A reaction in which one or more reactive *reaction intermediates* (frequently *radicals*) are continuously regenerated, usually through a repetitive cycle of elementary steps (the "propagation steps"). For example, in the chlorination of methane by a radical *mechanism*, $Cl^{\cdot}$ is continuously regenerated in the chain propagation steps:

$$\left.\begin{array}{l} \mathrm{Cl\bullet + CH_4 \longrightarrow HCl + H_3C\bullet} \\ \mathrm{H_3C\bullet + Cl_2 \longrightarrow CH_3Cl + Cl\bullet} \end{array}\right. \quad \text{Propagation steps}$$

In chain polymerization reactions, reactive intermediates of the same type, generated in successive steps or cycles of steps, differ in molecular mass, as in

$$\mathrm{RCH_2\dot{C}HPh + H_2C{=}CHPh \longrightarrow RCH_2CHPhCH_2\dot{C}HPh.}$$

See also *chain transfer, initiation, termination*.

CHAIN TRANSFER

The abstraction, by the *radical* end of a growing chain-polymer, of an atom from another molecule. The growth of the polymer chain is thereby terminated but a new radical, capable of chain propagation and polymerization,is simultaneously created. For the example of olefin polymerization cited for a *chain reaction*, the reaction

$$\mathrm{RCH_2\dot{C}HPh + CCl_4 \longrightarrow RCH_2CHClPh + Cl_3C\bullet}$$

represents a chain transfer, the radical $\mathrm{Cl_3C\bullet}$ propagating further polymerization:

$$\mathrm{CH_2{=}CHPh + Cl_3C\bullet \longrightarrow Cl_3CCH_2\dot{C}HPh}$$

$$\mathrm{Cl_3CCH_2\dot{C}HPh + CH_2{=}CHPh \longrightarrow Cl_3CCH_2CHPhCH_2\dot{C}HPh} \quad \text{etc.}$$

See also *telomerization*.

CHARGE DENSITY

The probability (per unit volume) of unit charge being in an infinitesimal volume element around a given point.

See also *electron density*.

CHARGE POPULATION

The net electric charge on a specified atom in a molecule, as determined by some prescribed definition: it is not physically observable.

See also *electron density*.

CHARGE TRANSFER COMPLEX

A *complex* whose nature is indirectly inferred mainly from optical absorption (or absorptions) corresponding to electronic transition(s) to an excited state in which there is a partial transfer of electronic charge from the *electron donor* to the *electron acceptor* moiety.

$$\mathrm{D + A \rightleftharpoons DA \xrightarrow{h\nu} D^{\delta+}A^{\delta-}}$$

The term need not be taken to imply that charge transfer is responsible for *bond*ing in such complexes. Whilst complexes between molecules of high *electron affinity* and low *ionization energy* are frequently observed, there is still disagreement concerning the cause of the attraction between the moieties.

CHELATE

See *chelation*.

CHELATION

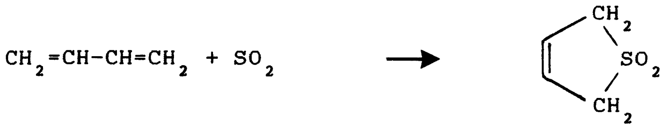
The formation or presence of *bonds* (or other attractive forces) from two or more separate *binding sites* within the same *ligand* to a single central atom. A *molecular entity* in which there is chelation (and the corresponding *chemical species*) is called a "chelate". The terms bidentate, terdentate ... multidentate are used to indicate the number of potential binding sites of the ligand, at least two of which must be used by the ligand in forming a "chelate". For example, the bidentate ethylenediamine forms a chelate with Cu^I in which both nitrogen atoms of ethylenediamine are bonded to copper. (The use of the term is often restricted to metallic central atoms.)

The phrase "separate binding sites" is intended to exclude cases such as $[PtCl_3(CH_2=CH_2)]^-$, ferrocene, and tricarbonyl(benzene)chromium in which ethene, the cyclopentadienyl group, and benzene are considered to present single binding sites to the respective metal atom, and which are not normally thought of as chelates.

See also *cryptand*.

CHELETROPIC REACTION

A form of *cycloaddition* across the terminal atoms of a fully *conjugated system* with formation of two new σ-bonds to a single atom of the ("monocentric") reagent. There is a formal loss of one π-bond in the substrate and an increase in *co-ordination number* of the relevant atom of the reagent. An example is the *addition* of sulfur dioxide to butadiene:



The reverse of this type of reaction is designated "cheletropic elimination".

WOODWARD and HOFFMANN (1969).

CHELOTROPIC REACTION

Alternative (and etymologically more correct) name for *cheletropic reaction*.

DEWAR (1971).

CHEMICAL FLUX

A concept related to *rate of reaction*, particularly applicable to the progress in one direction only of component reaction steps in a complex system or to the progress in one direction of reactions in a system at dynamic equilibrium (in which there are no observable concentration changes with time.) Chemical flux (φ) is a derivative with respect to time, and has the dimensions of amount of substance per unit volume transformed per unit time.

The sum of all the chemical fluxes leading to destruction of B is designated the "total chemical flux out of B" (symbol $\Sigma\varphi_{-B}$); the corresponding formation of B by concurrent elementary reactions is the "total chemical flux into B" (symbol $\Sigma\varphi_B$).

For the mechanism

$$A + B \underset{-1}{\overset{1}{\rightleftharpoons}} C$$

$$C + D \xrightarrow{2} E$$

the total chemical flux into C is caused by the single reaction (1):

$$\Sigma\varphi_C = \varphi_1$$

whereas the chemical flux out of C is a sum over all reactions that remove C:

$$\Sigma\varphi_{-C} = \varphi_{-1} + \varphi_2$$

where φ_{-1} is the "chemical flux out of C into B" and φ_2 is the "chemical flux out of C into E".

The rate of appearance of C is then given by

$$\frac{d[C]}{dt} = \Sigma\varphi_{C} - \Sigma\varphi_{-C}$$

In this system φ_1 (or $\Sigma\varphi_{-A}$) can be regarded as the hypothetical rate of decrease in the concentration of A due to the single (uni-directional) reaction (1) proceeding in the assumed absence of all other reactions.

For an *irreversible reaction* $A \xrightarrow{1} P$,

$$-\frac{d[A]}{dt} = \varphi_1$$

If two substances A and P are in *chemical equilibrium* ($A \rightleftharpoons P$), then

$$\Sigma\varphi_{A} = \Sigma\varphi_{-A} = \Sigma\varphi_{P} = \Sigma\varphi_{-P}$$

and

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = 0$$

GOLD (1979).

See also *order of reaction, rate-limiting step, steady state.*

CHEMICAL REACTION

A process that results in the interconversion of *chemical species*. Chemical reactions may be *elementary reactions* or *stepwise reactions*. (It should be noted that this definition includes experimentally observable interconversions of conformers).

Detectable chemical reactions normally involve sets of *molecular entities*, as indicated by this definition, but it is often conceptually convenient to use the term also for changes involving single molecular entities (i.e. "microscopic chemical events").

See also *identity reaction.*

CHEMICAL RELAXATON

If the equilibrium of a *chemical reaction* is disturbed by a sudden change, especially of some external parameter (such as temperature, pressure, or electric field strength), the system will readjust itself to a new position of the chemical equilibrium. The readjustment is known as chemical relaxation.

In many cases, and in particular when the displacement from equilibrium is slight, the progress of the system towards equilibrium can be expressed as a first-order law

$$[c_t - (c_{eq})_2] = [(c_{eq})_1 - (c_{eq})_2]\ e^{-t/\tau}$$

where $(c_{eq})_1$ and $(c_{eq})_2$ are the equilibrium concentrations of one of the *chemical species* involved in the reaction before and after the change in the external parameter, and c_t is its concentration at time t. The time parameter τ, named relaxation time, is simply related to the *rate constants* of the chemical reactions involved.

Measurements of relaxation times by relaxation methods [involving a temperature jump (T-jump), pressure jump, or electric field jump or a periodic disturbance of an external parameter, as in ultrasonic techniques] are used especially to follow the kinetics of very fast reactions.

See LEFFLER and GRUNWALD (1963).

CHEMICAL SPECIES

A set of chemically identical atomic or molecular structural units in a solid array or of chemically identical *molecular entities* that can explore the same set molecular energy levels on the time scale of the experiment.

For example, two conformational isomers may interconvert sufficiently slowly to be detectable by separate nmr spectra and hence to be considered to be separate chemical species on a time scale governed by the radiofrequency of the spectrometer used. On the other hand, in a slow *chemical reaction* the same mixture of conformers may behave as a single *chemical species*, i.e., there is virtually complete equilibrium population of the total set of molecular energy levels belonging to the two conformers.

Except where the context requires otherwise, the term is taken to refer to a set of molecular entities containing isotopes in their natural abundance.

The wording of the definition given in the first paragraph is intended to embrace both cases such as graphite, sodium chloride, or a surface oxide where the basic structural units are not capable of isolated existence, as well as those cases where they are.

In common chemical usage, and in this Glossary, generic and specific chemical names (such as *radical* or hydroxide ion) or chemical formulae refer either to a chemical species or to a molecular entity.

CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION

See *CIDNP*.

CHEMOSELECTIVE, CHEMOSELECTIVITY

Chemoselectivity is the preferential reaction of a chemical reagent with one of two or more different functional groups. A reagent has a high chemoselectivity if reaction occurs with only a limited number of different functional groups. For example, sodium borohydride is a more chemoselective reducing agent than is lithium aluminium hydride. The concept has not been defined in more quantitative terms.

See TROST (1980).

CHROMOPHORE

One of the groupings within a *molecular entity* to which the colour of a substance is attributed, or, in modern terms, the region in a molecular entity in which an electronic transition is thought to be more or less localized. The more restricted concept arose out of the empiricism of dyestuff chemistry.

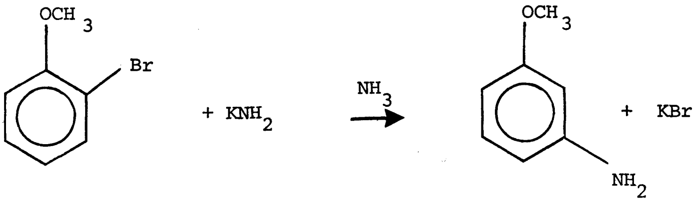
WITT (1876).

CIDNP *(Chemically induced dynamic nuclear polarization)*

An effect sometimes encountered in the nmr spectra of products of reactions that proceed by way of free *radical* intermediates, when these spectra are recorded while the reaction is taking place or immediately thereafter. The effect is manifest in the form of a distortion of the intensity of nmr absorption signals, the appearance of signals in emission, or abnormal intensity ratios in spin multiplets. These *transient* spectral abnormalities result from a non-Boltzmann distribution of nuclear spin populations, attributed to spin correlation effects within *radical pairs* which are the precursors of the observed products. Since the spin populations of the products rapidly attain a normal Boltzmann distribution, the effect decays rapidly after reaction is complete.

CINE-SUBSTITUTION

A substitution reaction (generally *aromatic*) in which the *entering group* takes up a position adjacent to that occupied by the *leaving group*. For example,



See also *tele-substitution*.

CLASS(a) METAL ION

A metal ion that combines preferentially with *ligands* containing ligating atoms that are the lightest of their Periodic Group.

See also *class(b) metal ion, hard acid*.

CLASS(b) METAL ION

A metal ion that combines preferentially with *ligands* containing ligating atoms other than the lightest of their Periodic Group.

See also *class(a) metal ion, hard acid*.

CLATHRATE

See *guest, host, inclusion compound*.

COEFFICIENT IN THE RATE EQUATION

See *kinetic equivalence*.

COLLIGATION

The formation of a covalent *bond* by the combination or recombination of two *radicals* (the reverse of *unimolecular homolysis*). For example:

$$\cdot OH + H_3C\cdot \longrightarrow CH_3OH.$$

See also *dimerization.*

COMMON-ION EFFECT (ON RATES)

A reduction in the *rate of reaction* of a *substrate* RX in solution [by a path that involves a *pre-equilibrium* with formation of R^+ (or R^-) ions as *reaction intermediates*] caused by the addition to the reaction mixture of an electrolyte solute containing the "common ion" X^- (or X^+). For example, the rate of *solvolysis* of diphenylmethyl chloride in acetone-water is reduced by the addition of salts of the common ion Cl^- which causes a decrease in the quasi-equilibrium concentration of the diphenylmethyl cation in the scheme:

$$RCl \underset{-1}{\overset{1}{\rightleftharpoons}} R^+ + Cl^- \qquad \text{(free ions, \underline{not} ion pairs)}$$

$$R^+ + OH_2 \xrightarrow{2} ROH + H^+\text{(solvated)}$$

provided $\varphi_2 \gg \varphi_{-1}$ (where φ = *chemical flux*).

This phenomenon is directly related to - and a consequence of - the familiar common-ion effect on *ionization* equilibria, commonly met in the context of electrolyte solubility for example.

COMPLEMENTARY BINDING SITES

See *binding site*.

COMPLEX

A *molecular entity* formed by a loose *association* involving two or more component molecular entities (ionic or uncharged), or the corresponding *chemical species*. The binding between the components is normally weaker than in a covalent *bond*.

The term has also been used with a variety of shades of meaning in different contexts: it is therefore best avoided when a more explicit alternative is applicable. For the different usage of "complex" in inorganic chemistry, see IUPAC INORGANIC RULES (1970); Rule 2.24.

See also *adduct, charge transfer complex, electron-donor-acceptor complex, encounter* *complex, inclusion complex, σ-adduct, π-adduct, transition state.*

COMPOSITE REACTION

A *chemical reaction* for which the expression for the rate of disappearance of a reactant (or rate of appearance of a product) involves rate constants of more than a single *elementary reaction*. Examples are "opposing reactions" (where rate constants of two opposed *chemical fluxes* are involved), "parallel reactions" (for which the rate of disappearance of any product is governed by the rate constants relating to several simultaneous reactions to form different respective products from a single set of reactants), and *stepwise reactions*.

COMPROPORTIONATION

The reverse of *disproportionation*.

CONCERTED (PROCESS)

Two or more *primitive changes* are said to be concerted (or to constitute a concerted process) if they occur within the same *elementary reaction*. Such changes will normally (though perhaps not inevitably) be "energetically coupled". (In the present context the term "energetically coupled" means that the simultaneous progress of the primitive changes involves a *transition state* of lower energy than that for their successive occurrence.)

See also *bifunctional catalysis, potential energy reaction surface, synchronous.*

CONDENSATION REACTION

A (usually stepwise) reaction in which two or more reactants (or remote reacting sites within the same *molecular entity*) yield a single main product with accompanying formation of water or of some other small molecule, e.g. ammonia, ethanol, acetic acid, hydrogen sulfide.

The *mechanism* of many condensation reactions has been shown to comprise consecutive *addition* and *elimination reactions*, as in the base-catalysed formation of *trans*-but-2-enal (crotonaldehyde) from acetaldehyde, via 3-hydroxybutanal (aldol). The overall reaction in this example is known as the aldol condensation.

CONFIGURATION

See IUPAC ORGANIC RULES (1979)

CONFORMATION

See IUPAC ORGANIC RULES (1979)

CONJUGATE ACID-BASE PAIR

The *Brønsted acid* BH^+ formed on protonation of a base B is called the conjugate acid of B, and B is the conjugate base of BH^+. (The conjugate acid always carries one unit positive charge more than the base, but the absolute charges of the species are immaterial to the definition.) For example: the Brønsted acid HCl and its conjugate base Cl^- constitute a conjugate acid-base pair.

CONJUGATED SYSTEM

See *conjugation*.

CONJUGATION

An alternating sequence (in a *line formula*) of single and multiple *bonds* that contains at least two multiple bonds. The structural unit containing such a sequence is called a "conjugated system". In more recent usage the term has been applied to the overlap of atomic p orbitals of three or more adjacent atoms.

See also *delocalization, homoconjugation, resonance.*

CONJUGATION MECHANISM

See *electromeric effect*.

CONNECTIVITY

In a chemical context, the information content of a *line formula*, but omitting any indication of *bond* multiplicity.

CONROTATORY

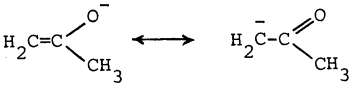
See *electrocyclic reaction*.

CONTACT ION PAIR

See *ion pair*.

CONTRIBUTING STRUCTURE

The definition is based on the valence-bond formulation of the quantum-mechanical idea of the wavefunction of a molecule as composed of a linear combination of wave functions, each representative of a formula containing *bonds* that are only single, double, or triple with a particular pairing of electron spins. Each such formula represents a contributing structure to the total wave function, and the degree to which each contributes is indicated by the square of its coefficient in the linear combination. The contributing structures themselves thus have a purely formal significance: they are the components from which wave functions can be built. Structures may be covalent (or non-polar) or ionic (or polar). The representation is frequently kept rather qualitative so that we speak of important or major contributing structures and minor contributing structures. For example, two major non-equivalent contributing structures for the conjugate base of acetone are



See also *delocalization*, *Kekule structure*, *resonance*.

CO-ORDINATE COVALENCE (Co-ordinate link)

See *co-ordination*.

CO-ORDINATION

The formation of a covalent *bond*, the two shared electrons of which have come from only one of the two parts of the *molecular entity* linked by it, as in the reaction between a *Lewis acid* and a *Lewis base* to form a *Lewis adduct*; alternatively, the bonding formed in this way. In the former sense, it is the reverse of *unimolecular heterolysis*.

(The origin of the bonding electrons has by itself no bearing on the character of the bond formed. Thus, the formation of methyl chloride from a methyl cation and a chloride ion involves co-ordination; the resultant bond obviously differs in no way from the C-Cl bond in methyl chloride formed by any other path, e.g. by *colligation* of a methyl radical and a chlorine atom.)

See also *dipolar bond*, *π-adduct*.

CO-ORDINATION NUMBER

The co-ordination number of a specified atom in a *chemical species* is the number of other atoms directly linked to that specified atom [cf. IUPAC INORGANIC RULES (1970); Rule 0.2]. For example, the co-ordination number of carbon in methane is four. (The term is used in a different sense in the crystallographic description of ionic crystals.)

CORONATE

See *crown*.

COSPHERE

See *cybotactic region*.

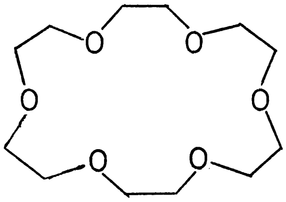
CRITICAL MICELLE CONCENTRATION (CMC)

See IUPAC MANUAL APPENDIX II (1972).

See also *inverted micelle*.

CROWN

A *molecular entity* comprising a monocyclic *ligand* assembly that contains three or more *binding sites* held together by covalent *bonds* and capable of binding a *guest* in a central (or nearly central) position. The *adducts* formed are sometimes known as "coronates". The best known members of this group are macrocyclic polyethers, such as "18-crown-6", containing several repeating units $-CR_2CR_2O-$ (where R is most commonly H), and known as crown ethers.



"18-crown-6"

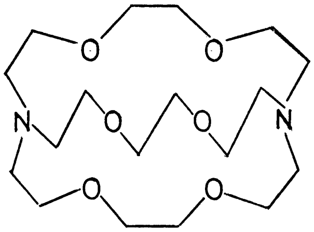
See also *host*.

PEDERSEN (1967).

CRYPTAND

A *molecular entity* comprising a cyclic *ligand* assembly that contains three or more *binding sites* held together by covalent *bonds*, and which defines a molecular cavity in such a way as to bind (and thus "hide" in the cavity) another molecular entity, the *guest* (a cation, an anion or a neutral species), more strongly than do the separate parts of the assembly (at the same total concentration of binding sites). The *adduct* thus formed is called a "cryptate". The term is usually restricted to bicyclic or oligocyclic molecular entities.

Example:



Corresponding monocyclic ligand assemblies (*crowns*) are sometimes included in this group, if they can be considered to define a cavity in which a guest can hide. Coplanar cyclic polydentate ligands, such a porphyrins, are not normally regarded as cryptands.

See also *host*.

DIETRICH, LEHN and SAUVAGE (1969).

For a contribution to the evolving terminology, see also VOGTLE (1980).

CRYPTATE

See *cryptand*.

CURTIN-HAMMETT PRINCIPLE

In a *chemical reaction* that yields one product from one conformational isomer and a different product from another conformational isomer (and provided these two isomers are rapidly interconvertible relative to the rate of product formation, whereas the products do not interconvert) the product composition is not solely dependent on the relative proportions of the conformational isomers in the *substrate*; it is controlled by the difference in standard Gibbs energies of the respective *transition states*.

It is also true that the product composition is formally related to the relative concentrations of the conformational isomers (i.e. the conformational equilibrium constant) and the respective rate constants of their reactions: these parameters are generally - though not invariably - unknown.

ELIEL (1962); see also SEEMAN et al.(1980).

See also *chemical species*.

CYBOTACTIC REGION

That part of a solution in the vicinity of a solute molecule in which the ordering of the solvent molecules is modified by the presence of the solute molecule. The term solvent "cosphere" of the solute has also been used.

See also *solvation*.

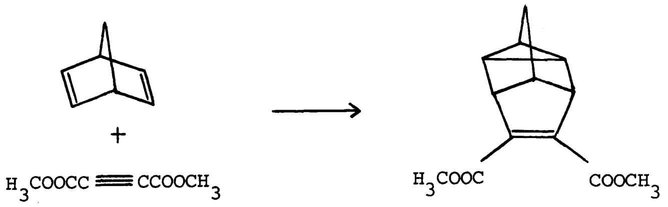
STEWART and MORROW (1927).

CYCLOADDITION

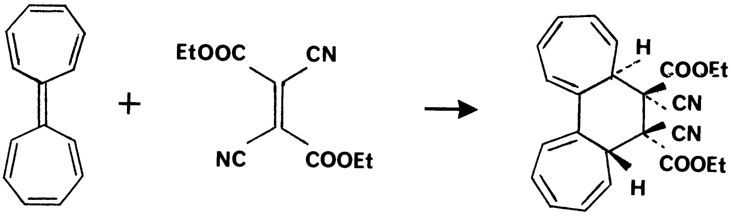
A reaction in which two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a single cyclic *adduct* in which there is a net reduction in the bond multiplicity.

The following two systems of notation have been used for the more detailed specification of cycloadditions, of which the second, more recent, system is preferred:

(1) An (i+j+ ...)cycloaddition is a reaction in which two or more molecules (or parts of the same molecule) respectively provide units of i, j, ... linearly connected atoms: these units become joined at their respective termini by new σ-bonds so as to form a cycle containing (i+j+...) atoms. In this notation, (a) a Diels-Alder reaction is a (4+2)cycloaddition, (b) the initial reaction of ozone with an alkene is a (3+2)cycloaddition, and (c) the reaction shown below is a (2+2+2)cycloaddition. (N.B.: Round brackets (...) are used in the description based on numbers of atoms.)



(2) The symbolism [i+j+...]cycloaddition identifies the numbers i, j... of electrons in the interacting units that participate in the transformation of reactants to products. In this notation the reactions (a) and (b) of the preceding paragraph would both be described as [2+4]cycloadditions, and (c) as a [2+2+2]cycloaddition. The symbol a or s (a = *antarafacial*, s = suprafacial) is often added (usually as a subscript) after the number to designate the stereochemistry of addition to each fragment. A subscript specifying the orbitals, viz., σ, π (*sigma*,*pi* with their usual significance) or ω (for an orbital associated with a single atom only), may be added a a subscript before the number. Thus the normal Diels-Alder reaction is a $[4_s+2_s]$ or $[{}_{\pi}4_s + {}_{\pi}2_s]$cycloaddition, whilst the reaction



would be a $[14_a+2_s]$ or $[_\pi 14_a + {}_\pi 2_s]$cycloaddition.

(N.B. Square brackets [...] are used in the description based on numbers of electrons.)

Cycloadditions may be *pericyclic reactions* or (non-*concerted*) *stepwise reactions*.

See also *cheletropic reaction*.

See HUISGEN (1968); WOODWARD and HOFFMANN (1969).

CYCLOELIMINATION

The reverse of *cycloaddition*. The term is preferred to the synonyms "cycloreversion", "retro-addition", and "retrocycloaddition".

CYCLOREVERSION

See *cycloelimination*.

DATIVE BOND

See *co-ordination*.

DECOMPOSITION, CHEMICAL

The breakdown of a single entity (normal molecule, *reaction intermediate*, etc.) into two or more fragments.

DE-ELECTRONATION

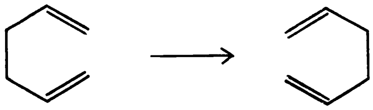
See *oxidation*(1).

DEGENERATE CHEMICAL REACTION

See *identity reaction*.

DEGENERATE REARRANGEMENT

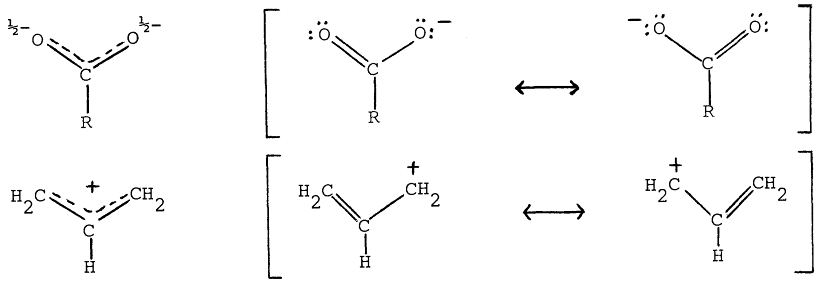
A *molecular rearrangement* in which the principal product is indistinguishable from the principal reactant. The term includes both "degenerate *intramolecular* rearrangements" and reactions that involve *intermolecular* transfer of atoms or groups ("degenerate intermolecular rearrangements"): both are degenerate *isomerizations*. The occurrence of degenerate rearrangements may be detectable by isotopic labelling or by dynamic NMR techniques. For example: the [3,3]*sigmatropic* rearrangement of 1,5-hexadiene,



See also *fluxional, molecular rearrangement, valence tautomerism*.

DELOCALIZATION

A quantum-mechanical concept directly associated with the Uncertainty Principle, most usually applied in organic chemistry to describe the π-bonding in a *conjugated system*. This bonding is not localized: instead, each link has a "fractional double bond character" or *bond order*. There is a corresponding "delocalization energy", identifiable with the stabilization of the system compared with a hypothetical alternative in which formal (localized) single and double *bonds* are present. Some degree of delocalization is always present, and can be estimated by quantum-mechanical calculations. The effects are particularly evident in *aromatic* systems and in symmetrical *molecular entities* in which a lone pair of electrons or a vacant p orbital is conjugated with a double bond (e.g. carboxylate ions, nitro compounds, the allyl cation). Delocalization in such species may be represented by partial bonds or as *resonance* (here symbolized by a two-headed arrow) between *contributing structures*, e.g.



These examples also illustrate the concomitant delocalization of charge in ionic conjugated systems. Analogously, delocalization of the spin of an unpaired electron occurs in conjugated *radicals*.

See also *mesomerism*.

DETACHMENT

The reverse of an *attachment*.

See also *electron attachment*.

DETAILED BALANCING, PRINCIPLE OF

When equilibrium is reached in a reaction system (containing however many components and reaction paths) as many atoms, in their respective *molecular entities*, will pass forwards as backwards along each individual path in a given finite time interval. Accordingly, the *mechanism* of a reaction in the reverse direction must in every detail be the reverse of the mechanism in the forward direction (provided always that the system is at or near equilibrium): it need not be true when the system is far from equilibrium.

The principle of detailed balancing is a consequence for macroscopic systems of the principle of *microscopic reversibility*.

DIFFUSION-CONTROLLED RATE

See *encounter-controlled rate, macroscopic diffusion control, microscopic diffusion control*.

DIMERIZATION

The reaction of a *molecular entity* A to give a molecular entity A_2. For example:

$$H_3C\bullet + \bullet CH_3 \longrightarrow CH_3CH_3, \qquad \text{or} \qquad 2\ CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)CH_2COCH_3$$

+ DIPOLAR-APROTIC SOLVENT

A solvent with a relatively high relative permittivity (or dielectric constant), greater than ca. 15, that cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds, e.g. dimethyl sulfoxide. The term (and its alternative "polar-aprotic solvent") is a misnomer and should therefore be discouraged. Such solvents are usually not *aprotic* but *protophilic* (and/or weakly *protogenic*). In describing a solvent it is better to be explicit about its essential properties, e.g., dipolar and non-hydroxylic.

DIPOLAR BOND

A *bond* formed (actually or conceptually) by *co-ordination* of two neutral moieties, e.g.,

$$R_3N: + \ddot{\underset{\cdot\cdot}{O}}: \longrightarrow R_3N^+\text{-}O^-$$

The term is preferred to the obsolescent or obsolete synonyms "co-ordinate link", "co-ordinate covalence", "dative bond", "semipolar double bond".

+ ***DIRADICAL***

See *biradical*.

DIRECT EFFECT

See *field effect*.

DISMUTATION

See *disproportionation*.

DISPROPORTIONATION

Any *chemical reaction* of the type A + A ⟶ A' + A", where A, A' and A" are different *chemical species*. For example:

$$2ArH^{+\cdot} \longrightarrow ArH + ArH^{2+}$$

The reverse of disproportionation is called "comproportionation".

A special case of disproportionation (or "dismutation") is "radical disproportionation", exemplified by

$$\cdot CH_2CH_3 + \cdot CH_2CH_3 \longrightarrow CH_2{=}CH_2 + CH_3CH_3$$

Reactions of the more general type

$$R\dot{C}HCH_3 + R'\dot{C}HCH_3 \longrightarrow RCH{=}CH_2 + R'CH_2CH_3$$

are also loosely described as radical disproportionations.

(A somewhat more restricted usage of the term prevails in inorganic chemistry.)

DISROTATORY

See *electrocyclic reaction*.

DISSOCIATION

(1) The separation of a *molecular entity* into two or more molecular entities (or any similar separation within a polyatomic molecular entity). Examples include *unimolecular heterolysis* and *homolysis*, and the separation of the constituents of an *ion pair* into free ions.

(2) The separation of the constituents of any aggregate of molecular entities.

In both senses dissociation is the reverse of *association*.

DRIVING FORCE

The decrease in Gibbs energy on going from the reactants to the products of a *chemical reaction* (-ΔG).

E_T-VALUE

See *Z-value*.

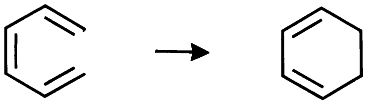
EFFECTIVE MOLARITY (or ***Effective concentration***)

The ratio of the first-order rate constant of an *intramolecular* reaction involving two functional groups within the same *molecular entity* to the second-order *rate constant* of an analogous *intermolecular elementary reaction*. This ratio has the dimensions of concentration.

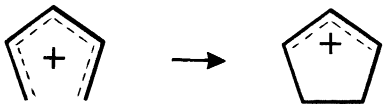
See also *intramolecular catalysis*.

ELECTROCYCLIC REACTION

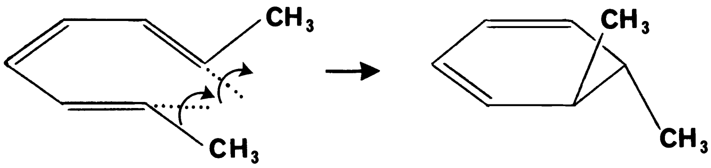
A *molecular rearrangement* that involves the formation of a σ-bond between the termini of a fully *conjugated* linear π-electron system (or a linear fragment of a π-electron system) and a decrease by one in the number of π-bonds, or the reverse of that process. For example:



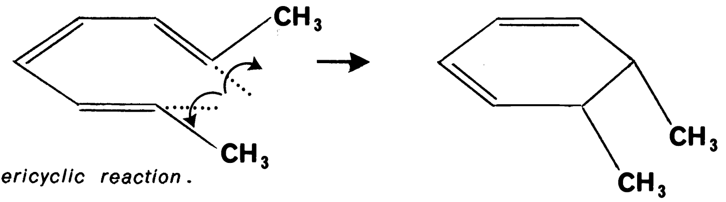
or



The stereochemistry of such a process is termed "conrotatory" (or *antarafacial*) if the interacting termini of the conjugated system both rotate in the same sense, e.g.



or "disrotatory (or suprafacial) if one terminus rotates in a clockwise and one in a counter-clockwise sense, e.g.



See also *pericyclic reaction*.

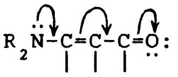
ELECTROFUGE

A *leaving group* that does not carry away the bonding electron pair. For example, in the nitration of benzene by NO_2^+, H^+ is the electrofuge.

See also *electrophile*, *nucleofuge*.

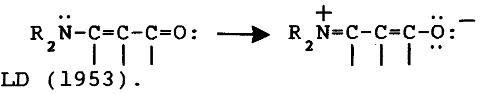
+ *ELECTROMERIC EFFECT* (obsolescent)

A molecular polarizability effect occurring by an *intramolecular* electron displacement (sometimes called the "conjugative mechanism" and, previously, the "tautomeric mechanism") characterized by the substitution of one electron pair for another within the same atomic octet of electrons. It can be indicated by curved arrows symbolizing the displacement of electron pairs, as in



$$R_2\ddot{N}-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=\underset{\cdot\cdot}{O}:$$

which represents the hypothetical electron shift



$$R_2\ddot{N}-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=O: \longrightarrow R_2\overset{+}{N}=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-\underset{\cdot\cdot}{\ddot{O}}:^-$$

See INGOLD (1953).

ELECTRON ACCEPTOR

(1) A substance to which an electron may be transferred; for example,

1,4-dinitrobenzene or the 1,1'-dimethyl-4,4'-bipyridylium di-cation.

\+ (2) A Lewis acid. This usage is discouraged.

ELECTRON AFFINITY

The energy released when an additional electron (without excess energy) attaches itself to a *molecular entity* (usually an electrically neutral molecular entity). (The direct measurement of this quantity involves molecular entities in the gas phase.)

ELECTRON ATTACHMENT

The combination of a *molecular entity* with an electron, resulting in a molecular entity of (algebraically) increased negative charge. (It is not an *attachment*, as defined in this Glossary.)

See also *oxidation*(1),*reduction*.

ELECTRON DENSITY

The electron probability distribution in a *molecular entity*. If $P(x,y,z)\mathrm{d}x\mathrm{d}y\mathrm{d}z$ is the probability of finding an electron in the volume element $\mathrm{d}x\mathrm{d}y\mathrm{d}z$ at the point with co-ordinates x,y,z, then $P(x,y,z)$ is the electron density. For many purposes (e.g., X-ray scattering, forces on atoms) the system behaves exactly as if the electrons were smeared out into a continuously distributed charge. The term has frequently been wrongly applied to negative *charge population*.

See also *charge density*.

ELECTRON DETACHMENT

The reverse of an *electron attachment.*

ELECTRON DONOR

(1) A *molecular entity* that can transfer an electron to another molecular entity, or the corresponding *chemical species.*

\+ (2) A Lewis base. This usage is discouraged.

+ *ELECTRON-DONOR-ACCEPTOR COMPLEX*

A term sometimes employed instead of *charge transfer complex* or *Lewis adduct*. Its use is discouraged.

See also *adduct, co-ordination*.

ELECTRONATION

See *reduction*.

ELECTRONEGATIVITY

A measure of the power of an atom or a group of atoms to attract electrons from other parts of the same *molecular entity*. The concept has been quantified by a number of authors, including especially Pauling and Mulliken.

See ATKINS (1974).

ELECTROPHILE, ELECTROPHILIC

An electrophile (or electrophilic reagent) is a reagent that forms a *bond* to its reaction partner (the *nucleophile*) by accepting both bonding electrons from that reaction partner.

An "electrophilic *substitution reaction*" is a *heterolytic* reaction in which the reagent supplying the entering group acts as an electrophile. For example

$$\underset{}{C_6H_6} + \underset{\text{electrophile}}{NO_2^+} \longrightarrow C_6H_5NO_2 + \underset{\textit{electrofuge}}{H^+}$$

Electrophilic reagents are *Lewis acids*. "Electrophilic catalysis" is *catalysis* by a *Lewis acid*.

The term "electrophilic" is also used to designate the apparent polar character of certain *radicals*, as inferred from their higher relative reactivities with reaction sites of higher *electron density*.

See also *electrophilicity*.

ELECTROPHILICITY

(1) The property of being *electrophilic* (see *electrophile*).

(2) The relative reactivity of an electrophilic reagent. (It is also sometimes referred to as "electrophilic power".) Qualitatively, the concept is related to *Lewis acidity*. However, whereas Lewis acidity is measured by relative equilibrium constants, electrophilicity is measured by relative *rate constants* for reactions of different electrophilic reagents towards a common *substrate* (usually involving attack at a carbon atom).

See also *nucleophilicity*.

ELEMENT EFFECT

The ratio of the rate constants of two reactions that differ only in the identity of the element of the atom in the *leaving group* by which the leaving group is attached to the rest of the *substrate* molecule. As for *isotope effects*, a ratio of unity is thought of as a "null effect".

ELEMENTARY REACTION

A one-step reaction or a *reaction step* that has no *reaction intermediate*.

See also *stepwise reaction*.

ELIMINATION REACTION

The reverse of an *addition reaction*.

See also *α-elimination*.

ENANTIOSELECTIVITY

See *stereoselectivity*.

ENCOUNTER COMPLEX

A *complex* of *molecular entities* produced at an *encounter-controlled rate*. When the complex is formed from two molecular entities it is called an "encounter pair". A distinction between (larger) encounter complexes and encounter pairs may be relevant in some cases, e.g. for mechanisms involving *preassociation*.

ENCOUNTER-CONTROLLED RATE

A *rate of reaction* corresponding to the rate of encounter of the reacting *molecular entities*. This is also known as a "diffusion-controlled rate" since rates of encounter are themselves controlled by diffusion rates (which in turn depend on the viscosity of the *medium* and the dimensions of the reactant molecular entities).

For a *bimolecular* reaction betwen solutes in water at 25°C an encounter-controlled rate is calculated to have a second-order *rate constant* of the order of 10^{10} dm^3 mol^{-1} s^{-1}. (The encounter-controlled rate depends also upon the concentrations of the reactants).

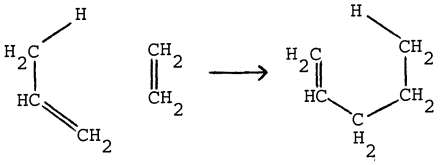
See also *microscopic diffusion control*.

ENCOUNTER PAIR

See *encounter complex*.

ENE REACTION

The addition of an olefin (or some other compound with a double bond) having an allylic hydrogen (the "ene") to a compound with a multiple bond (the "enophile") with transfer of the allylic hydrogen and a concomitant reorganization of bonding, as illustrated below for propene (the "ene") and ethylene (ethene; the "enophile"). The reverse process is a "retro-ene" reaction.



ENERGY OF ACTIVATION, E_a (Arrhenius energy of activation; activation energy)

An operationally defined quantity expressing the dependence of a rate constant on temperature according to

$$E_a = RT^2\left(\frac{\partial \ln k}{\partial T}\right)_p$$

as derived from the "Arrhenius equation", $k = A \exp(-E_a/RT)$, where A is termed the "pre-exponential factor".

See also *enthalpy of activation*.

ENERGY PROFILE

See *Gibbs energy diagram, potential energy profile*.

ENOPHILE

See *ene reaction*.

ENTERING GROUP

An atom or *group* that forms a *bond* to what is considered to be the main part of the *substrate* during a reaction. For example: the attacking *nucleophile* in a bimolecular nucleophilic *substitution reaction*.

See also *leaving group.*

ENTHALPY OF ACTIVATION, $\Delta H^\ddagger$

The standard enthalpy difference between the *transition state* and the ground state of the reactants at the same temperature and pressure. It is related to the temperature coefficient of the rate constant according to the equation:

$$\Delta H^\ddagger = RT^2\left(\frac{\partial \ln k}{\partial T}\right)_p - RT$$

$$= E_a - RT$$

$$= -R\left(\frac{\partial \ln(k/T)}{\partial(1/T)}\right)_p$$

where E_a is the *energy of activation*, providing that rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm^{-3}, measured at a fixed temperature and pressure). If $\ln k$ is expressed as

$\ln k = (a/T) + b + c\ln T + dT,$

then $\Delta H^{\ddagger} = -aR + (c-1)RT + dRT^2$.

If the concentration units are mol dm^{-3} at the temperature of each experiment, the true and apparent enthalpies of activation differ by $(n-1)/\alpha RT^2$, where n is the *order of reaction*, and α the thermal expansivity.

Strictly speaking, the quantity defined is the enthalpy of activation at constant pressure, from which the enthalpy of activation at constant volume can be deduced.

See also *entropy of activation, Gibbs energy of activation*.

ENTROPY OF ACTIVATION, $\Delta S^{\ddagger}$

The standard entropy difference between the *transition state* and the ground state of the reactants, at the same temperature and pressure.

It is related to *Gibbs energy of activation* and *enthalpy of activation* by the equations

$$\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta G^{\ddagger})/T$$

$$= \Delta H^{\ddagger}/T - R\ln(k/h) + R\ln(k/T)$$

or, if ln k is expressed as $\ln k = a/T + b + c\ln T + dT$,

$$\Delta S^{\ddagger} = R[b - \ln(k/h) + (c-1)(1 + \ln T) + 2dT]$$

provided that rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm^{-3}, measured at a fixed temperature and pressure). The numerical value of $\Delta S^{\ddagger}$ depends on the standard state (and therefore on the concentration units) selected.

Strictly speaking, the quantity defined is the entropy of activation at constant pressure from which an entropy of activation at constant volume can be deduced.

The information represented by the entropy of activation may alternatively be conveyed by the pre-exponential factor A (see *energy of activation*).

EQUILIBRIUM CONTROL

See *thermodynamic control*.

EQUILIBRIUM ISOTOPE EFFECT

See *isotope effect.*

EXCIMER

An (electronically) excited-state dimer which is usually dissociative in the ground state.

See also *exciplex.*

EXCIPLEX

An (electronically) excited-state *complex* of fixed stoichiometry, formed from two or more *molecular entities* (not all of which are chemically identical), and which is usually dissociative in the ground state.

EXTERNAL ION RETURN

See *ion pair return*.

EXTERNAL RETURN

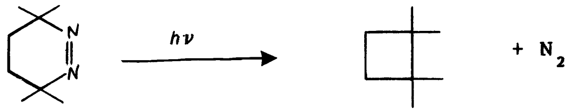
See *ion-pair return*.

EXTRUSION REACTION

A reaction in which an atom or *group* Y connected to two other atoms or groups X and Z is lost from a molecule, leading to a product in which X is bonded to Z, e.g.,

$$X\text{-}Y\text{-}Z \longrightarrow X\text{-}Z + Y$$

or



The reverse of an extrusion reaction is called an *insertion reaction*.

FIELD EFFECT

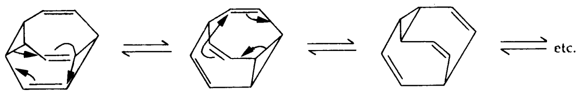
An experimentally observable effect (on reaction rates, etc.) of *intramolecular* coulombic interaction between the centre of interest and a remote pole or dipole, by direct action through space rather than through bonds. The magnitude of the field effect (or "direct effect") is dependent on the intensity, orientation, and shortest distance between the centre of interest and the remote pole or dipole. An approach to its calculation was described by KIRKWOOD and WESTHEIMER (1938).

See also *inductive effect*.

FLUXIONAL

A fluxional *chemical species* undergoes rapid *degenerate rearrangements* (generally detectable only by spectroscopic line-shape analysis).

Example:



Bullvalene (10!/3 forms)

See also *valence tautomerism*.

FRACTIONATION FACTOR, ISOTOPIC

The ratio $(x_1/x_2)_A/(x_1/x_2)_B$, where x is the abundance, expressed as the atom fraction of the isotope distinguished by the subscript numeral, when the two isotopes are equilibrated between two different *chemical species* A and B (or between specific sites A and B in the same or different chemical species). The term is most commonly met in connection with deuterium solvent *isotope effects* when the fractionation factor φ expresses the ratio

$$\varphi = (x_D/x_H)_{\text{solute}}/(x_D/x_H)_{\text{solvent}}$$

for the exchangeable hydrogen atoms in the chemical species (or sites) concerned. The concept is also applicable to *transition states*.

FRAGMENTATION

(1) The *heterolytic* cleavage of a molecule according to the general reaction a-b-c-d-X$\longrightarrow$a-b + c=d + :X, where a-b is an *electrofuge* and :X is a *nucleofuge* (which may emerge from the reaction in combined form), and the middle group c-d affords the unsaturated fragment c=d. For example,

$$Ph_3C.CO_2H + H^+ \longrightarrow Ph_3C^+ + CO + H_2O$$

GROB (1969).

(2) The breakdown of a *radical* into a diamagnetic molecule and a smaller radical, e.g., $X{-}Y{-}Z\cdot \rightarrow X{=}Y + Z\cdot$

(3) The breakdown of a *radical ion* in a mass spectrometer or in solution, forming an ion of lower molecular mass and a radical, e.g.,

$$[(CH_3)_3C{-}OH]^{+\cdot} \rightarrow (CH_3)_2C{=}\overset{+}{O}H + H_3C\cdot \quad \text{(mass spectrometer)}$$

$$[ArBr]^{-\cdot} \rightarrow Ar\cdot + Br^- \quad \text{(solution)}.$$

FREE ENERGY

See *Gibbs energy* ...

This change conforms to the recommendations of IUPAC MANUAL (1979).

FREE RADICAL

See *radical*.

FRONTIER ORBITALS

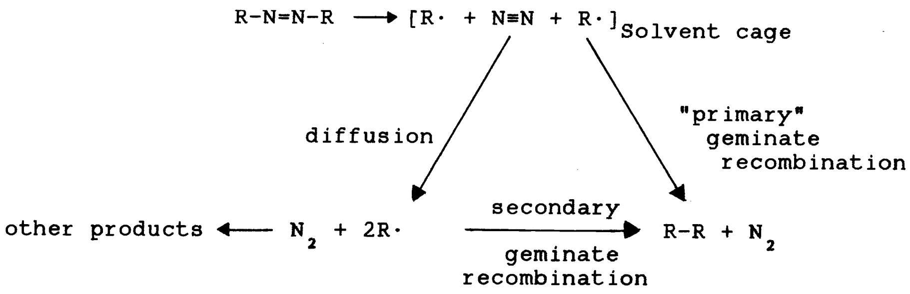
The *H*ighest-energy *O*ccupied *M*olecular *O*rbital (HOMO) (filled or partly filled) and *L*owest-energy *U*noccupied *M*olecular *O*rbital (LUMO) (completely or partly vacant) of a *molecular entity*. Examination of the mixing of frontier orbitals of reacting molecular entities affords an approach to the interpretation of reaction behaviour; this constitutes a simplified perturbation *molecular orbital* theory of chemical behaviour.

GEMINATE PAIR

See *radical pair.*

GEMINATE RECOMBINATION

The reaction with each other of two *transient molecular entities* produced from a common precursor in solution. If reaction occurs before any separation by diffusion has occurred, this is termed "primary geminate recombination". If the mutually reactive entities have been separated, and come together by diffusion, this is termed "secondary geminate recombination". For example,



See also *cage, ion-pair return.*

GENERAL ACID CATALYSIS

The *catalysis* of a chemical reaction by a series of *Brønsted acids* (which may include the solvated hydrogen ion) so that the rate of the catalysed part of the reaction is given by $\sum k_{HA}[HA]$ multiplied by some function of *substrate* concentrations. (The acids HA are unchanged by the overall reaction.) General catalysis by acids can be experimentally distinguished from *specific catalysis* by hydrogen ions by observation of the *rate of reaction* as a function of buffer concentration.

See also *catalysis, catalytic coefficient, intramolecular catalysis, pseudo-catalysis, specific catalysis.*

GENERAL BASE CATALYSIS

The acceleration of a chemical reaction by a series of *Brønsted bases* (which may include the *lyate ion*) so that the rate of the catalysed part of the reaction is given by $\sum k_B[B]$ multiplied by some function of *substrate* concentrations.

See also *general acid catalysis*.

GIBBS ENERGY DIAGRAM

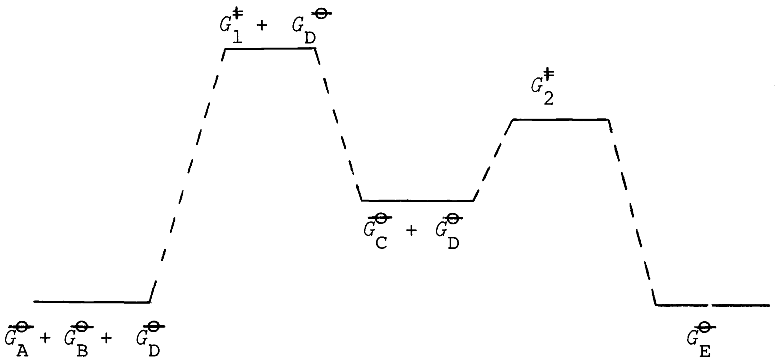
A diagram showing the relative standard Gibbs energies of reactants, *transition states, reaction intermediates*, and products, in the same sequence as they occur in a *chemical reaction*. These points are often connected by a smooth curve (a "Gibbs energy profile", commonly still referred to as a "free energy profile") but experimental observation can provide information on relative standard Gibbs energies only at the maxima and minima and not at configurations between them. The abscissa expresses the sequence of reactants, products, reaction intermediates and transition states but is otherwise undefined.

Contrary to statements in many text books, the highest point on a Gibbs energy diagram does not necessarily correspond to the transition state of the *rate-limiting step*. For example, in a *stepwise reaction* consisting of two reaction steps

$$(1) \quad A + B \rightleftharpoons C$$

$$(2) \quad C + D \longrightarrow E$$

one of the transition states of the two reaction steps must (in general) have a higher standard Gibbs energy than the other, whatever the concentration of D in the system. However, the value of that concentration will determine which of the reaction steps is rate-limiting.



See also *potential energy profile, potential energy reaction surface*.

GIBBS ENERGY OF ACTIVATION, ($\Delta G^{\ddagger}$) (Gibbs free energy of activation)

The standard Gibbs energy difference between the *transition state* of a reaction (either an *elementary reaction* or a *stepwise reaction*) and the ground state of the reactants. It is calculated from the experimental rate constant k via the conventional form of the absolute rate equation:

$$\Delta G^{\ddagger} = RT(\ln \mathbf{k}/h - \ln k/T)$$

where $\mathbf{k}$ is the Boltzmann constant and h the Planck constant

(k/h = 2.08358×10^{10} K^{-1} s^{-1}). The values of rate constants, and hence Gibbs energies of activation, depend upon the choice of concentration units (or of the thermodynamic standard state).

See also *entropy of activation*.

GIBBS ENERGY PROFILE

See *Gibbs energy diagram*.

GROUP

A defined linked collection of atoms within a *molecular entity*. This use of the term in physical organic and general chemistry is less restrictive than the definition adopted for the purpose of nomenclature of organic compounds. [See IUPAC ORGANIC RULES (1969), Section C].

See also *substituent group*.

GROUP ELECTRONEGATIVITY

See *substituent electronegativity*.

GRUNWALD-WINSTEIN EQUATION

The *linear Gibbs energy relation*

$$\lg (k_s/k_0) = mY$$

expressing the dependence of the rate of *solvolysis* of a *substrate* on *ionizing power* of the solvent. The rate constant k_0 applies to the reference solvent (ethanol-water, 80:20, v/v) and k_s to the solvent S, both at 25°. The parameter m is characteristic of the substrate and is assigned the value unity for *tert*-butyl chloride. The value Y is intended to be a quantitative measure of the ionizing power of the solvent S. The equation has also been applied to reactions other than solvolysis. [For the definition of other Y-scales, see BENTLEY and SCHLEYER (1977)].

GRUNWALD and WINSTEIN (1948); FAINBERG and WINSTEIN (1956).

See also *polarity*, *Z-value*.

GUEST

An organic or inorganic ion or compound that occupies a cavity, cleft or pocket within the molecular structure of a *host molecular entity* and forms a *complex* with it or which is trapped in a cavity within the crystal structure of a host.

See also *crown*, *cryptand*, *inclusion compound*.

HALF-LIFE

In a kinetic experiment, the time required for the concentration of a particular reactant to fall to one half of its initial value. (Its dependence on initial concentration depends upon the *order of reaction*. It is independent of initial concentration only for a first-order process.)

See also *mean life-time*.

HAMMETT ACIDITY FUNCTION

See *acidity function*.

HAMMETT EQUATION (or ***Hammett relation***)

See *σ-value*.

HAMMOND PRINCIPLE (or ***Hammond postulate***)

The hypothesis that, when a *transition state* leading to an unstable *reaction* *intermediate* (or product) has nearly the same energy as that intermediate, the two are interconverted with only a small reorganization of molecular structure. Essentially the same idea is sometimes referred to as "Leffler's assumption", namely, that the transition state bears the greater resemblance to the less stable species (reactant or reaction intermediate/product).

HAMMOND (1955); LEFFLER (1953).

HARD ACID

A *Lewis acid* with an acceptor centre of low *polarizability*. It preferentially associates with *hard bases* rather than with "soft bases", in a qualitative sense. For example, the hard O- (or N-) bases are preferred to their S- (or P-) analogues. Conversely a "soft acid" possesses an acceptor centre of high polarizability and exhibits the reverse preference of a partner for *coordination*. These preferences are not defined in a quantitative sense.

See also *class(a) metal ion, hard base*.

HARD BASE

A *Lewis base* with a donor centre (e.g. an O atom) of low *polarizability* and with vacant orbitals of high energy; the converse applies to "soft bases".

See also *hard acid*.

HEAT CAPACITY OF ACTIVATION ($\Delta C_p^{\ddagger}$)

A quantity related to the temperature coefficient of $\Delta H^{\ddagger}$ (*enthalpy of activation*) and $\Delta S^{\ddagger}$ (*entropy of activation*) according to the equations:

$$\Delta C_p^{\ddagger} = \left(\frac{\partial \Delta H^{\ddagger}}{\partial T}\right)_p = T\left(\frac{\partial \Delta S^{\ddagger}}{\partial T}\right)_p$$

If the rate constant is expressible in the form $\ln k = a/T + b + c\ln T + dT$, then

$$\Delta C_p^{\ddagger} = (c-1)R + 2dRT$$

See KOHNSTAM (1967).

HETEROCONJUGATION

(1) Association between a base and the conjugate acid of a different base through a *hydrogen bond* ($\mathrm{B'...HB^{+}}$ or $\mathrm{A'H...A^{-}}$).

(2) Some authors refer to *conjugated systems* containing a hetero-atom, e.g. pyridine, as "heteroconjugated systems". This usage is discouraged since it inappropriately suggests an analogy to *homoconjugation*(2), which conflicts with the currently accepted definition of that term.

HETEROLYSIS, HETEROLYTIC

The cleavage of a bond so that both bonding electrons remain with one of the two fragments between which the *bond* is broken, e.g.

$$\overset{\curvearrowright}{\mathrm{A}\!\rightarrow\!\mathrm{B}} \longrightarrow \mathrm{A}^{+} + \mathrm{B}^{-}$$

Heterolysis of a bond (not forming part of a ring) in the *unimolecular* reaction of an electrically neutral *molecular entity* results in the formation of two oppositely charged ions (cf. *homolysis*).

Heterolytic bond fission is a feature of many *bimolecular* reactions in solution (e.g., *electrophilic* substitution, *nucleophilic* substitution).

See also *heterolytic bond dissociation energy*.

HETEROLYTIC BOND DISSOCIATION ENERGY

The energy required to break a given *bond* of some specific compound by *heterolysis*. For the *dissociation* of a neutral molecule AB in the gas phase into A^+ and B^- the heterolytic bond dissociation energy $D(A^+B^-)$ is the sum of the *bond dissociation energy*, $D(A-B)$, and the adiabatic *ionization energy* of the *radical* A· minus the *electron affinity* of the radical B·.

HETEROVALENT HYPERCONJUGATION

See *hyperconjugation*.

HIDDEN RETURN

See *ion-pair return*.

HOFMANN RULE

"The principal olefin formed in the decomposition of quaternary ammonium hydroxides that contain different primary alkyl groups is always ethylene, if an ethyl group is present." Originally given in this limited form by A. W. Hofmann, the rule has since been extended and modified as follows: "When two or more alkenes can be produced in a *β-elimination reaction*, the alkene having the smallest number of alkyl groups attached to the double bond carbon atoms will be the predominant product." This orientation described by the Hofmann rule is observed in elimination reactions of quaternary ammonium salts and tertiary sulfonium salts, and in certain other cases.

Hofmann (1851)

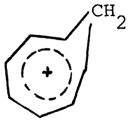
See also *Zaitsev rule*.

HOMO

See *frontier orbitals*.

HOMOAROMATIC

Whereas in an *aromatic* molecule there is continuous overlap of p-orbitals over a cyclic array of atoms, in a homoaromatic molecule there is a formal discontinuity in this overlap resulting from the presence of a single sp^3 hybridized atom within the ring; p-orbital overlap apparently bridges this sp^3 centre, and features associated with aromaticity are manifest in the properties of the compound. Pronounced homoaromaticity is not normally associated with neutral molecules, but mainly with species bearing a formal electrical charge, e.g., the "homotropylium" cation $C_8H_9^+$



In bis-, tris-, (etc.) homoaromatic species, two, three, (etc.) single sp^3 centres separately interrupt the π-electron system.

See also *homoconjugation*(2).

HOMOCONJUGATION

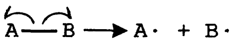
(1) Association between a base and its *conjugate acid* through a *hydrogen bond* ($B...HB^+$ or $AH...A^-$).

(2) The orbital overlap of two π-systems separated by a non-conjugating group, such as CH_2.

See also *homoaromatic*.

HOMOLYSIS

The cleavage of a *bond* ("homolytic cleavage" or "homolytic fission") so that each of the molecular fragments between which the bond is broken retains one of the bonding electrons. A *unimolecular* reaction involving homolysis of a bond (not forming part of a cyclic structure) in a *molecular entity* containing an even number of (paired) electrons results in the formation of two *radicals*:



$$A{-}B \longrightarrow A\cdot + B\cdot$$

It is the reverse of *colligation*. Homolysis is also commonly a feature of *bimolecular substitution reactions* (and of other reactions) involving radicals and molecules.

See also *bond dissociation energy, heterolysis.*

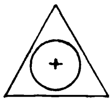
HOST

A *molecular entity* that forms *complexes* with organic or inorganic *guests*, or a *chemical species* that can accommodate guests within cavities of its crystal structure. Examples include *cryptands* and *crowns* (where there are ion-dipole attractions between heteroatoms and positive ions), *hydrogen-bonded* molecules that form "clathrates" (e.g. hydroquinone and water), and host molecules of *inclusion compounds* (e.g. urea or thiourea). *Van der Waals forces* bind the guest to the host molecule in clathrates and inclusion compounds.

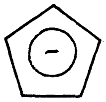
HÜCKEL (4*n* + 2) RULE

Monocyclic systems of trigonally hybridized atoms that contain $(4n+2)$ π-electrons (where n is a non-negative integer) will exhibit *aromatic* character.

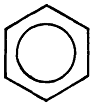
This rule is derived from the Hückel MO calculations on planar monocyclic conjugated hydrocarbons $(CH)_m$ where m is an integer equal to or greater than 3) according to which $(4n + 2)$ π-electrons are contained in a closed-shell system. Examples of systems that obey the Hückel rule include:



Cyclopropenyl
cation
(m=3, n=0)



Cyclopentadienyl
anion
(m=5, n=1)



Benzene

(m=6, n=1)

Systems containing $4n$ π-electrons (such as cyclobutadiene and the cyclopentadienyl cation) are "antiaromatic".

See also *conjugation, Möbius aromaticity.*

HYDRATION

Addition of water or of the elements of water (i.e. H and OH) to a *molecular entity*. For example, hydration of ethene:

$$H_2C{=}CH_2 + H_2O \longrightarrow CH_3CH_2OH$$

See also *aquation*.

HYDROGEN BOND

The hydrogen bond is a form of *association* between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. Both electronegative atoms are usually (but not necessarily) from the first row of the periodic table, i.e., N,O, or F. Hydrogen bonds may be *intermolecular* or *intramolecular*. With a few exceptions, usually involving fluorine, the associated energies are less than 20-25 kJ mol^{-1} (5-6 kcal mol^{-1}).

HYDROLYSIS

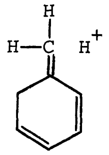
Solvolysis by water.

HYDROPHOBIC INTERACTION

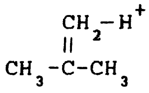
The tendency of hydrocarbons (or of *lipophilic* hydrocarbon-like groups in solutes) to form *intermolecular* aggregates in an aqueous *medium*, and analogous *intramolecular* interactions. The name arises from the attribution of the phenomenon to the apparent repulsion between water and hydrocarbons. The misleading alternative term "hydrophobic *bond*" is discouraged.

HYPERCONJUGATION

In the formalism that separates bonds into σ and π types, hyperconjugation is the interaction of σ-bonds with a π network. This interaction is customarily illustrated by *contributing structures*, e.g. for toluene (below), sometimes said to be an example of "heterovalent" or "sacrificial hyperconjugation", so named because the contributing structure contains one two-electron bond less than the normal *Lewis formula* for toluene.



The concept of hyperconjugation is also extended to *carbenium ions* and *radicals*, where the interaction is now between σ-bonds and an unfilled or partly filled π- or p-orbital. A contributing structure illustrating this for the *tert*-butyl cation is:



$$\begin{array}{c} CH_2\text{-}H^+ \\ \| \\ CH_3\text{-}C\text{-}CH_3 \end{array}$$

This is sometimes called an example of "isovalent hyperconjugation" (the contributing structure containing the same number of two-electron bonds as the normal Lewis formula).

Both structures shown are also examples of "no-bond resonance".

See also *sigma,pi*.

HYPSOCHROMIC

See *bathochromic*.

IDENTITY REACTION

A *chemcial reaction* whose products are chemically identical with the reactants.

See also *degenerate rearrangement*.

+ IMENE

See *nitrene*.

+ IMIDOGEN

See *nitrene*.

+ IMIDONIUM ION

See *nitrenium ion*.

+ IMIN

See *nitrene*.

+ IMINE RADICAL

See *nitrene*.

INCLUSION COMPOUND (or ***Inclusion complex***)

A *complex* in which one component (the *host*) forms a crystal lattice containing spaces in the shape of long tunnels or channels in which *molecular entities* of a second *chemical species* (the *guest*) are located. There is no bonding between guest and host, the attraction being generally due to *van der Waals forces*. If the spaces in the host lattice are enclosed on all sides so that the guest species are "trapped", as in a cage, such compounds are known as "clathrates" or "cage compounds".

INDUCTIVE EFFECT

An experimentally observable effect (on *rates of reaction*, etc.) of the transmission of charge through a chain of atoms by electrostatic induction. Although the term has been taken by some authors to include the *field effect*, there is a theoretical distinction between these two effects as models for the coulombic interaction between a given site within a *molecular entity* and a remote pole or dipole within the same entity, and various methods of experimental distinction have been discussed. Some effects called "inductive" in the older literature are now considered to be field effects.

See also *mesomeric effect*.

+ ***INDUCTOMERIC EFFECT*** (obsolescent)

A molecular *polarizability* effect occurring by the inductive mechanism of electron displacement.

See INGOLD (1953).

INERT

Stable and *unreactive*.

INHIBITION

The decrease in *rate of reaction* brought about by the addition of a substance (inhibitor), by virtue of its effect on the concentration of a reactant, *catalyst* or *reaction intermediate*. For example, molecular oxygen and *p*-benzoquinone can act as "inhibitors" in many reactions involving *radicals* as intermediates by virtue of their ability to act as *scavengers* towards these radicals.

If the rate of a reaction in the absence of inhibitor is v_0 and that in the presence of a certain amount of inhibitor is v, the degree of inhibition (i) is given by

$$i = (v_0 - v)/v_0$$

INITIATION

A reaction or process generating free *radicals* (or some other reactive *reaction intermediates* which then participate in a *chain reaction*. For example, in the chlorination of alkanes by a *radical mechanism* the initiation step is the *dissociation* of molecular chlorine.

INSERTION REACTION

A *chemical reaction* of the general type

$$\text{X-Z} + \text{Y} \longrightarrow \text{X-Y-Z}$$

in which a connecting atom or *group* Y replaces the bond joining the parts X and Z of the reactant XZ. An example is the *carbene* insertion reaction

$$R_3C\text{-}H + H_2C: \longrightarrow R_3C\text{-}CH_3$$

The reverse of an insertion reaction is called an *extrusion reaction*.

See also *α-addition*.

INTERMEDIATE

See *reaction intermediate*.

INTERMOLECULAR

(1) Descriptive of any process that involves a transfer (of atoms, *groups*, electrons, etc.) or of interactions between different *molecular entities*.

(2) Relating to a comparison between different molecular entities.

See also *intramolecular*.

INTERNAL ION-PAIR RETURN

See *ion-pair return*.

INTERNAL RETURN

See *ion-pair return*.

INTIMATE ION PAIR

See *ion pair*.

INTRAMOLECULAR

(1) Descriptive of any process that involves a transfer (of atoms, *groups*, electrons, etc.) or of interactions between different parts of the same *molecular entity*.

(2) Relating to a comparison between atoms or groups within the same molecular entity.

See also *intermolecular*.

INTRAMOLECULAR CATALYSIS

The acceleration of a chemical transformation at one site of a *molecular entity* through involvement of another functional ("catalytic") *group* in the same molecular entity, without that group appearing to have undergone change in the reaction product. The use of the term should be restricted to cases for which analogous *intermolecular catalysis* by *chemical species* bearing that catalytic group is observable. Intramolecular catalysis can be detected and expressed in quantitative form by a comparison of the reaction rate with that of a strictly comparable model compound in which the catalytic group is absent, or by measurement of the *effective molarity* of the catalytic group.

See also *neighbouring-group participation*.

INVERSE KINETIC ISOTOPE EFFECT

See *isotope effect*.

INVERSE MICELLE

See *inverted micelle*

INVERTED MICELLE

The reversible formation of association colloids from surfactants in non-polar solvents leads to aggregates termed inverted (or inverse, reverse, or reversed) *micelles*. Such association is often of the type

$$\text{Monomer} \rightleftharpoons \text{Dimer} \rightleftharpoons \text{Trimer} \rightleftharpoons \ldots\ldots \rightleftharpoons n\text{-mer}$$

and the phenomenon of *critical micelle concentration* (or an analogous effect) is consequently not observed.

In an inverted micelle the *polar groups* of the surfactants are concentrated in the interior and the *lipophilic* groups extend towards and into the non-polar solvent.

ION PAIR

A pair of oppositely charged ions held together by coulombic attraction without formation of a covalent *bond*. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc.

Following Bjerrum, oppositely charged ions with their centres closer together than a distance

$$q = (8.36 \times 10^6\ z_+z_-/\epsilon_r T)\ \mathrm{pm}$$

are considered to constitute an ion pair ("Bjerrum ion pair"). [z_+z_- are the charges of the ions, and ϵ_r is the relative permittivity (or dielectric constant) of the medium.]

An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule), is designated as a "tight ion pair" (or "intimate" or "contact ion pair"). A tight ion pair of X^+ and Y^- is symbolically represented as X^+Y^-.

By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a "loose ion pair", symbolically represented as $X^+ \| Y^-$. The members of a loose ion pair can readily interchange with other free or loosely paired ions in the solution. This interchange may be detectable (e.g., by isotopic labelling) and thus afford an experimental distinction between tight and loose ion pairs.

A further conceptual distinction has sometimes been made between two types of loose ion pairs. In "solvent-shared ion pairs" the ionic constituents of the pair are separated by only a single solvent molecule, whereas in "solvent-separated ion pairs" more than one solvent molecule intervenes. However, the term "solvent-separated ion pair" must be used and interpreted with care since it has also widely been used as a less specific synonym for "loose ion pair".

See also *common-ion effect, dissociation, ion-pair return*.

ION-PAIR RETURN

The combination of a pair of ions to re-form the corresponding covalent *molecular entity*.

If the ions are paired as a tight *ion-pair* and re-combine without prior separation into a loose ion pair, this is called "internal ion-pair return":

$$\begin{array}{ccc} R^+Z^- & \rightleftharpoons & RZ \\ \text{tight ion} & & \text{covalent} \\ \text{pair} & & \text{molecule} \end{array}$$

It is a special case of "primary *geminate recombination*".

If the ions are paired as a loose ion pair and form the covalent chemical species via a tight ion pair, this is called "external ion-pair return":

$$\begin{array}{ccccc} R^+ \| Z^- & \rightleftharpoons & R^+Z^- & \rightleftharpoons & RZ \\ \text{loose ion} & & \text{tight ion} & & \text{covalent} \\ \text{pair} & & \text{pair} & & \text{molecule} \end{array}$$

It is a special case of "secondary geminate recombination".

When the covalent molecule RZ is re-formed without partial racemization (if the group R is suitably chiral) or without other direct evidence of prior formation of a tight ion pair, the internal ion-pair return is sometimes called a "hidden return".

External ion-pair return is to be distinguished from "external ion return", the (reversible) process whereby dissociated ion are converted into loose ion pairs:

$$R^+ + Z^- \longrightarrow R^+ \| Z^-$$

IONIZATION

The generation of one or more ions. It may occur, e.g., by loss of an electron from a neutral *molecular entity*, by the *unimolecular heterolysis* of such an entity into two or more ions, or by a heterolytic *substitution reaction* involving neutral molecules, such as

$$CH_3CO_2H + H_2O \longrightarrow H_3O^+ + CH_3CO_2^-$$

$$Ph_3CCl + AlCl_3 \longrightarrow Ph_3C^+ + AlCl_4^-$$

$$Ph_3CCl \longrightarrow Ph_3C^+Cl^- \quad (\textit{ion pair}, \text{ in benzene})$$

The loss of an electron from a singly, doubly, etc. charged cation is called second, third, etc. ionization. This terminology is used especially in mass spectrometry.

See also *ionization energy*.

IONIZATION ENERGY

The minimum energy required to remove an electron from an isolated *molecular entity* (in its vibrational ground state) in the gaseous phase. If the resulting molecular entity is considered to be in its vibrational ground state, one refers to the energy as the "adiabatic ionization energy". If the molecular entity produced possesses the vibrational energy determined by the Franck-Condon principle (according to which the electron ejection takes place without an accompanying change in molecular geometry), the energy is called the "vertical ionization energy". The name ionization energy is preferred to the somewhat misleading earlier name "ionization potential".

See also *ionization*.

IONIZATION POTENTIAL

See *ionization energy*.

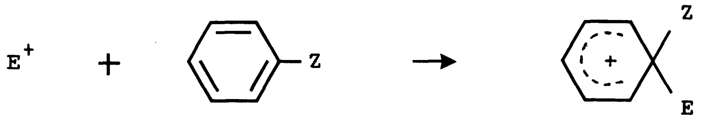
IONIZING POWER

A qualitative term to denote the tendency of a particular solvent to promote *ionization* of an uncharged solute. The term has been used both in a kinetic and in a thermodynamic context. (It should be noted that ionization is not synonymous with *dissociation*.)

See also *Grunwald-Winstein equation*.

IPSO-ATTACK

The attachment of an entering group to a position in an *aromatic* compound already carrying a *substituent group* (other than hydrogen). The entering group may displace that substituent group but may also itself be expelled or migrate to a different position in a subsequent step. For example:



where E^+ is an *electrophile* and Z is a substituent (other than hydrogen).

ISOENTROPIC

A reaction series is said to be isoentropic if the individual reactions of the series have the same *entropy of activation*.

ISOKINETIC RELATIONSHIP

When a series of structurally related substrates undergo the same general reaction or when the reaction conditions for a single substrate are changed in a systematic way, the *enthalpies* and *entropies of activation* sometimes satisfy the relation

$$\Delta H^{\ddagger} - \beta \Delta S^{\ddagger} = \text{constant}$$

where the parameter β is independent of temperature. This equation (or some equivalent form) is said to represent an "isokinetic relationship". The temperature $T = \beta$ (at which all substrates of a series obeying the isokinetic relationship react at the same rate) is termed the "isokinetic temperature".

See LEFFLER (1955).

ISOMERIZATION

A *chemical reaction*, the principal product of which is isomeric with the principal reactant. An *intramolecular* isomerization that involves the breaking and making of bonds is a special case of a *molecular rearrangement*. Isomerization does not necessarily imply molecular rearrangement (e.g., in the case of the interconversion of conformational isomers).

ISOSBESTIC POINT

This term is usually employed with reference to a set of absorption spectra, plotted on the same chart for a set of solutions in which the sum of the concentrations of two principal absorbing components, A and B, is constant. The curves of absorbance against wavelength (or frequency) for such a set of mixtures often all intersect at one or more points, called isosbestic points.

Isosbestic points are commonly met when electronic spectra are taken (a) on a solution in which a *chemical reaction* is in progress (in which case the two absorbing components concerned are a reactant and a product, A + B), or (b) on a solution in which the two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component, typically the concentration of hydrogen ions (e.g., an acid-base indicator equilibrium $A \rightleftharpoons B + H^{+}_{aq}$). The effect may also appear (c) in the spectra of a set of solutions of two unrelated non-interacting components having the same total concentration. In all these examples, A (and/or B) may be either a single *chemical species* or a mixture of chemical species present in an invariant proportion.

If A and B are single chemical species, isosbestic points will appear at all wavelengths at which their molar absorption coefficients (formerly called extinction coefficients) are the same. (A more involved identity applies when A and B are mixtures of constant proportion.)

If absorption spectra of the types considered above intersect not at one or more isosbestic points but over a range of wavelengths, this is prima facie evidence in case (a) for the formation of a *reaction intermediate* in substantial concentration ($A \rightarrow C \rightarrow B$), in case (b) for the involvement of a third absorbing species in the equilibrium, e.g.

$$A \rightleftharpoons B + H^{+}_{aq} \rightleftharpoons C + 2H^{+}_{aq},$$

or in case (c) for some interaction of A and B (e.g., $A + B \rightleftharpoons C$).

ISOTOPE EFFECT

The ratio of the rate or equilibrium constants of two reactions that differ only in the isotopic composition of one or more of their otherwise chemically identical components, i.e. $k_{\mathrm{light}}/k_{\mathrm{heavy}}$ ("kinetic isotope effect") and $K_{\mathrm{light}}/K_{\mathrm{heavy}}$ ("equilibrium isotope effect"). The use of the reciprocal ratios to express isotope effects is discouraged.

A distinction can be made between *intermolecular* isotope effects (when a comparison is made between isotopically different reactant *molecular entities*) and *intramolecular* isotope effects (when the different isotopes occupy chemically equivalent alternative reactive sites within the same molecular entity, so that the reaction results in isotopically distinguishable products).

A kinetic isotope effect is termed "normal" or "inverse" according to whether $k_{\mathrm{light}}/k_{\mathrm{heavy}}$ is larger or smaller than unity. (The use of the term "normal" must not be interpreted too literally: inverse isotope effects are the "norm" for certain types of reaction.)

The absence of isotopic discrimination for rate or equilibrium constants ($k_{light}/k_{heavy} = 1$ or $K_{light}/K_{heavy} = 1$) is, strictly speaking, a "unity isotope effect". It is more commonly thought of as a "null isotope effect", on the grounds that there is zero isotopic effect on the corresponding standard Gibbs energy change, i.e. that an isotope <u>effect</u> exists only when the ratio of rate or equilibrium constants differs from unity.

A kinetic isotope effect attributable to isotopic substitution of an atom to which a *bond* is made or broken in the *rate-limiting step* or in a *pre-equlibrium* step of a specified reaction is termed a "primary kinetic isotope effect". For example, $k_B/k_{B'}$, is the primary kinetic isotope effect for the reactions

$$\text{A-B} + \text{C} \xrightarrow{k_B} \text{A} + \text{B-C}$$

$$\text{A-B'} + \text{C} \xrightarrow{k_{B'}} \text{A} + \text{B'-C}$$

where B and B' are the light and heavy isotopes, respectively. The corresponding isotope effect on the equilibrium constant of such a reaction is called a "primary equlibrium isotope effect".

A kinetic isotope effect attributable to isotopic substitution of an atom to which bonds are neither made nor broken in the rate-limiting step or in a pre-equilibrium of a specified reaction is termed a "secondary kinetic isotope effect". For example, $k_D/k_{D'}$, is a secondary kinetic isotope effect for the reactions:

$$\text{D-A-B} + \text{C} \xrightarrow{k_D} \text{D-A} + \text{B-C}$$

$$\text{D'-A-B} + \text{C} \xrightarrow{k_{D'}} \text{D'-A} + \text{B-C}$$

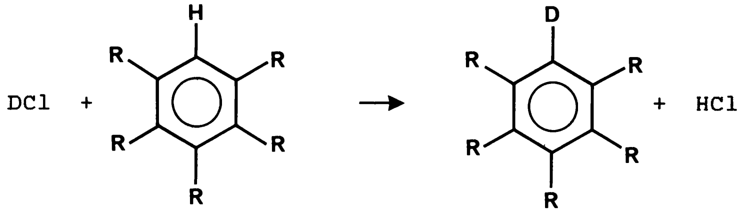
where D and D' are the light and heavy isotopes, respectively. One speaks of α, β (etc.) secondary isotope effects where α, β (etc.) denote the position of isotopic substitution relative to the reaction centre. The corresponding isotope effect on the equilibrium constant of such a reaction is called a "secondary equilibrium isotope effect".

A "solvent isotope effect" is any kinetic or equilibrium isotope effect resulting from a change in the isotopic composition of the solvent.

See also *fractionation factor*.

ISOTOPE EXCHANGE

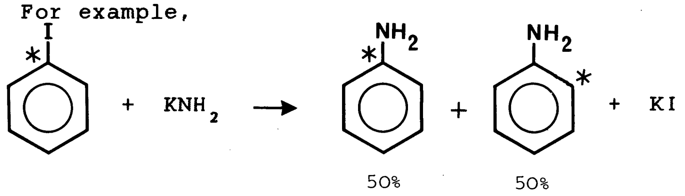
A *chemical reaction* in which the reactant and product *chemical species* are chemically identical but have different isotopic composition. In such a reaction the isotope distribution tends towards equilibrium (as expressed by *fractionation factors*) as a result of transfers of isotopically different atoms or *groups*. For example,



ISOTOPIC SCRAMBLING

The approach to or achievement of an equilibrium distribution of isotopes within a specified set of atoms in a *chemical species* or group of chemical species. For example,

(a)



(b) $(PhN^{*}{\equiv}N)^{+} \longrightarrow (PhN^{*}{\equiv}N)^{+} + (PhN{\equiv}N^{*})^{+}$

(* denotes position of an isotopically different atom)

See also *fractionation factor*.

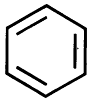
ISOVALENT HYPERCONJUGATION

See *hyperconjugation*.

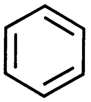
KEKULÉ STRUCTURE *(for aromatic compounds)*

One of the *contributing structures* of an *aromatic molecular entity* (such as benzene), with fixed alternating single and double bonds, in which interactions between multiple bonds are assumed to be absent.

For benzene,



and



are the Kekulé structures.

KINETIC CONTROL *(of product composition)*

The term characterizes conditions (including reaction times) that lead to reaction products in a proportion governed by the relative rates of the parallel (forward) reactions leading to their formation.

See also *thermodynamic control*.

KINETIC ELECTROLYTE EFFECT ***(Kinetic ionic strength effect)***

The general effect of an added electrolyte (i.e. an effect other than, or in addition to, that due to its possible involvement as a reactant or *catalyst*) on the observed rate constant of a reaction in solution. At low concentrations (when only long-range coulombic forces need to be considered) the effect on a given reaction is determined only by the ionic strength

$I = (1/2) \sum c_i z_i^2$ (c_i = concentration, z_i = charge, for ion i)

of the solution and not by the chemical identity of the ions. For practical purposes, this concentration range is roughly the same as the region of validity of the Debye-Hückel limiting law for activity coefficients. At higher concentrations, the effect of an added electrolyte depends also on the chemical identity of the ions. Such specific action can usually be interpreted as the incursion of *reaction paths* involving an ion of the electrolyte as reactant or catalyst, in which case the action is not properly to be regarded just as a kinetic electrolyte effect.

Kinetic electrolyte effects are sometimes (too restrictively and therefore incorrectly) referred to as kinetic "salt effects".

A kinetic electrolyte effect ascribable solely to the influence of the ionic strength on activity coefficients of ionic reactants and transition states is called a "primary kinetic electrolyte effect"

A kinetic electrolyte effect arising from the influence of the ionic strength of the solution upon the *pre-equilibrium* concentration of an ionic species that is involved in a subsequent *rate-limiting step* of a reaction is called a "secondary kinetic electrolyte effect". A common case encountered in practice is the effect on the concentration of hydrogen ion (acting as catalyst) produced from the *ionization* of a weak acid in a buffer solution.

See also *common ion effect, order of reaction*.

KINETIC EQUIVALENCE

Two reaction schemes are kinetically equivalent if they imply the same *rate law*.

For example, consider the two schemes (i) and (ii) for the formation of C from A:

$$\text{(i)}\quad \mathrm{A} \underset{k_{-1},\ \mathrm{OH}^-}{\overset{k_1,\ \mathrm{OH}^-}{\rightleftharpoons}} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

Providing that B does not accumulate as a *reaction intermediate*

$$\frac{d[\mathrm{C}]}{dt} = \frac{k_1 k_2\,[\mathrm{A}][\mathrm{OH}^-]}{k_2 + k_{-1}\,[\mathrm{OH}^-]} \qquad \ldots\ldots\ (1)$$

$$\text{(ii)}\quad \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \xrightarrow[\mathrm{OH}^-]{k_2} \mathrm{C}$$

Providing that B does not accumulate as a reaction intermediate

$$\frac{d[\mathrm{C}]}{dt} = \frac{k_1 k_2\,[\mathrm{A}][\mathrm{OH}^-]}{k_{-1} + k_2[\mathrm{OH}^-]} \qquad \ldots\ldots\ (2)$$

Both equations for d[C]/d*t* (rate laws) are of the form:

$$\frac{d[\mathrm{C}]}{dt} = \frac{r[\mathrm{A}][\mathrm{OH}^-]}{1 + s[\mathrm{OH}^-]} \qquad \ldots\ldots\ (3)$$

where r and s are constants (sometimes called "coefficients in the rate equation"). They are identical in their dependence on concentrations and do not distinguish whether OH^- catalyses the formation of B or is involved in its further transformation to C. The two schemes are therefore kinetically equivalent under conditions to which the stated provisos apply.

KINETIC ISOTOPE EFFECT

See *isotope effect*.

KOSOWER Z-VALUE

See *Z-value*.

LABILE

The term has loosely been used to describe either a relatively *unstable* and *transient chemical species* or (less commonly) a relatively *stable* but *reactive* species. It must therefore not be used without explanation of the intended meaning, and is best avoided altogether.

LEAST NUCLEAR MOTION, PRINCIPLE OF

The hypothesis that, for given reactants, the reactions involving the smallest change in nuclear positions will have the lowest *energy of activation*.

(It is also often simply referred to as principle of least motion.)

See HINE (1977).

LEAVING GROUP

An atom or *group* (charged or uncharged) that becomes detached from an atom in what is considered to be the residual or main part of the *substrate* in a specified reaction.

For example, in the heterolytic *solvolysis* of benzyl bromide in acetic acid

$$PhCH_2Br + AcOH \longrightarrow PhCH_2OAc + HBr$$

the leaving group is Br^-; in the reaction

$$MeS^- + PhCH_2\overset{+}{N}Me_3 \longrightarrow MeSCH_2Ph + Me_3N$$

it is Me_3N; in the *electrophilic* nitration of benzene, it is H^+. The term has meaning only in relation to a specified reaction. The leaving group is not, in general, the same as the *substituent group* present in the substrate (e.g. bromine and trimethylammonio in the substrates of the first two examples above).

A slightly different usage of the term prevails in the (non-mechanistic) naming of *transformations*, where the actual substituent group present in the substrate (and also in the product) is referred to as the leaving group.

See also *electrofuge, entering group, nucleofuge*.

LEFFLER'S ASSUMPTION

See *Hammond principle*.

LEVELLING EFFECT

The tendency of a solvent to make all *Brønsted acids* whose *acidity* exceeds a certain value appear equally acidic. It is due to the complete transfer to a *protophilic* solvent of a proton from a dissolved acid stronger than the conjugate acid of the solvent. The only acid present to any significant extent in all such solutions is the *lyonium ion*. For example, the solvent water has a levelling effect on the acidities of $HClO_4$, HCl, and HI: aqueous solutions of these acids at the same (moderately low) concentrations have the same acidities. A corresponding levelling effect applies to strong bases in *protogenic* solvents.

LEWIS ACID

A *molecular entity* (and the corresponding *chemical species*) that is an electron-pair acceptor and therefore able to react with a *Lewis base* to form a *Lewis adduct*, by sharing the electron pair furnished by the Lewis Base. For example:

$$\underset{\text{Lewis acid}}{Me_3B} \quad + \quad \underset{\text{Lewis base}}{:NH_3} \quad \longrightarrow \quad \underset{\text{Lewis adduct}}{Me_3\overset{-}{B}\text{-}\overset{+}{N}H_3}$$

See also *co-ordination, dipolar bond*.

LEWIS ACIDITY

The thermodynamic tendency of a substance to act as a *Lewis acid*. Comparative measures of this property are provided by the equilibrium constants for *Lewis adduct* formation of a series of Lewis acids with a common reference *Lewis base*.

See also *electrophilicity*.

LEWIS ADDUCT

The *adduct* formed between a *Lewis acid* and a *Lewis base*.

LEWIS BASE

A *molecular entity* (and the corresponding *chemical species*) able to provide a pair of electrons and thus capable of *co-ordination* to a *Lewis acid*, thereby producing a *Lewis adduct*.

LEWIS BASICITY

The thermodynamic tendency of a substance to act as a *Lewis base*. Comparative measures of this property are provided by the equilibrium constants for *Lewis adduct* formation for a series of Lewis bases with a common reference *Lewis acid*.

See also *nucleophilicity*.

LEWIS FORMULA (Electron dot or *Lewis structure)*

Molecular structures in which the valency electrons are shown as dots so placed that one pair of dots represents two electrons or one (single) covalent *bond* between two atoms, e.g. $\mathrm{H}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}{:}$. A double bond is represented by two pairs of dots etc. Dots representing non-bonded outer-shell electrons are placed adjacent to the atoms with which they are associated. Formal charges (e.g. +, −, 2+, etc.) are attached to atoms to indicate the difference between the positive nuclear charge (atomic number) and the total number of electrons (including those in inner shells), on the formal basis that bonding electrons are shared equally between the atoms they join. (Bonding pairs of electrons are sometimes denoted by lines, representing bonds, as in *line formulae*.)

LIFE-TIME

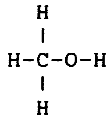
See *mean life-time, half-life*.

LIGAND

If it is possible to indicate a "central" atom in a polyatomic *molecular entity*, the atoms or *groups* bound to that atom are called ligands. (Cf. IUPAC INORGANIC RULES (1970); Rule 2.24). The term is generally used in connection with metallic "central" atoms.

LINE FORMULA

A two-dimensional representation of *molecular entities* in which atoms are shown joined by lines representing single *bonds*, without any indication or implication concerning the spatial direction of bonds. For example, methanol is represented as



$$\begin{array}{ccccccc} & & \mathrm{H} & & & & \\ & & | & & & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{H} \\ & & | & & & & \\ & & \mathrm{H} & & & & \end{array}$$

(The term should not be confused with the representation of chemical formulae by the "Wiswesser line notation", a method of string notation. Formulae in this notation are also known as "Wiswesser line formulae".)

LINEAR GIBBS ENERGY RELATION

A linear correlation between the logarithm of a rate constant or equilibrium constant for one series of reactions with the logarithm of the rate constant or equilibrium constant for a related series of reactions. Typical examples of such relations (frequently still known as "linear free energy relations") are the *Brønsted relation*, and the Hammett $\rho\sigma$ equation (see *σ-value*).

The name arises because the logarithm of an equilibrium constant (at constant temperature and pressure) is proportional to a standard Gibbs energy change, and the logarithm of a rate constant is a linear function of a *Gibbs energy of activation*.

LINEWEAVER-BURK PLOT

See *Michaelis-Menten kinetics*.

LIPOPHILIC

Literally, "fat-loving". Applied to *molecular entities* (or parts of molecular entities) having a tendency to dissolve in fat-like (e.g. hydrocarbon) solvents.

See also *hydrophobic interaction*.

LOOSE ION PAIR

See *ion pair*.

LUMO

See *frontier orbitals*.

LYATE ION

The anion produced by proton loss from a solvent molecule. For example, the hydroxide ion is the lyate ion of water.

LYONIUM ION

The cation produced by protonation of a solvent molecule. For example, $CH_3OH_2^+$ is the lyonium ion in methanol solution.

MACROSCOPIC DIFFUSION CONTROL

The limitation of the *rate of reaction* for a reaction in solution by the rate of mixing by diffusion of solutions of the two reactants. It can occur even when the reaction *rate constant* is several powers of ten less than for an *encounter-controlled rate*. Analogous (and even more important) effects of the limitation of reaction rates by the speed of mixing are encountered in heterogeneous (solid/liquid, solid/gas, liquid/gas) systems.

See also *microscopic diffusion control*.

'MAGIC ACID'

See *superacid*.

MARKOVNIKOV RULE

"In the addition of hydrogen halides to unsymmetrically constituted [unsaturated] hydrocarbons, the halogen atom becomes attached to the carbon bearing the lesser number of hydrogen atoms." Originally formulated by Markovnikov (Markownikoff) to generalize the orientation in additions of hydrogen halides to simple alkenes, this rule has been extended to polar *addition reactions* as follows. "In the *heterolytic* addition of a polar molecule to an alkene or alkyne, the more electronegative atom (or part) of the polar molecule becomes attached to the carbon atom bearing the smaller number of hydrogen atoms."

This rule has also been cast in semi-mechanistic terms as stating that the more electropositive part of the polar molecule becomes attached to the end of the multiple bond that would result in the more stable *carbenium ion* (whether or not a carbenium ion is actually formed as a *reaction intermediate* in the addition reaction). Addition in the opposite sense is commonly called "anti-Markovnikov addition", and has been observed especially when the reaction involves *homolysis* of the polar molecule.

MARKOWNIKOFF (1870)

MEAN LIFE-TIME

The average life-time of the *molecular entities* of a specified *chemical species*.

In a system at equilibrium the mean life-time τ (which governs and may be measured by spectral line broadening) of the molecular entities of a specific chemical species is given by the number of molecular entities (in a specified state or form) divided by the number of molecular entities leaving that state or form per unit time.

For a reacting system in which the decrease in concentration of a particular chemical species is governed by a first-order *rate law*, τ is the time taken for the concentration of that chemical species to fall to 1/e of its initial value. The mean-life time is then equal to the reciprocal of the sum of rate constants for all concurrent first-order reactions, i.e. $\tau = 1/\Sigma k$.

See also *chemical relaxation, half-life, rate of reaction.*

MECHANISM

A detailed description of the pathway leading from the reactants to the products of a reaction, including as complete a characterization as possible of the composition, structure and other properties of *reaction intermediates* and *transition states*. An acceptable mechanism of a specified reaction (and there may be a number of such alternative mechanisms not excluded by the evidence) must be consistent with the reaction stoichiometry, the *rate law*, and with all other available experimental data, such as the stereochemical course of the reaction. Inferences concerning the electronic and nuclear motions which dynamically interconvert successive species along the reaction path (as represented by curved arrows, for example) are often included in the description of a mechanism.

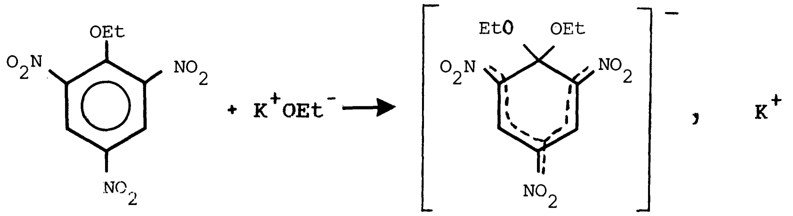
See also *Gibbs energy diagram*.

MEDIUM

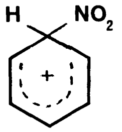
The phase (and composition of the phase) in which *chemical species* and their reactions are studied in a particular investigation.

MEISENHEIMER ADDUCT

A cyclohexadienyl derivative formed as *Lewis adduct* from a *nucleophile (Lewis base)* and an *aromatic* or heteroaromatic compound. In earlier usage the term "Meisenheimer complex" was restricted to the typical Meisenheimer alkoxide *adducts* of nitro-substituted aromatic ethers, e.g.,



Analogous cationic adducts, such as



considered to be *reaction intermediates* in *electrophilic* aromatic *substitution reactions*, are called "Wheland intermediates".

See also *σ-adduct*.

MESOMERIC EFFECT

The experimentally observable effect (on reaction rates, etc.) of a substituent due to the overlap of its p- or π-orbital with the p- or π-orbitals of the rest of the *molecular entity*. *Delocalization* is thereby introduced or extended, and electronic charge may flow to or from the substituent.

See also *field effect*, *inductive effect*.

See INGOLD (1953).

MESOMERISM

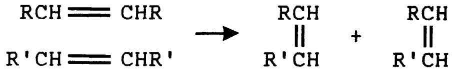
Essentially synonymous with *resonance*. The term is particularly associated with the picture of π-electrons as less localized in an actual molecule than in a *Lewis formula*.

The term is intended to imply that the correct representation of a structure is intermediate between two or more Lewis formulae.

See also *aromatic*(2), *delocalization*.

METATHESIS

A *bimolecular* process formally involving the exchange of a *bond* (or bonds) between similar interacting *chemical species* such that the bonding affiliations in the products are identical (or closely similar) to those in the reactants. For example:



$$\begin{matrix}\mathrm{RCH{=}CHR} \\ \mathrm{R'CH{=}CHR'}\end{matrix} \longrightarrow \begin{matrix}\mathrm{RCH} \\ \| \\ \mathrm{R'CH}\end{matrix} + \begin{matrix}\mathrm{RCH} \\ \| \\ \mathrm{R'CH}\end{matrix}$$

(The term has its origin in inorganic chemistry but this older usage is not applicable in organic chemistry.)

METHYLENE

See *carbene*.

METHYLIDYNE

See *carbyne*.

MICELLAR CATALYSIS

The acceleration of a *chemical reaction* in solution by the addition of a surfactant so that the reaction can proceed in the environment of surfactant aggregates. (Rate enhancements may be due to, for example, higher concentration of reactants in that environment, more favourable orientation and solvation of the species, enhanced rate constants in the micellar pseudophase of the surfactant aggregate.)

See also *catalyst*.

MICELLE

See IUPAC MANUAL APPENDIX II (1972).

MICHAELIS-MENTEN KINETICS

The dependence of an initial *rate of reaction* upon the concentration of a *substrate* [S] that is present in large excess over the concentration of an enzyme or other *catalyst* (or reagent) E with the appearance of saturation behaviour following the Michaelis-Menten equation,

$$v = V[\mathrm{S}]/(K_\mathrm{m} + [\mathrm{S}]),$$

where v is the observed initial rate, V is its limiting value at substrate saturation (i.e., $[\mathrm{S}] \gg K_\mathrm{m}$), and K_m the substrate concentration when $v = V/2$. The definition is experimental, i.e. it applies to any reaction that follows an equation of this general form. The symbols V_max or v_max are sometimes used for V.

The parameters V and K_m (the "Michaelis constant") of the equation can be evaluated from the slope and intercept of a linear plot of v^{-1} against $[\mathrm{S}]^{-1}$ (a "Lineweaver-Burk plot").

A Michaelis-Menten equation is also applicable to the condition where E is present in large excess, in which case the concentration [E] appears in the equation instead of [S].

The term has sometimes been used to describe reactions that proceed according to the scheme

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_{cat}} \text{Products}$$

in which case $K_m = (k_{-1} + k_{cat})/k_1$ (Briggs-Haldane conditions). It has more usually been applied only to the special case in which $k_{-1} \gg k_{cat}$ and $K_m = k_{-1}/k_1 = K_s$; in this case K_m is a true dissociation constant (Michaelis-Menten conditions).

MICROSCOPIC CHEMICAL EVENT

See *chemical reaction*, *molecularity*.

MICROSCOPIC DIFFUSION CONTROL (Encounter control)

The observable consequence of the limitation that the rate of a *chemical reaction* in a homogeneous *medium* cannot exceed the rate of encounter of the reacting *molecular entities*.

If (hypothetically) a *bimolecular* reaction in a homogeneous medium occurred instantaneously when two reactant molecular entities made an encounter, the rate of the reaction would be an *encounter-controlled rate*, determined solely by rates of diffusion of the reactants. Such a hypothetical "fully diffusion-controlled rate" is also said to correspond to "total microscopic diffusion control", and represents the asymptotic limit of the *rate of reaction* as the *rate constant* for the chemical conversion of the *encounter pair* into product (or products) becomes infinitely large.

"Partial microscopic diffusion control" is said to operate in a homogeneous reaction when the rates of chemical conversion and of encounter are comparable. (The degree of microscopic diffusion control cannot usually be determined with any precision.)

See also *macroscopic diffusion control*.

MICROSCOPIC REVERSIBILITY, PRINCIPLE OF

"At equilibrium, any microscopic chemical event occurs with the same frequency as the reverse of that event."

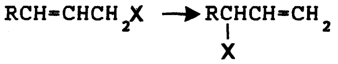
See also *chemical reaction*, *detailed balancing*.

MIGRATION

(1) The (usually *intramolecular*) transfer of an atom or *group* during the course of a *molecular rearrangement*.

(2) The movement of a *bond* to a new position, within the same *molecular entity*, is known as "bond migration".

Allylic rearrangements, e.g.,



$$RCH{=}CHCH_2X \rightarrow RCHCH{=}CH_2 \text{ (with X below the first CH)}$$

exemplify both types of migration.

MINIMUM STRUCTURAL CHANGE, PRINCIPLE OF

See *molecular rearrangement*.

MÖBIUS AROMATICITY

A monocyclic array of orbitals in which there is a single out-of-phase overlap (or, more generally, an odd number of out-of-phase overlaps) reveals the opposite pattern of *aromatic* character to Hückel systems; with 4*n* electrons it is stabilized (aromatic), whereas with 4*n* + 2 it is destabilized (antiaromatic). No examples of ground state Möbius systems are known, but the concept has been applied to *transition states* of *pericyclic reactions* [see *aromatic*(3)].

The name is derived from the topological analogy of such an arrangement of orbitals to a Möbius strip.

HEILBRONNER (1964), ZIMMERMAN (1971).

See also *Hückel (4n + 2) rule.*

MOLECULAR ENTITY

Any chemically or isotopically distinct atom, molecule, ion, *ion pair*, *radical*, *radical ion*, *complex*, conformer etc., capable of identification as a separately distinguishable entity.

It depends on the context with what degree of precision a molecular entity is to be described. For example, "hydrogen molecule" is an adequate definition of a certain molecular entity for some purposes, whereas for others it is necessary to distinguish the electronic state and/or vibrational state and/or nuclear spin, etc. of the hydrogen molecule.

See also *chemical species*.

MOLECULAR ORBITAL

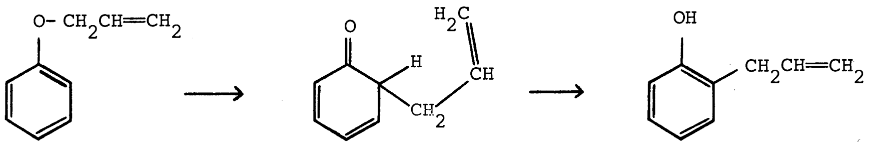
A one-electron wave function describing an electron moving in the effective field provided by the nuclei and all other electrons of a *molecular entity* of more than one atom. Such molecular orbitals can be transformed in prescribed ways into component functions to give "localized molecular orbitals". Molecular orbitals can also be described, in terms of the number of nuclei (or "centres") encompassed, as two-centre, multi-centre, etc., molecular orbitals.

An orbital is usually depicted by sketching contours on which the wave function has a constant value (contour map) or by indicating schematically the envelope of the region of space in which there is an arbitrarily fixed high (say 95%) probability of finding the electrons occupying the orbital, giving also the algebraic sign (+ or −) of the wave function in each part of that region.

MOLECULAR REARRANGEMENT

The term is traditionally applied to any reaction that violates the so-called "principle of minimum structural change". According to this over-simplified hypothesis, *chemical species* do not isomerize in the course of a *transformation*, i.e. a *substitution reaction* or the change of a functional *group* of a chemical species into a different functional group does not involve the making or breaking of more than the minimum number of *bonds* required to effect that transformation. For example, any new substituents should enter the precise positions previously occupied by displaced groups.

The simplest type of rearrangement is an *intramolecular* reaction in which the product is isomeric with the reactant (one type of "intramolecular isomerization"). An example is the first step of the Claisen rearrangement:



The definition of molecular rearrangement also includes changes in which there is a *migration* of an atom or bond (unexpected on the basis of the principle of minimum structural change), as in the reaction

$$CH_3CH_2CH_2Br + AgOAc \longrightarrow (CH_3)_2CHOAc + AgBr$$

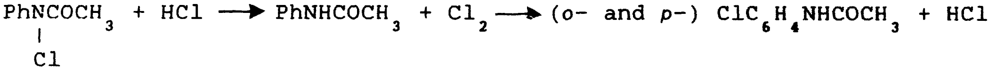
where the *rearrangement stage* can formally be represented as the "1,2-shift" of hydride between adjacent carbon atoms in the *carbenium ion*

$$\mathrm{CH_3CH_2\overset{+}{C}H_2 \longrightarrow CH_3\overset{+}{C}HCH_3}$$

as well as reactions in which an *entering group* takes up a different position from the *leaving group*, with accompanying "bond migration". An example of the latter type is the "allylic rearrangement":

$$\mathrm{(CH_3)_2C{=}CHCH_2Br + OH^- \longrightarrow (CH_3)_2C(OH)CH{=}CH_2 + Br^-}$$

A distinction is made between "intramolecular rearrangements" (or "true molecular rearrangements") and "*intermolecular* rearrangements" (or "apparent rearrangements"). In the former case the atoms and groups that are common to a reactant and a product never separate into independent fragments during the rearrangement stage (i.e., the change is intramolecular), whereas in an "intermolecular rearrangement a migrating group is completely free from the parent molecule and is re-attached to a different position in a subsequent step, as in the Orton reaction:



$$\mathrm{Ph\underset{\underset{\displaystyle Cl}{|}}{N}COCH_3 + HCl \longrightarrow PhNHCOCH_3 + Cl_2 \longrightarrow (\mathit{o}\text{- and }\mathit{p}\text{-})\ ClC_6H_4NHCOCH_3 + HCl}$$

MOLECULARITY

The number of reactant *molecular entities* that are involved in the "microscopic chemical event" constituting an *elementary reaction*. (For reactions in solution this number is always taken to exclude molecular entities that form part of the *medium* and which are involved solely by virtue of their *solvation* of solutes.) A reaction with a molecularity of <u>one</u> is called "unimolecular", one with a molecularity of <u>two</u> "bimolecular" and of <u>three</u> "termolecular".

See also *chemical reaction, order of reaction*.

MULTI-CENTRE BOND

Representation of some *molecular entities* solely by localized two-electron two-centre *bonds* appears to be unsatisfactory. Instead, multi-centre bonds have to be considered in which electron pairs occupy orbitals encompassing three or more atomic centres. Examples include the three-centre bonds in diborane, the delocalized π-bonding of benzene, and *bridged carbocations*.

MULTI-CENTRE REACTION

A synonym for *pericyclic reaction*. The number of "centres" is the number of atoms in the *transition state* that are breaking old single *bonds* and/or forming new bonds to atoms to which they were not previously bonded. This number does not necessarily correspond to the ring size of the transition state for the pericyclic reaction. Thus, a Diels-Alder reaction is a "four-centre reaction". This terminology has largely been superseded by the more detailed one developed for the various pericyclic reactions.

See *cycloaddition, sigmatropic rearrangement*.

MULTIDENT

See *ambident.*

NARCISSISTIC REACTION

A *chemical reaction* that can be described as the conversion of a reactant into its mirror image, without rotation or translation of the product, so that the product enantiomer actually coincides with the image of the reactant molecule with respect to a fixed mirror plane. Examples of such reactions are cited under the entries *fluxional* and *degenerate rearrangement*.

SALEM (1971).

NEIGHBOURING-GROUP PARTICIPATION

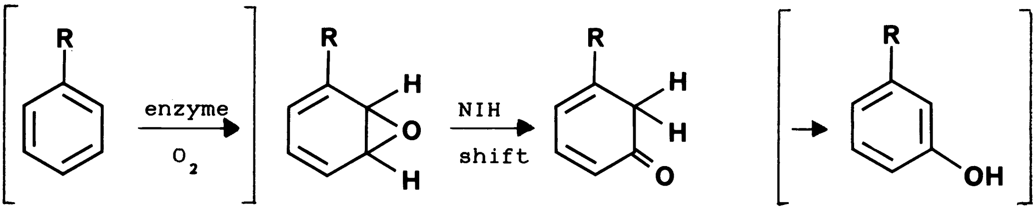
The direct interaction of the reaction centre (usually, but not necessarily, an incipient *carbenium centre*) with the lone pair of electrons of an atom or with the electrons of a σ- or π-bond contained within the parent molecule but not conjugated with the reaction centre. A distinction is sometimes made between n-, σ- and π-participation.

The associated rate increase is known as "anchimeric assistance". "Synartetic acceleration" is the special case of anchimeric assistance ascribed to participation by electrons binding a substituent to a carbon atom in a β- position relative to a *leaving group* attached to the α-carbon atom. According to the underlying model, these electrons then provide a three-centre bond (or "bridge") "fastening together" (as the word "synartetic" is intended to suggest) the α- and β-carbon atoms between which the charge is divided in the intermediate *bridged carbocation* formed (and in the *transition state* preceding its formation). The term synartetic acceleration is not now widely used.

See also *intramolecular catalysis, multi-centre bond*.

NIH SHIFT

The *intramolecular* hydrogen *migration* accompanying the *molecular rearrangement* of arene oxides to cyclohexadienones, thought to be the central step in the enzymatic hydroxylation of aromatic rings.



(NIH stands for National Institutes of Health where the shift was discovered.)

NITRENE

Generic name for $\ddot{H}N$: and substitution derivatives thereof, containing electrically neutral one-co-ordinate nitrogen with four non-bonding electrons. Two of these are paired; the other two may have parallel spins (triplet state) or antiparallel spins (singlet state). The name is the strict analogue of *carbene* and, as a generic name, it is preferred to a number of alternatives proposed ("imene", "imine radical", "azene", "azylene", "azacarbene", "imin", "imidogen").

See LWOWSKI (1970).

NITRENIUM ION

A structure, real or hypothetical, representing a nitrogen cation that contains at least one two-co-ordinate nitrogen atom, i.e. NH_2^+ and substitution derivatives thereof. (Cf. *carbenium ion*.) Like nitrenes, from which nitrenium ions can be considered to be derived by addition of H^+ or R^+, nitrenium ions can exist in singlet or triplet states. (Use of the alternative name "imidonium ion" is not recommended.)

NO-BOND RESONANCE

See *hyperconjugation*.

NORMAL KINETIC ISOTOPE EFFECT

See *isotope effect*.

NUCLEOFUGE

A *leaving group* that carries away the bonding electron pair. For example, in the *hydrolysis* of an alkyl chloride, Cl^- is the nucleofuge.

See also *electrofuge, nucleophile*.

NUCLEOPHILE, NUCLEOPHILIC

A nucleophile (or nucleophilic reagent) is a reagent that forms a bond to its reaction partner (the *electrophile*) by donating both bonding electrons.

A "nucleophilic *substitution reaction*" is a *heterolytic* reaction in which the reagent supplying the *entering group* acts as a nucleophile. For example

$$\mathrm{EtCl} + \underset{\text{nucleophile}}{\mathrm{MeO}^-} \longrightarrow \mathrm{EtOMe} + \underset{\textit{nucleofuge}}{\mathrm{Cl}^-}$$

Nucleophilic reagents are *Lewis bases*.

Nucleophilic catalysis is catalysis by a Lewis base, involving formation of a *Lewis adduct* as a *reaction intermediate*. For example, the *hydrolysis* of acetic anhydride in aqueous solution catalysed by pyridine:

$$\mathrm{C_5H_5N} + \mathrm{(CH_3CO)_2O} \longrightarrow [\mathrm{C_5H_5NCOCH_3}]^+ + \mathrm{CH_3CO_2}^-$$

$$[\mathrm{C_5H_5NCOCH_3}]^+ + \mathrm{H_2O} \longrightarrow \mathrm{C_5H_5N} + \mathrm{CH_3CO_2H} + \mathrm{H^+_{aq}}$$

The term "nucleophilic" is also used to designate the apparent polar character of certain *radicals*, as inferred from their higher relative reactivity with reaction sites of lower electron density.

See also *electrophilic, nucleophilicity*.

NUCLEOPHILICITY

(1) The property of being *nucleophilic*.

(2) The relative reactivity of a *nucleophilic* reagent. (It is also sometimes referred to as "nucleophilic power".) Qualitatively, the concept is related to *Lewis basicity*. However, whereas Lewis basicity is measured by relative equilibrium constants,

$$\mathrm{B{:}} + \mathrm{A} \overset{K}{\rightleftharpoons} \overset{+}{\mathrm{B}}-\overset{-}{\mathrm{A}}$$

nucleophilicity of a Lewis base is measured by relative rate constants of different nucleophilic reagents towards a common *substrate*, most commonly involving formation of a bond to carbon,

$$\mathrm{B{:}} + \mathrm{A{-}Z} \xrightarrow{k} \overset{+}{\mathrm{B}}-\mathrm{A} + \mathrm{Z{:}}^-$$

See also *electrophilicity*.

'ONIUM' ION

A cation containing a "central" atom that bears a formal positive charge and is bonded to one univalent atom or group more than is normal for a neutral molecule containing that "central" atom. The suffix "-onium" occurs in the names of specific ions, e.g. $\mathrm{NR_4}^+$, tetra-alkylammonium; $\mathrm{SR_3}^+$, trialkylsulfonium; where R = alkyl.

See also *carbenium ion, carbonium ion*.

OPPOSING REACTIONS

See *composite reactions*.

OPTICAL YIELD

See *stereoselectivity*.

ORBITAL

See *molecular orbital*.

ORBITAL SYMMETRY

The behaviour of an atomic or a localized *molecular orbital* under a molecular symmetry operation characterizes its orbital symmetry. For example, under a reflection in an appropriate symmetry plane, the phase of the orbital may be unchanged (symmetric), or it may change sign, i.e., the positive and negative lobes are interchanged (antisymmetric).

A principal context for the use of orbital symmetry is the discussion of chemical changes that involve "conservation of orbital symmetry". If a certain symmetry element (e.g. the reflection plane) is retained during a molecular reorganization (even involving bond rupture), an orbital must retain its symmetry type with respect to this retained symmetry feature. This principle permits the qualitative construction of correlation diagrams to show how molecular orbitals transform (and how their energies change) during idealized chemical changes (e.g. *cycloadditions*).

An idealized single bond is a σ-bond, i.e., it has cylindrical symmetry, whereas a p-orbital or π-bond orbital has π-symmetry, i.e., it is antisymmetric with respect to reflection in a plane passing through the atomic centres with which it is associated. In ethylene, the π-bonding orbital is symmetric with respect to reflection in a plane perpendicular to and bisecting the C-C bond, whereas the π^*-antibonding orbital is antisymmetric with respect to this operation.

Considerations of orbital symmetry are frequently grossly simplified in that, for example, the π orbitals of a carbonyl group would be treated as having the same symmetry as those of ethylene, and the fact that the carbonyl group in (e.g.) camphor, unlike that in formaldehyde, has no mirror planes would be ignored. These simplified considerations nevertheless afford the basis of one approach to the understanding of the rules which indicate whether *pericyclic reactions* are likely to occur under thermal or photochemical conditions.

WOODWARD and HOFFMANN (1969)

See also *sigma,pi*.

ORDER OF REACTION

If the *rate of reaction* (v) for any reaction can be expressed by an empirical differential rate equation (or *rate law*) which contains a factor of the form $k[A]^\alpha[B]^\beta$ (expressing in full the dependence of the rate of reaction on the concentrations [A], [B] ...) where α,β are constant exponents (independent of concentration and time) and k is a constant, then the reaction is said to be of order α with respect to A, of order β with respect to B,..., and of (total or overall) order $n = (\alpha+\beta+ \ldots)$. The exponents α,β ... can be positive or negative integral or rational non-integral numbers. They are the reaction orders with respect to A,B, ... and are sometimes called "partial orders of reaction". Orders of reaction deduced from the dependence of initial rates of reaction on concentration are called "orders of reaction with respect to concentration"; orders of reaction deduced from the dependence of the rate of reaction on time of reaction are called "orders of reaction with respect to time".

The concept of order of reaction is also applicable to chemical rate processes occurring in systems for which concentration changes (and hence rates of reaction) are not themselves measurable, provided it is possible to measure a *chemical flux*. For example, if there is a dynamic equilibrium according to the equation aA pP and if a chemical flux is experimentally found (e.g. by nmr line shape analysis) to be related to concentrations by the equation

$$\varphi_{-A}/a = k[A]^\alpha[L]^\lambda \ldots$$

then the corresponding reaction is of order α with respect to A ... and of total (or overall) order n $(= \alpha + \lambda + \ldots.)$.

The proportionality factor k above is called the (nth order) "rate coefficient".

Rate coefficients referring to (or believed to refer to) *elementary reactions* are called "rate constants".

The (overall) order of a reaction cannot be deduced from measurements of a "rate of appearance" or "rate of disappearance" at a single value of the concentration of a species whose concentration is constant (or effectively constant) during the course of the reaction. If the overall rate of reaction is, for example, given by

$$v = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}$$

but if [B] stays constant, then the order of the reaction (with respect to time), as observed from the concentration change of A with time, will be α, and the rate of disappearance of A can be expressed in the form

$$v_{\mathrm{A}} = k_{\mathrm{obs}}[\mathrm{A}]^{\alpha}$$

The proportionality factor k_{obs} deduced from such an experiment is called the "observed rate coefficient", and it is related to the $(\alpha + \beta)$th order rate coefficient k by the equation

$$k_{\mathrm{obs}} = k[\mathrm{B}]^{\beta}$$

For the common case when $\alpha = 1$, k_{obs} is often referred to as a "pseudo-first order rate coefficient" (k_{ψ}).

For a simple (*elementary*) reaction a partial order of reaction is the same as the stoichiometric number of the reactant concerned and must therefore be a positive integer (see *rate of reaction*). The overall order is then the same as the *molecularity*. For *stepwise reactions* there is no general connection between stoichiometric numbers and partial orders. Such reactions may have more complex rate laws, so that an apparent order of reaction may vary with the concentrations of the *chemical species* involved and with the progress of the reaction: in such cases it is not useful to speak of orders of reaction, although apparent orders of reaction may be deducible from initial rates.

In a *stepwise reaction*, orders of reaction may in principle always be assigned to the elementary steps.

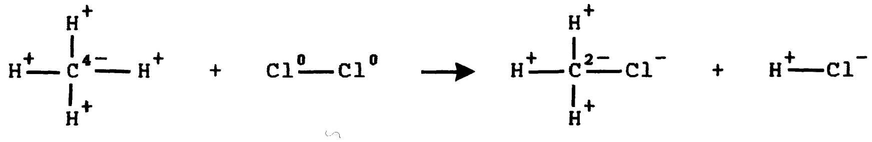
See also *kinetic equivalence*.

OXIDATION

(1) The complete net removal of one or more electrons from a *molecular entity* (also called "de-electronation").

(2) The above definition can be adapted to *chemical reactions* in which a complete electron transfer does not occur but which, by custom and in current usage, are termed oxidations. In this application "oxidation numbers" are considered. These are defined (IUPAC INORGANIC RULES, 1970) in terms of a formal model in which both electrons of a covalent electron-pair *bond* between non-identical atoms are assigned to the more electronegative atom (except that all elements in a Group of the Periodic Table are considered to have the same electronegativity as the first element of the Group). The formal charges on the individual atoms in a molecular entity which are thus calculated are called oxidation numbers. The use of this concept in oxidation reactions is illustrated by the example below, where an increase in the algebraic (positive) charge (or a decrease in the negative charge) on an atom implies its oxidation. For instance, the carbon atom of methane can be considered to have lost electrons on going from methane to chloromethane. In this sense it can be said that methane has been oxidized. In the converse sense, the reverse reactions are "reductions".

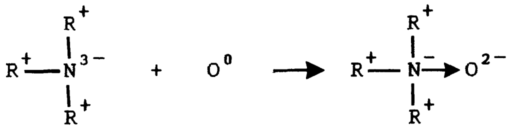
(a)



$$\mathrm{H^{+}{-}\underset{\displaystyle H^{+}}{\overset{\displaystyle H^{+}}{C^{4-}}}{-}H^{+} + Cl^{0}{-}Cl^{0} \longrightarrow H^{+}{-}\underset{\displaystyle H^{+}}{\overset{\displaystyle H^{+}}{C^{2-}}}{-}Cl^{-} + H^{+}{-}Cl^{-}}$$

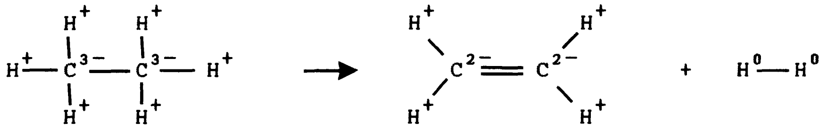
(C^{4-} oxidized to C^{2-})

(b)



(N^{3-} oxidized to N^{-})

(c)



(C^{3-} oxidized to C^{2-})

See also *oxidation level*.

See HENDRICKSON, CRAM and HAMMOND (1970).

(3) As a less general but intuitively simpler alternative to (2), oxidation can be described as a *transformation* of an organic *substrate* that can notionally be dissected into steps or *primitive changes* consisting of the removal of one or several electrons from the substrate followed or preceded by gain or loss of water and/or hydrogen ions or hydroxide ions, or by *nucleophilic* substitution by water or its reverse and/or by an *intramolecular molecular rearrangement*.

This formal definition allows the original idea of oxidation (combination with oxygen), together with its extension to removal of hydrogen, as well as processes closely akin to this type of transformation (and generally regarded in current usage of the term in organic chemistry to be oxidations and to be effected by "oxidizing agents") to be descriptively related to definition (1).

The oxidations listed as examples under (2) are then considered as follows:

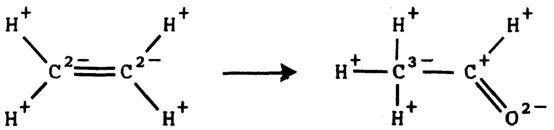
(a) $CH_4 - 2e^- - H^+ + OH^- = CH_3OH \xrightarrow[\text{of hydrolysis}]{\text{reversal}} CH_3Cl$

(b) $R_3N - 2e^- + OH^- - H^+ = R_3NO$

(c) $C_2H_6 - 2e^- - 2H^+ = CH_2{=}CH_2$

OXIDATION LEVEL

The term is applied as a qualitative indication of whether a particular organic *transformation* can be deemed to be an *oxidation*(2) or *reduction*, on the basis of the sum of the "oxidation numbers" of corresponding groups of carbon atoms in *substrate* and product. For example, the sum of the oxidation numbers of the two carbon atoms in each of the *molecular entities* ethene, ethanol and chloroethane is -4, and they are accordingly said to be at the same oxidation level. In ethane the corresponding sum is -6, and ethane is at a lower oxidation level. In ethyne, ethanal and dichloroethane these sums are -2, and these are at a common higher oxidation level than the other two groups of compounds. Accordingly the transformation of ethene to ethanal is an oxidation:



Oxidation levels can be misleading guides since they refer only to the carbon atoms of the molecular entities.

OXIDATION NUMBER

See IUPAC INORGANIC RULES, (1970), Rule O.1.

See also *oxidation*(2)

PARALLEL REACTIONS

See *composite reaction*.

PARTIAL RATE FACTOR

The rate of substitution at one specific site in an *aromatic* compound relative to the rate of substitution at one position in benzene. For example, the partial rate factor f_p^Z for *para*-substitution in a monosubstituted benzene C_6H_5Z is related to the rate constants $k(C_6H_5Z)$ and $k(C_6H_6)$ for the total reaction (i.e. at all positions) of C_6H_5Z and benzene, respectively, and % *para* (the percentage of *para*-substitution in the total product formed from C_6H_5Z) by the relation

$$f_p^{\mathrm{Z}} = \frac{6k(\mathrm{C_6H_5Z})}{k(\mathrm{C_6H_6})} \frac{\%\ para}{100}$$

Similarly for *meta*-substitution:

$$f_m^{\mathrm{Z}} = \frac{6k(\mathrm{C_6H_5Z})}{2k(\mathrm{C_6H_6})} \frac{\%\ meta}{100}$$

(The symbols p_f^Z, m_f^Z, o_f^Z are also in use.) The term can be extended to other substituted *substrates* undergoing parallel reactions at different sites with the same reagent according to the same *rate law*.

INGOLD (1953); STOCK and BROWN (1963).

See also *selectivity*.

PERICYCLIC REACTION

A *chemical reaction* in which *concerted* reorganization of *bonding* takes place throughout a cyclic array of continuously bonded atoms. It may be viewed as a reaction proceeding through a fully *conjugated* cyclic *transition state*. The term embraces a variety of processes, including *cycloadditions*, *cheletropic reactions*, *electrocyclic* and *sigmatropic rearrangements*, etc. (provided they are concerted).

See also *multi-centre reaction*.

PERSISTENT

See *transient*.

pH-RATE PROFILE

A plot of observed rate constant, or more usually its decadic logarithm, against pH of solution, other variables being kept constant.

PHASE-TRANSFER CATALYSIS

The phenomenon of rate enhancement of a reaction between *chemical species* located in different phases (immiscible liquids or solid and liquid) by addition of a small quantity of an agent (called the "phase-transfer *catalyst*") that extracts one of the reactants, most commonly an anion, across the interface into the other phase so that reaction can proceed. These catalysts are salts of *"onium ions"* (e.g. tetra-alkylammonium salts) or agents that complex inorganic cations (e.g. *crown* ethers). The catalyst cation is not consumed in the reaction although an anion exchange does occur.

PHENONIUM ION

See *bridged carbocation*.

PHOTOLYSIS

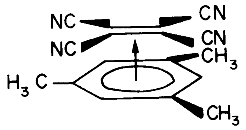
The cleavage of one or more covalent *bonds* in a *molecular entity* resulting from absorption of light, or a photochemical process in which such cleavage is an essential part. For example:

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot$$

The term has also been expanded so as to specify the method of irradiation ("laser photolysis", "flash photolysis"). It is recommended that this usage should not be extended beyond these examples.

π-ADDUCT (pi-Adduct)

An *adduct* formed by electron-pair donation from a π-orbital into a σ-orbital, or from a σ-orbital into a π-orbital, or from a π-orbital into a π-orbital. For example:



Such an adduct has commonly been known as a "π-complex", but, as the bonding is not necessarily weak, it is better to avoid the term *complex*, in accordance with the recommendation in this Glossary.

See also *co-ordination*.

π-BOND (pi-Bond)

See *sigma,pi*.

+ *π-COMPLEX (pi-Complex)*

See *π-adduct*.

π-ORBITAL (pi-Orbital)

See *sigma,pi*.

+ *POLAR-APROTIC (SOLVENT)*

See *dipolar-aprotic*.

POLAR EFFECT

An effect of a *substituent group* (on *rates of reaction*, etc.) having its origin in the *substituent electronegativity*. (There are also other substituent effects, e.g. *steric effects*.)

See also *field effect, inductive effect, mesomeric effect*.

POLAR SOLVENT

See *polarity*.

POLARITY

When applied to a solvent, this rather ill-defined term is synonymous with *ionizing power*.

See also *Grunwald-Winstein equation, Z-value*.

POLARIZABILITY

The ease of distortion of the electron cloud of a *molecular entity* by an electric field (such as that due to the proximity of a charged reagent). It is experimentally measured as the ratio of induced dipole moment (μ_{ind}) to the field E which induces it:

$$\alpha = \mu_{ind}/E$$

In ordinary usage the term refers to the "mean polarizability", i.e., the average over three rectangular axes of the molecule. Polarizabilities in different directions (e.g. along the bond in Cl_2, called "longitudinal polarizability", and in the direction perpendicular to the bond, called "transverse polarizability") can, at least in principle, be distinguished.

See INGOLD (1953).

POLYDENT

See *ambident*.

POTENTIAL-ENERGY PROFILE

A curve describing the variation of the potential energy of the system of atoms that make up the reactants and products of a reaction, as a function of one geometric co-ordinate, and corresponding to the "energetically easiest passage" from reactants to products (i.e. along the line produced by joining the paths of steepest descent from the *transition state* to the reactants and to the products). For an *elementary reaction* the relevant geometric co-ordinate is the *reaction co-ordinate*; for a *stepwise reaction* it is the succession of reaction co-ordinates for the successive individual *reaction steps*. (The reaction co-ordinate is sometimes approximated by a quasi-chemical index of reaction progress, such as "degree of atom transfer" or *bond order* of some specified *bond*.)

See also *potential-energy reaction surface, Gibbs energy diagram*.

POTENTIAL-ENERGY REACTION SURFACE

A geometric hypersurface on which the potential energy of a set of reactants is plotted as a function of the co-ordinates representing the molecular geometry of the system.

For simple systems two such co-ordinates (characterizing two variables that change during the progress from reactants to products) can be selected, and the potential energy plotted as a contour map.

For simple *elementary reactions*, e.g. $A\text{-}B + C \longrightarrow A + B\text{-}C$, the surface can show the potential energy for all values of the A, B, C geometry, providing that the ABC angle is fixed.

For more complicated reactions a different choice of two co-ordinates is sometimes preferred, e.g. the *bond orders* of two different *bonds*. Such a diagram is often arranged so that reactants are located at the bottom left corner and products at the top right. If the trace of the representative point characterizing the route from reactants to products follows two adjacent edges of the diagram, the changes represented by the two co-ordinates take place in distinct succession; if the trace leaves the edges and crosses the interior of the diagram, the two changes are *concerted*. In many qualitative applications it is convenient (although not strictly equivalent) for the third co-ordinate to represent standard Gibbs energy rather than potential energy. (Some reservations concerning the diagrammatic use of Gibbs energies are noted under *Gibbs energy diagram*).

The energetically easiest route from reactants to products on the potential -energy contour map defines the *potential-energy profile*.

ALBERY (1967); MORE O'FERRALL (1970); JENCKS (1972).

See also *reaction co-ordinate*.

PRE-ASSOCIATION

A step on the *reaction path* of some *stepwise reactions*

$$A \longrightarrow B \xrightarrow{+C} \text{Product}$$

in which the *molecular entity* C is already present in an *encounter pair* or *encounter complex* with A during the formation of B from A, e.g.

$$A+C \xrightleftharpoons{\text{pre-association}} \underset{\text{complex}}{\underset{\text{encounter}}{(A...C)}} \longrightarrow \underset{\text{complex}}{\underset{\text{encounter}}{(B...C)}} \xrightarrow{\text{rapid}} \text{Product}$$

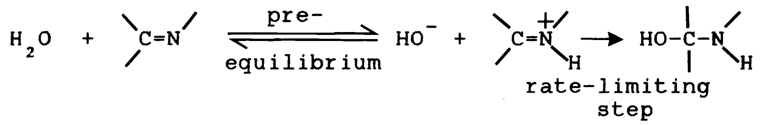
The *chemical species* C may but does not necesarily assist the formation of B from A (which may itself be a *bimolecular* reaction with some other reagent). If it does not, C is described as being present as a spectator, and hence such a mechanism is sometimes referred to as a "spectator mechanism".

Pre-association is important when B is too short-lived to permit B and C to come together by diffusion.

See also *microscopic diffusion control*.

PRE-EQUILIBRIUM (or *Prior equilibrium*)

A reversible step or reversible sequence of steps preceding the *rate-limiting step* in a *stepwise reaction*. For example



See also *kinetic equivalence*.

PRE-EXPONENTIAL FACTOR

See *energy of activation*, *entropy of activation*.

PRIMARY EQUILIBRIUM ISOTOPE EFFECT

See *isotope effect*.

PRIMARY KINETIC ELECTROLYTE EFFECT

See *kinetic electrolyte effect*.

PRIMARY KINETIC ISOTOPE EFFECT

See *isotope effect*.

PRIMITIVE CHANGE

One of the conceptually simpler molecular changes into which an *elementary reaction* can be notionally dissected. Such changes include *bond* rupture, bond formation, internal rotation, change of bond length or bond angle, bond *migration*, redistribution of charge, etc.

The concept of primitive changes is helpful in the detailed verbal description of elementary reactions, but a primitive change does not represent a process that is by itself observable as a component of an elementary reaction.

PRIOR EQUILIBRIUM

See *pre-equlibrium*.

PROMOTION

See *pseudo-catalysis*.

PROPAGATION

See *chain reaction*.

PROTIC

See *protogenic*.

PROTOGENIC (SOLVENT)

Capable of acting as a proton donor (strongly or weakly acidic as a *Brønsted acid*). The term is preferred to the synonym "protic" or the more ambiguous expression "acidic" by itself.

+ *PROTOLYSIS*

This term has been used synonymously with *proton-transfer reaction*. Because of its misleading similarity to *hydrolysis*, *photolysis*, etc., its use is discouraged.

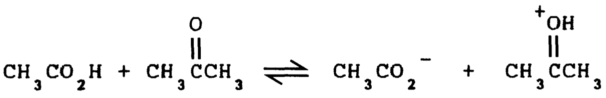
See also *autoprotolysis*.

PROTON AFFINITY

The energy released in the gas-phase reaction (real or hypothetical) between a proton and the *molecular entity* concerned (usually an electrically neutral molecule) to give the *conjugate acid* of that species.

PROTON-TRANSFER REACTION

A *chemical reaction*, the main feature of which is the *intermolecular* or *intramolecular* transfer of a proton from one *binding site* to another. For example,



$$CH_3CO_2H + CH_3\overset{\overset{O}{\|}}{C}CH_3 \rightleftharpoons CH_3CO_2^- + CH_3\overset{\overset{^+OH}{\|}}{C}CH_3$$

In the detailed description of proton-transfer reactions, especially of rapid proton transfers between electronegative atoms, it should always be specified whether the term is used to refer to the overall process (including the more-or-less *encounter-controlled* formation of a *hydrogen-bonded complex* and the separation of the products; see *microscopic diffusion control*) or just to the proton-transfer event (including solvent rearrangement) by itself.

See also *autoprotolysis*, *tautomerism*.

PROTOPHILIC (SOLVENT)

Capable of acting as proton acceptor, strongly or weakly basic (as a *Brønsted base*).

PROTOTROPIC REARRANGEMENT (or *Prototropy*)

See *tautomerism*.

PSEUDO-CATALYSIS

If an acid or base is present in nearly constant concentration throughout a reaction in solution (owing to buffering or the use of a large excess) it may be found to increase the rate of that reaction and also to be consumed during the process. The acid or base is then not a *catalyst* and the phenomenon cannot be called *catalysis* according to the well-established meaning of these terms in chemical kinetics, although the *mechanism* of such a process is often intimately related to that of a catalysed reaction. It is recommended that the term pseudo-catalysis be used in these and analogous cases (not necessarily involving acids or bases). For example, if a *Brønsted acid* accelerates the *hydrolysis* of an ester to a carboxylic acid and an alcohol, this is properly called acid catalysis, whereas the acceleration, by the same acid, of hydrolysis of an amide should be described as pseudo-catalysis by the acid: the "acid pseudo-catalyst" is consumed during the reaction through formation of an ammonium ion. The terms "general acid pseudo-catalysis" and "general base pseudo-catalysis" may be used as the analogues of *general acid catalysis* and *general base catalysis*.

The term "base-promoted" has sometimes been used for reactions that are pseudo-catalysed by bases. However, the term "promotion" also has a different meaning in other chemical contexts.

PSEUDO-FIRST ORDER RATE COEFFICIENT

See *order of reaction*.

+ PSEUDOMOLECULAR REARRANGEMENT

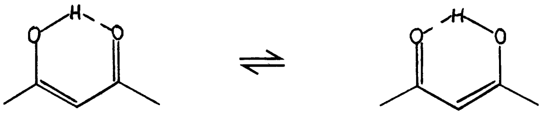
The use of this awkwardly formed term is discouraged. It is synonymous with "intermolecular rearrangement".

See *molecular rearrangement*.

PSEUDOPERICYCLIC

A *concerted transformation* is pseudopericyclic if the primary changes in bonding occur within a cyclic array of atoms at one (or more) of which non-bonding and bonding atomic orbitals interchange roles.

A formal example is the enol $\rightleftharpoons$ enol prototropy of 2,4-pentanedione (acetylacetone).



Since the atomic orbitals that interchange roles are orthogonal, such a reaction does not proceed through a fully *conjugated transition state* and is thus not a *pericyclic reaction* and therefore not governed by *orbital symmetry* restrictions applicable to pericyclic reactions.

ROSS, SEIDERS and LEMAL (1976).

+ PSEUDO-UNIMOLECULAR

An ambiguous term without clear meaning.

See *unimolecular, order of reaction*.

PYROLYSIS

Thermolysis, usually associated with exposure to a high temperature.

QUANTUM YIELD

The number of moles transformed in a specified process, physically (e.g. by emission of photons) or chemically, per mole of photons absorbed by the system.

See CALVERT and PITTS (1966)

RADICAL (or *Free radical*)

A *molecular entity* possessing an unpaired electron such as $\cdot CH_3$, $\cdot SnH_3$, $\cdot Cl$ (or $Cl\cdot$). (In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if this is possible.) Paramagnetic metal ions are not normally regarded as radicals.

At least in the context of physical organic chemistry, it seems desirable to cease using the adjective "free" in the general name of this type of *chemical species* and *molecular entity*, so that the term "free radical" may in future be restricted to those radicals which do not form parts of *radical pairs*.

It should, however, also be noted that the name "radical", by itself, is used in the nomenclature of organic compounds [IUPAC ORGANIC RULES (1969), Section A] to describe a hydrocarbon residue forming part of a molecule. (For example, the side chain in 3-methylpentane is a methyl radical). In physical or mechanistic organic chemistry such a part of a molecule would usually be called a *substituent group* or *group*, notwithstanding the more restrictive use of the word "group" in the nomenclature of organic compounds.

See also *biradical*.

RADICAL ANION

See *radical ion*.

RADICAL CATION

See *radical ion*.

RADICAL CENTRE(S)

The atom (or group of atoms) in a polyatomic radical on which an unpaired electron is largely localized. *Attachment* of a monovalent atom to a radical centre gives a molecule for which it is possible to write a *Lewis formula* in which the normal stable valencies are assigned to all atoms.

RADICAL COMBINATION

See *colligation*.

RADICAL DISPROPORTIONATION

See *disproportionation*.

RADICAL ION

A *radical* that carries an electric charge. A positively charged radical is called a "radical cation" (e.g., the benzene radical cation $C_6H_6^{\bullet +}$); a negatively charged radical is called a "radical anion" (e.g.. the benzene radical anion $C_6H_6^{\bullet -}$ or the benzophenone radical anion $Ph_2\dot{C}-O^-$).

Unless the positions of unpaired spin and charge can be associated with specific atoms, superscript dot and charge designations should be placed in the order $\cdot+$ or $\cdot-$ suggested by the name "radical ion", or - if the typography allows it - with the charge designation directly above the centrally placed dot (e.g. $C_3H_6^{\overset{+}{\bullet}}$).

RADICAL PAIR (or **Geminate pair**)

The term is used to identify two *radicals* in close proximity in liquid solution, with a solvent *cage*. They may be formed simultaneously by some *unimolecular* process, e.g., peroxide decomposition, or they may have come together by diffusion. Whilst the radicals are together, correlation of the unpaired electron spins of the two species cannot be ignored: this correlation is responsible for *CIDNP* phenomena.

RADIOLYSIS

The cleavage of one or several bonds resulting from exposure to high-energy radiation. The term has also been used to refer to the irradiation itself ("pulse radiolysis"). It is recommended that this usage should not be extended.

RATE COEFFICIENT

See *order of reaction*.

RATE CONSTANT

See *order of reaction*.

RATE LAW (or *Empirical differential rate equation*)

An expression for the *rate of reaction* of a particular reaction in terms of concentrations of *chemical species* and constant parameters (normally *rate coefficients* and partial *orders of reaction*) only. For examples of rate laws see equations (1) to (3) under *kinetic equivalence*, and equation (1) under *steady state*.

RATE OF APPEARANCE

See *rate of reaction*.

RATE OF CONSUMPTION

See *rate of reaction*.

RATE OF DISAPPEARANCE

See *rate of reaction*.

RATE OF REACTION

For the general *chemical reaction*

$$aA + bB \ldots \longrightarrow pP + qQ \ldots$$

occurring under constant-volume conditions, without an appreciable build-up of *reaction intermediates*, the rate of reaction (v) is defined as

$$v = -\frac{1}{a}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \frac{1}{p}\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = \frac{1}{q}\frac{\mathrm{d}[\mathrm{Q}]}{\mathrm{d}t}$$

where symbols placed inside square brackets denote concentrations (conventionally expressed in units of mol dm^{-3}). The symbols R and r are also commonly used in place of v. It is recommended that the unit of time should always be the second.

In such a case the rate of reaction differs from the rate of increase of concentration of a product P by a constant quotient (its coefficient in the stoichiometric equation, p) and from the rate of decrease of concentration of reactant A by the quotient a. [It should be noted that all coefficients in the stoichiometric equation are positive; those for products (p, q, ...) will therefore differ in sign from the stoichiometric numbers defined in IUPAC MANUAL (1979).]

The quantity $\dot{\xi}$ ($= \frac{\mathrm{d}\xi}{\mathrm{d}t}$) defined by the equation

$$\dot{\xi} = -\frac{1}{a}\frac{\mathrm{d}n_\mathrm{A}}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}n_\mathrm{B}}{\mathrm{d}t} = \frac{1}{p}\frac{\mathrm{d}n_\mathrm{P}}{\mathrm{d}t} = \frac{1}{q}\frac{\mathrm{d}n_\mathrm{Q}}{\mathrm{d}t}$$

(where n_A designates the amount of substance A, conventionally expressed in units of mol) may be called the "rate of conversion" and is appropriate when the use of concentrations is inconvenient, e.g. under conditions of varying volume. In a system of constant volume, the rate of reaction is equal to the rate of conversion per unit volume throughout the reaction.

For a *stepwise reaction* this definition of "rate of reaction" (and "extent of reaction", ξ) will apply only if there is no accumulation of intermediate or formation of side products. It is therefore recommended that the term "rate of reaction" be used only in cases where it is experimentally established that these conditions apply. More generally, it is recommended that, instead, the terms "rate of disappearance" or "rate of consumption" of A (i.e. $-\mathrm{d}[\mathrm{A}]/\mathrm{d}t$, the rate of decrease of concentration of A) or "rate of appearance" of P (i.e. $\mathrm{d}[\mathrm{P}]/\mathrm{d}t$, the rate of increase of concentration of product P) be used depending on the concentration change of the particular *chemical species* that is actually observed. In some cases reference to the *chemical flux* observed may be more appropriate.

The symbol v (without lettered subscript) should be used only for rate of reaction; v with a lettered subscript (e.g. v_A) refers to a rate of appearance or rate of disappearance (e.g. of the chemical species A).

N.B.: This definition is consistent with CODATA (1974) recommendations and with IUPAC MANUAL APPENDIX V(1981), but differs from the unconventional terminology in the earlier IUPAC MANUAL (1979).

See also *chemical relaxation, mean life time, order of reaction*.

RATE-CONTROLLING STEP

See *rate-limiting step*.

RATE-DETERMINING STEP

See *rate-limiting step*.

RATE-LIMITING STEP (or **Rate-controlling step**)

If for a *stepwise reaction*

$$\mathrm{A} + \mathrm{B} \xrightleftharpoons{K_1} \mathrm{C} + \mathrm{D} \xrightleftharpoons{K_2} \ldots \xrightleftharpoons[k_{-g}]{k_g} \mathrm{G} \xrightarrow{k_j + (\mathrm{X})} \mathrm{P} \xrightarrow{k_m} \mathrm{Q} \ \ldots$$

step 1 step 2 step g step j step m

which corresponds to a sequence of *elementary reactions* in a homogeneous system, the *rate of reaction* (v) can be expressed by:

$$v = F([\mathrm{A}],[\mathrm{B}],[\mathrm{C}],[\mathrm{D}],\ \ldots\ldots,\ K_1,K_2,\ \ldots.) \times k_j\ [\mathrm{X}]$$

where F is, to a good approximation, a function only of the concentrations and of the equilibrium constants K for the *pre-equilibrium* that precede the step j, then step j is called the rate-limiting step.

In such a sequence, step j is the earliest step for which the forward *chemical flux* (divided, if appropriate, by the corresponding stoichiometric number) does not greatly exceed the rate of formation of the final reaction product (similarly divided), if the overall process is irreversible.

Under the conditions $\Sigma\varphi_G > \Sigma\varphi_P$ and $\varphi_{-g} \approx \varphi_j$, the chemical flux φ_g will not be greatly in excess of φ_j; and neither step g nor step j is separately rate-limiting. In such cases the two steps have been described as "jointly rate-limiting". The definition can be extended to some more complicated kinetic situations, but the concept is not always valid. Some of the extensions are obvious (e.g., when step j leads to an equilibrating mixture of products). In some other cases the analysis becomes too complicated to be practically useful.

The term "rate-limiting" does not imply that such a step imposes an upper limit on the rate of reaction (as under conditions of saturation in *Michaelis-Menten kinetics*). For this reason, the synonym "rate-controlling step", although not widely used at present, is preferable where there is a possibility of such confusion.

The term "rate-determining step" has been used both as a synonym for "rate-limiting step" and with a more restricted meaning. It is therefore ambiguous and we advise caution concerning its use. For heterogeneous systems the above analysis may require explicit inclusion of mass transfer.

See also *macroscopic diffusion control, microscopic diffusion control*.

REACTION

See *chemical reaction*.

REACTION CO-ORDINATE

A geometric parameter that changes during the conversion of one (or more) reactant *molecular entities* to one (or more) product molecular entities and whose value can be taken as a measure of the progress of an *elementary* *reaction*. (For example, a *bond* length or bond angle or a combination of bond lengths and/or bond angles; it is sometimes approximated by a non-geometric parameter, such as the *bond order* of some specified bond.)

In the formalism of "*transition state* theory", the reaction co-ordinate is that co-ordinate in a set of curvilinear co-ordinates obtained from the conventional ones for the reactants which, for each *reaction step*, leads smoothly from the configuration of the reactants through that of the transition state to the configuration of the products. The reaction co-ordinate is typically chosen to parallel the path of minimum potential energy from reactants to products.

The term has also been used interchangeably with the term *transition co-ordinate*, applicable to the co-ordinate in the immediate vicinity of the potential energy maximum. Being more specific, the name transition co-ordinate is to be preferred in that context.

See MARCUS (1966).

See also *potential-energy profile, potential-energy reaction surface*.

REACTION INTERMEDIATE

A *molecular entity* with a lifetime appreciably longer than a molecular vibration (corresponding to a local potential energy minimum of depth greater than RT) that is formed (directly or indirectly) from the reactants and reacts further to give (either directly or indirectly) the products of a *chemical reaction*; also the corresponding *chemical species*.

See also *reaction step, elementary reaction, stepwise reaction*.

REACTION MECHANISM

See *mechanism*.

REACTION PATH

(1) A synonym for *mechanism*.

(2) A trajectory on the *potential energy surface*.

REACTION STAGE

A set of one or more (possibly experimentally not separable) *reaction steps* leading to and/or from a detectable or presumed *reaction intermediate*.

REACTION STEP

An *elementary reaction*, constituting one of the stages of a *stepwise reaction*, in which a *reaction intermediate* (or, for the first step, the reactants) is converted to the next reaction intermediate (or, for the last step, the products) in the sequence of intermediates between reactants and products.

See also *rate-limiting step, reaction stage.*

REACTIVE, REACTIVITY

As applied to a *chemical species*, the terms express a kinetic property. A species is said to be more reactive or to have a higher reactivity in some given context than some other (reference) species if it has a larger rate constant for a specified *elementary reaction* with the same reaction partner. The term has meaning only by reference to some explicitly stated or implicitly assumed standard.

The term is also more loosely used as a phenomenological description not restricted to elementary reactions. When applied in this sense the property under consideration may reflect not only rate constants but also equilibrium constants for *pre-equilibria*.

See also *stable, unreactive, unstable.*

REACTIVITY INDEX

Any numerical index derived from quantum - mechanical model calculations that permits the prediction of relative reactivities of different molecular sites. Many indices are in use, based on a variety of theories and relating to various types of reaction. The more successful applications have been to the *substitution reactions* of *conjugated systems* where relative reactivities are determined largely by changes of π-electron energy.

REARRANGEMENT

See *degenerate rearrangement, molecular rearrangement, sigmatropic rearrangement.*

REARRANGEMENT STAGE

The *elementary reaction* or *reaction stage* (of a *molecular rearrangement*) in which there is both making and breaking of *bonds* between atoms common to a reactant and a reaction product. If the rearrangement stage consists of a single elementary reaction, this is a "rearrangement step".

REDUCTION

The complete transfer of one or more electrons to a *molecular entity* (also called "electronation"), and, more generally, the reverse of the processes described under *oxidation* (2), (3).

REGIOSELECTIVE, REGIOSELECTIVITY

A regioselective reaction is one in which a chemical change occurs preferentially at one of several possible sites in a molecule (usually involving at each site a functional *group* of the same structural type). Reactions are termed completely (100%) regioselective if the discrimination is complete or partially (x%) regioselective if the product of reaction at one site predominates over the products of reaction at other sites. The discrimination may also semi-quantitatively be referred to as high or low regioselectivity.

(Originally, the term was restricted to *addition* reactions of unsymmetrical reagents to unsymmetrical alkenes.)

RELAXATION

See *chemical relaxation.*

RESONANCE

In the context of chemistry, the term refers to the representation of the electronic structure of a molecular system in terms of *contributing structures*. Resonance among contributing structures means that the wave function is approximately represented by "mixing" the wave functions of contributing structures. The concept is the basis of the quantum-mechanical valence bond method. The resulting stabilization is linked to the quantum-mechanical concept of "resonance energy". The term resonance is also used to refer to the *delocalization* phenomenon itself.

See ATKINS (1974).

See also *mesomerism.*

RESONANCE EFFECT

See *mesomeric effect.*

RESONANCE ENERGY

See *resonance.*

+ RETROADDITION

See *cycloelimination.*

\+ ***RETROCYCLOADDITION***

See *cycloelimination*.

RETRO-ENE REACTION

See *ene reaction*.

REVERSE MICELLE (or ***Reversed micelle***)

See *inverted micelle*.

ρ-VALUE

A measure of the susceptibility to the influence of *substituent groups* on the rate constant or equilibrium constant of a particular organic reaction involving a family of related *substrates*. Defined by Hammett for the effect of ring substituents in *meta*- and *para*- positions on *aromatic* side-chain reactions by the empirical "$\rho\sigma$ - equation" of the general form

$$\mathrm{lg}\ \frac{k_X}{k_H} = \rho\sigma_X$$

in which σ_X is a constant characteristic of the substituent X and of its position in the reactant molecule.

More generally, ρ-values (modified with appropriate subscripts and superscripts) are used to designate the susceptibility of reaction series for families of various organic compounds, and not only for aromatic series, to any substituent effects, as given by the use of any modified set of *σ-constants* in an empirical $\rho\sigma$-correlation.

Reactions with a positive ρ-value are accelerated (or the equilibrium constants of analogous equilibria are increased) by substituents with positive σ-constants. Since the sign of σ was defined so that substituents with a positive σ-value increase the acidity of benzoic acid, such substituents are generally described as attracting electrons away from the aromatic ring. It follows that reactions with a positive ρ-value are considered to involve a *transition state* (or reaction product) such that the difference in energy between this state and the reactants is decreased by a reduction in electron density at the reactive site of the substrate.

See also *Taft equation*.

ρσ-EQUATION ***(rho-sigma Equation)***

See *rho-value*.

SACRIFICIAL HYPERCONJUGATION

See *hyperconjugation*.

\+ ***SALT EFFECT***

See *kinetic electrolyte effect*.

SAYTZEFF RULE

See *Zaitsev rule*.

SCAVENGER

A substance that reacts with (or otherwise removes) a trace component (as in the scavenging of trace metal ions) or traps a reactive *reaction intermediate*.

See also *inhibition*.

SCRAMBLING

See *isotopic scrambling*.

SECONDARY EQULIBRIUM ISOTOPE EFFECT

See *isotope effect*.

SECONDARY KINETIC ELECTROLYTE EFFECT

See *kinetic electrolyte effect*.

SECONDARY KINETIC ISOTOPE EFFECT

See *isotope effect*.

SELECTIVITY

The discrimination shown by a reagent in competitive attack on two or more *substrates* or on two or more positions in the same substrate. It is quantitatively expressed by ratios of *rate constants* of the competing reactions, or by the decadic logarithms of such ratios.

SELECTIVITY FACTOR

A quantitative representation of *selectivity* in *aromatic substitution reactions* (usually *electrophilic*, for mono-substituted benzene derivatives). If the *partial rate factor*, (f), expresses the reactivity of a specified position in the aromatic compound PhX relative to that of a single position in benzene, then the selectivity factor S_f expressing descrimination between *p*- and *m*-positions in PhX) is defined as

$$S_f \; = \; \lg\,(f_p^{\,X}/f_m^{\,X}).$$

STOCK and BROWN (1963).

σ-ADDUCT (sigma-Adduct)

The product formed by the *attachment* of an *electrophilic* or *nucleophilic entering group* or of a *radical* to a ring carbon atom of an *aromatic* species such that a new σ-bond is formed and the original *conjugation* is disrupted. (This has generally been called a "σ-complex", but *adduct* is more appropriate than *complex* according to the definitions given.) The term may also be used for analogous adducts to unsaturated (and *conjugated*) systems in general.

See also *Meisenheimer adduct*.

SIGMA, PI (σ,π)

The terms are symmetry designations, π molecular orbitals being antisymmetric with respect to a defining plane containing at least one atom (e.g. the molecular plane of ethene), and σ molecular orbitals symmetric with respect to the same plane. In practice the terms are used both in this rigorous sense (for orbitals encompassing the entire molecule) and also for localized two-centre orbitals or bonds, and it is necessary to make a clear distinction between these two usages.

Considering two-centre bonds, a π-bond has a nodal plane that includes the internuclear bond axis, whereas a σ-bond has no such nodal plane. (A δ-bond in organometallic or inorganic *molecular species* has two nodes).

Such two-centre orbitals may take part in molecular orbitals of σ- or π-symmetry. For example, the methyl group in propene contains three C-H bonds, each being of local σ-symmetry (i.e. without a nodal plane including the internuclear axis), but these three "σ-bonds" can in turn be combined to form a set of group orbitals one of which has π-symmetry with respect to the principal molecular plane and can accordingly interact with the two-centre orbital of π-symmetry (π-bond) of the double-bonded carbon atoms, to form a molecular orbital of π-symmetry.

Such interaction between the CH_3 group and the double bond is an example of what is called *hyperconjugation*. This cannot rigorously be described as "σ - π conjugation" since σ and π here refer to different defining planes, and interaction between orbitals of different symmetries (with respect to the same defining plane) is forbidden.

See also JORGENSEN and SALEM (1973).

σ-BOND (sigma-Bond)

See *sigma,pi*.

σ-CONSTANT (sigma-Constant)

Hammett's substituent constant, defined as lg (K_a/K_a^0), where K_a is the ionization constant of a *meta-* or *para-*substituted benzoic acid in water at 25°C, and K_a^0 that of benzoic acid itself.

The term is also in use as a collective description for related substituent constants, applicable to restricted ranges of observations, of which σ^+, σ^- and σ^0 are typical. Such constituent constants are designated by the letter σ with various subscripts and superscripts. They are defined in the references cited below.

In a qualitative sense, a large positive σ-value implies high electron-withdrawing power, etc.

See also *ρ-value, Taft equation*.

See CHAPMAN and SHORTER (1972), JOHNSON (1973), SHORTER (1973).

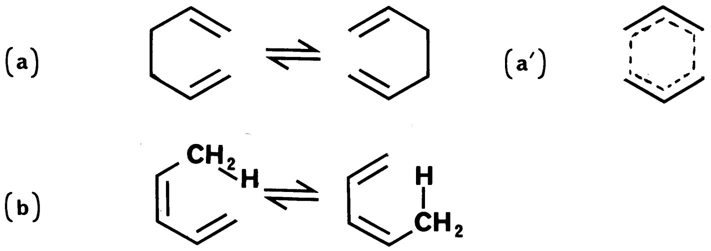
σ-ORBITAL (sigma-Orbital)

See *sigma,pi.*

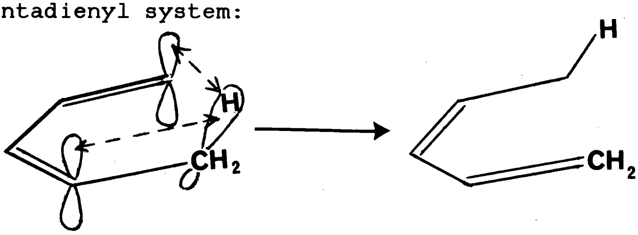
SIGMATROPIC REARRANGEMENT

A *molecular rearrangement* that involves both the creation of a new *σ-bond* between previously not directly linked atoms and the breaking of an existing σ-bond. There is normally a concurrent relocation of π-bonds in the molecule concerned, but the total number of π- and σ-bonds does not change. The term was originally restricted to *intramolecular pericyclic reactions*, and many authors use it with this connotation. It is, however, also applied in a more general, purely structural, sense.

If such a reaction is intramolecular, its *transition state* may be visualized as an *association* of two fragments connected at their termini by two partial σ-bonds, one being broken and the other being formed as, for example, the two allyl fragments in (a'). Considering only atoms within the (real or hypothetical) cyclic array undergoing reorganization, if the numbers of these in the two fragments are designated i and j, then the rearrangement is said to be a sigmatropic change of order [i,j] (conventionally [i] ⩽[j]). Thus the rearrangement (a) is of order [3,3], whilst reaction (b) is a [1,5]sigmatropic shift of hydrogen. (N.B.: By convention square brackets [...] here refer to numbers of atoms, in contrast with current usage in the context of *cycloaddition*.)



The descriptors a and s (*antarafacial* and suprafacial) may also be annexed to the numbers i and j; (b) is then described as a [1s, 5s] sigmatropic rearrangement, since it is suprafacial with respect both to the hydrogen atom and to the pentadienyl system:



The prefix "homo" (meaning one extra atom, interrupting *conjugation* - cf. "homoaromatic") has frequently been applied to sigmatropic rearrangements, but is misleading.

See also *cycloaddition*, *tautomerism*.

SILYLENE

(1) An uncharged di-co-ordinate silicon compound in which silicon is linked to two adjacent groups by covalent bonds and possesses two non-bonding electrons. (The definition is analogous to that given for *carbene*.)

(2) The silanediyl group ($H_2Si<$), analogous to the methyl group ($H_2C<$).

SOFT ACID

See *hard acid*.

SOFT BASE

See *hard base*.

SOLVATION

Any stabilizing interaction of a solute (or solute moiety) and the solvent or a similar interaction with solvent of groups of an insoluble material (i.e., the ionic groups of an ion-exchange resin). Examples of such interactions are generally electrostatic and *van der Waals forces*, as well as chemically more specific effects such as *hydrogen bond* formation.

See also *cybotactic region*.

SOLVENT ISOTOPE EFFECT

See *isotope effect*.

SOLVENT POLARITY

See *Grunwald-Winstein equation*, *ionizing power*, *Z-value*.

SOLVENT-SEPARATED ION PAIR

See *ion pair*.

SOLVENT-SHARED ION PAIR

See *ion pair*.

SOLVOLYSIS

Generally, reaction with a solvent, or with a *lyonium ion* or *lyate ion*, involving the rupture of one or more bonds in the reacting solute. More specifically the term is used for *substitution*, *elimination* and *fragmentation* reactions in which a solvent species is the *nucleophile*, ("alcoholysis" if the solvent is an alcohol, etc.).

SOMO

A Singly Occupied Molecular Orbital (usually the half-filled *HOMO* of a *radical*).

See also *frontier orbitals*.

SPECIES

See *chemical species*.

SPECIFIC CATALYSIS

The acceleration of a reaction by a unique *catalyst*, rather than by a family of related substances. The term is most commonly used in connection with specific hydrogen-ion or hydroxide-ion (*lyonium ion* or *lyate ion*) catalysis.

See also *general acid catalysis, general base catalysis, pseudo-catalysis.*

SPECTATOR MECHANISM

See *pre-association*.

SPIN ADDUCT

See *spin trapping.*

SPIN COUNTING

See *spin trapping.*

SPIN LABEL

A stable paramagnetic *group* (typically a nitroxyl radical) that is attached to a part of another *molecular entity* whose microscopic environment is of interest and may be revealed by the electron spin resonance spectrum of the spin label.

When a simple paramagnetic molecular entity is used in this way without covalent attachment to the molecular entity of interest it it frequently referred to as a "spin probe".

SPIN PROBE

See *spin label*.

SPIN TRAPPING

In certain solution reactions a *transient radical* will interact with a diamagnetic reagent to form a more "persistent" radical. The product radical accumulates to a concentration where detection and, frequently, identification are possible by esr spectroscopy. The key reaction is usually one of *attachment*; the diamagnetic reagent is said to be a "spin trap", and the persistent product radical is then the "spin *adduct*". The procedure is referred to as spin trapping, and is used for monitoring reactions involving the intermediacy of *reactive* radicals at concentrations too low for direct observation. Typical spin traps are C-nitroso-compounds and nitrones, to which reactive radicals will rapidly add to form nitroxyl radicals. A quantitative development, in which essentially all reactive radicals generated in a particular system are intercepted, has been referred to as "spin counting". Spin trapping has also been adapted to the interception of radicals generated in both gaseous and solid phases. In these cases the spin adduct is in practice transferred to a liquid solution for observation in order to facilitate the interpretation of the esr spectra of the radicals obtained.

STABLE

As applied to *chemical species*, the term expresses a thermodynamic property, which is quantitatively measured by relative molar standard Gibbs energies. A chemical species A is more stable than is isomer B if $\Delta G^{o} > 0$ for the (real or hypothetical) reaction A → B, under stated conditions. If for two reactions

$$P \longrightarrow X + Y \qquad (\Delta G_1^{\ominus})$$

$$Q \longrightarrow X + Z \qquad (\Delta G_2^{\ominus})$$

$\Delta G_1^{\ominus} > \Delta G_2^{\ominus}$, P is more stable relative to the product Y than Q is relative to Z. Both in qualitative and quantitative usage the term stable is therefore always used by reference to some explicitly stated or implicitly assumed standard.

The term should not be used as a synonym for "unreactive" since a relatively more stable chemical species may nevertheless be more *reactive* than some reference species towards a given reaction partner.

See also *inert, unstable.*

STATIONARY STATE

See *steady state*.

STEADY STATE (or *Stationary state*)

(1) A *reactive reaction intermediate* (X) reaches a steady state in a reaction sequence when the processes leading to its formation and those resulting in its removal are nearly in balance (i.e., the *chemical flux* into X is nearly equal to the chemical flux out of X), so that the rate of its change of concentration is negligible compared with the rate of change of concentration of other species involved. For example, for a sequence of reactions

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{X}$$

$$\mathrm{X} + \mathrm{C} \xrightarrow{k_2} \mathrm{D}$$

involving one low-concentration reactive intermediate X, the Bodenstein steady-state approximation $d[\mathrm{X}]/dt = 0$ leads to the expression

$$\frac{d[\mathrm{D}]}{dt} = \frac{k_1 k_2 [\mathrm{A}][\mathrm{C}]}{k_{-1} + k_2[\mathrm{C}]} \qquad .....(1)$$

N.B.: The term is used with a more rigorous meaning by mathematicians.

(2) In a stirred flow reactor a steady state implies a regime such that all concentrations are independent of time.

STEPWISE REACTION

A *chemical reaction* with at least one *reaction intermediate* and involving at least two consecutive *elementary reactions*.

See also *composite reaction*.

STEREOCHEMICAL

Relating to isomerism due to differences in the spatial arrangement of bonds without any differences in *connectivity* or bond multiplicity between the isomers.

STEREOELECTRONIC

Pertaining to the dependence of the properties (especially the energy) of a *molecular entity* in a particular electronic state (or of a *transition state*) on relative nuclear geometry. The electronic ground state is usually considered, but the term can apply to excited states as well. Stereoelectronic effects arise from the different alignment of electronic orbitals in different arrangements of nuclear geometry.

STEREOELECTRONIC CONTROL

Control of the nature of the products of a *chemical reaction* (or of its rate) by *stereoelectronic* factors. The term is usually applied in the framework of an orbital approximation. The variations of *molecular orbital* energies with relative nuclear geometry (along a *reaction co-ordinate*) are then seen as consequences of variations in basis-orbital overlaps.

STEREOSELECTIVE, STEREOSELECTIVITY

A stereoselective reaction is one in which a chemical change occurs to form preferentially one of two or more alternative products that differ only in their stereochemistry. Reactions are termed (100%) stereoselective if the discrimination is complete or partially (x%) stereoselective if one product predominates. The discrimination may also semi-quantitatively be referred to as high or low stereoselectivity.

See ELIEL (1962).

[For the use of the term "stereoselective polymerization" see IUPAC POLYMERS (1974).]

See also *stereospecific*.

STEREOSPECIFIC

(1) A reaction is termed stereospecific if starting materials differing only in their stereoisomerism are thereby converted into stereoisomerically different products. According to this definition, a stereospecific process is necessarily *stereoselective* but not all stereoselective processes are stereospecific.

(2) The term has also been applied to describe a reaction of high (> 98%) stereoselectivity, but this usage is unnecessary and is discouraged.

See ELIEL (1962).

[For the use of the term "stereospecific polymerization" see IUPAC POLYMERS (**1981**)].

STERIC EFFECT

An increase (or decrease) in a rate constant (or in an equilibrium constant), relative to a model compound, as a result of a difference in *strain* between, on the one hand, reactants and, on the other hand, a *transition state* ("steric acceleration", "steric retardation") or reaction products. (The adjective "steric" is not to be confused with *stereochemical*).

STOICHIOMETRIC NUMBER

See *rate of reaction*.

STOPPED FLOW

A technique for following the kinetics of reactions in solution (usually in the millisecond time range and slower) in which two reacant solutions are rapidly mixed by being forced through a mixing chamber and the flow of the mixed solution along a uniform tube is then suddenly arrested. At a fixed position along the tube the solution is monitored (as a function of time following the stoppage of flow) by some method with a rapid response (e.g. photoelectric photometry).

STRAIN

Strain is present in a *chemical species* or *transition state* if the *bond* lengths, bond angles, or dihedral angles ("torsional strain") are different from their typical values in related molecules, or if the distances between non-bonded atoms are shorter than the sum of the van der Waals radii of the atoms.

It is quantitatively defined as the enthalpy of a structure relative to a strainless structure (real or hypothetical) made up from the same atoms with the same types of bonding. (The enthalpy of formation of cyclopropane is 53.6 kJ mol^{-1}, whereas the enthalpy of formation based on three "normal" methylene groups, from acyclic models, is -61.9 kJ mol^{-1}. On this basis cyclopropane is destabilized by 115.5 kJ mol^{-1} of strain energy.

SUBJACENT ORBITAL

The Next-to-Highest Occupied *Molecular Orbital* ("NHOMO"). Subjacent orbitals are sometimes found to play an important role in the interpretation of molecular interactions according to the *frontier orbital* approach.

See BERSON (1972).

SUBSTITUENT ELECTRONEGATIVITY

The power of a *substituent group* to attract electrons to itself in comparison with a reference substituent, such as -H or $-CH_3$.

See also *electronegativity*.

SUBSTITUENT GROUP

An atom or *group* of bonded atoms that can be considered to have replaced a hydrogen atom (or two hydrogen atoms in the special case of bivalent groups) in a parent *molecular entity* (real or hypothetical).

SUBSTITUTION REACTION

An *elementary* or *stepwise reaction* in which one atom or *group* in a *molecular entity* is replaced by another atom or group. For example,

$$CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$$

SUBSTRATE

A *chemical species* of particular interest, the reaction of which with some other chemical reagent is under observation (e.g., a compound that is transformed under the influence of a *catalyst*. The term should be used with care. Either the context or a specific statement should always make it clear which chemical species in a reaction is regarded as the substrate.

SUPERACID

A medium having a high *acidity*, generally greater than that of 100% sulfuric acid. The common superacids are made by dissolving a powerful *Lewis acid* (e.g. SbF_5) in a suitable *Brønsted acid*, such as HF or HSO_3F. (An equimolar mixture of HSO_3F and SbF_5 is known by the trade name "magic acid").

In a biochemical context "superacid catalysis" is sometimes used to denote catalysis by metal ions analogous to catalysis by hydrogen ions.

SUPRAFACIAL

See *antarafacial*.

SYN

See *anti*.

SYNARTETIC ACCELERATION

See *neighbouring-group participation*.

SYNCHRONOUS

A *concerted* process in which the *primitive changes* concerned (generally *bond* rupture and bond formation) have progressed to the same (or comparable) extent at the *transition state* is said to be synchronous. The term figuratively implies a more or less synchronized progress of the changes. However, the progress of a bonding change (or other primitive change) has not quantitatively been defined in terms of a single parameter applicable to different bonds or different bonding changes. (Changes in fractional bond order would, in principle, provide such an index, if it were possible to define them in a physically unambiguous fashion.) The concept is therefore in general only qualitatively descriptive and does not admit an exact definition except in cases of *concerted* processes involving changes in two identical bonds (i.e. between the same and/or structurally equivalent atoms) and then only if they have symmetrical transition states.

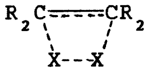
Thus the bimolecular isotope exchange

$$I^- + RI^* \longrightarrow I^{-*} + RI$$

may be an exactly synchronous process, and an *addition reaction*

$$R_2C{=}CR_2 + X_2 \longrightarrow XR_2C{-}CR_2X$$

may also conceivably be one, for instance if it involves a transition state in which the two C-X bond lengths, and the two angles XCC are equal.



(N.B.: The foregoing examples are not intended to convey a view as to the actual *mechanisms* of these reactions, which may or may not involve concerted and/or synchronous processes.)

The view is strongly held by some active workers in the field that the use of this term can be seriously misleading and is best avoided.

T-JUMP

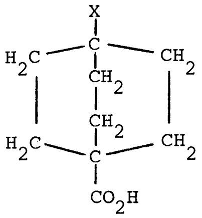
See *chemical relaxation.*

TAFT EQUATION

A $\rho\sigma$-equation with modified parameters ρ_I, σ_I, used in correlations of polar effects in reactions of aliphatic compounds,

$$\lg (k_X/k_H) = \rho_I\sigma_I$$

where $\sigma_I = \lg(K_X/K_H)$, referring to acid dissociation constants of the acids



or $\sigma_I = 0.262 \lg(K_X/K_H)$, referring to substituted acetic acids XCH_2COOH.

TAFT (1952, 1953)

See also *ρ-value, σ-constant.*

+ *TAUTOMERIC EFFECT (obsolete)*

See *electromeric effect.*

TAUTOMERISM

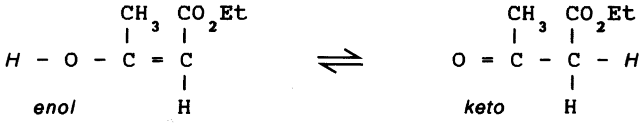
Isomerism of the general form:

$$G - X - Y = Z \rightleftharpoons X = Y - Z - G\cdot$$

where the isomers (called tautomers) are readily interconvertible; the atoms connecting the groups X, Y, Z are typically any of C, H, O or S, and G is a *group* which becomes an *electrofuge* or *nucleofuge* during isomerization. The commonest case, when the electrofuge is H^+, is also known as "prototropy". When the analogous isomerization involves the *migration* of anionic groups or of other cationic groups one also speaks of "anionotropy" and (less commonly) "cationotropy", respectively.

Examples, written so as to illustrate the general pattern given above, include:

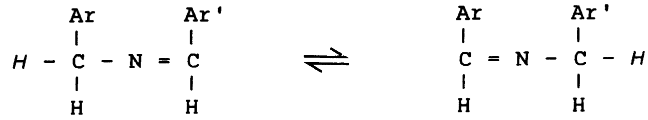
(a) keto - enol tautomerism, such as



$$\underset{enol}{H-O-\overset{CH_3}{\overset{|}{C}}=\underset{\underset{H}{|}}{\overset{CO_2Et}{\overset{|}{C}}}} \rightleftharpoons \underset{keto}{O=\overset{CH_3}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{CO_2Et}{\overset{|}{C}}}-H}$$

($G^+ = H^+$, X = O, Y = $C.CH_3$, Z = $CH.CO_2Et$

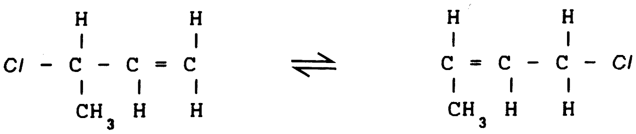
(b)



$H-\underset{H}{\overset{Ar}{C}}-N=\underset{H}{\overset{Ar'}{C}} \rightleftharpoons \underset{H}{\overset{Ar}{C}}=N-\underset{H}{\overset{Ar'}{C}}-H$

($G^+ = H^+$, X = CHAr, Y = N, Z = CHAr')

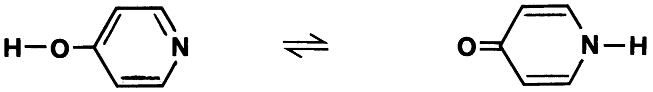
(c)



$Cl-\underset{CH_3}{\overset{H}{C}}-\underset{H}{C}=\underset{H}{\overset{H}{C}} \rightleftharpoons \underset{CH_3}{\overset{H}{C}}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-Cl$

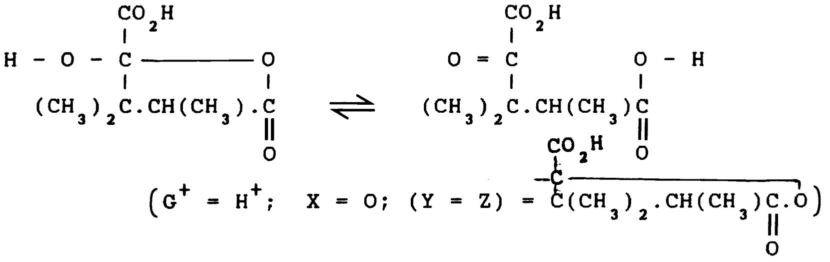
($G^- = Cl^-$, X = $CH.CH_3$, Y = CH, Z = CH_2)

The grouping Y may itself be a three-atom (or five-atom) chain extending the conjugation, as in



($G^+ = H^+$; X = O^-, Y = C-CH=CH; Z = N)

The double bond between Y and Z may be replaced by a ring, when the phenomenon is called ring-chain tautomerism, as in

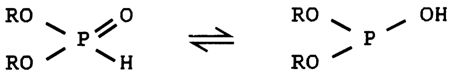


($G^+ = H^+$; X = O; (Y = Z) = $\overset{|}{\underset{}{C}}(CH_3)_2.CH(CH_3)C.O$)

Conceivable examples of isomerism of the type

$H-C\equiv N \rightleftharpoons \bar{C}\equiv\overset{+}{N}-H$

or



(involving the migration of H^+ to a *neighbouring* atom) are also sometimes considered to fall under the heading of tautomerism.

See INGOLD (1953)

See also *ambident, sigmatropic rearrangement, tautomerization, valence tautomerism*.

TAUTOMERIZATION

The *isomerization* by which tautomers are interconverted. It is a *heterolytic molecular rearrangement* and is frequently very rapid.

See *tautomerism*.

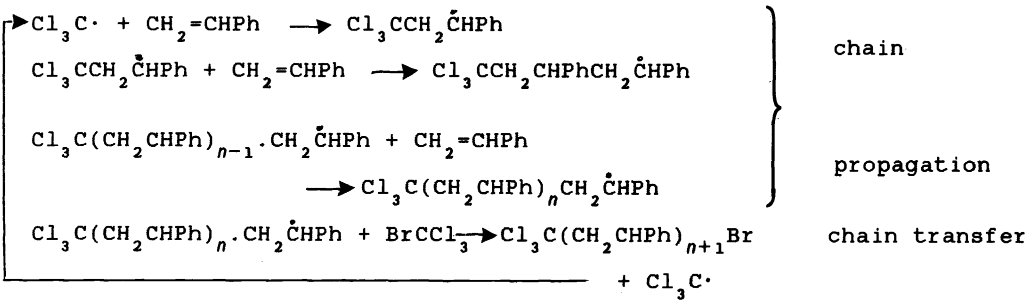
TELE-SUBSTITUTION

A *substitution reaction* in which the *entering group* takes up a position more than one atom away from the atom to which the *leaving group* was attached.

See also *cine-substitution*.

TELOMERIZATION

The formation of an *addition* oligomer, having uniform end groups X'...X", by a *chain reaction* in which a *chain transfer* limits the length of the polymer ("telomer") produced. An example is the polymerization of styrene in bromotrichloromethane solution (X' = CCl_3, X" = Br), where $Cl_3C\cdot$ radicals are formed in the initiation step) to produce $Cl_3C[CH_2CHPh]_nBr$, with *n* greater than 1 and often less than ca. 10:



$$\begin{aligned}
&Cl_3C\cdot + CH_2{=}CHPh \longrightarrow Cl_3CCH_2\dot{C}HPh \\
&Cl_3CCH_2\dot{C}HPh + CH_2{=}CHPh \longrightarrow Cl_3CCH_2CHPhCH_2\dot{C}HPh \\
&Cl_3C(CH_2CHPh)_{n-1}.CH_2\dot{C}HPh + CH_2{=}CHPh \longrightarrow Cl_3C(CH_2CHPh)_nCH_2\dot{C}HPh \\
&Cl_3C(CH_2CHPh)_n.CH_2\dot{C}HPh + BrCCl_3 \longrightarrow Cl_3C(CH_2CHPh)_{n+1}Br + Cl_3C\cdot
\end{aligned}$$

TERMINATION

The steps in a *chain reaction* in which *reactive reaction intermediates* are destroyed or rendered inactive, thus ending the chain.

TETRAHEDRAL INTERMEDIATE

A *reaction intermediate* in which an initially double-bonded carbon atom (typically a carbonyl carbon atom) has been transformed from a trigonal to a tetrahedral arrangement of *bonds*. For example, aldol in the *condensation reaction* of acetaldehyde, (but most tetrahedral intermediates have a more fleeting existence.)

THERMODYDNAMIC CONTROL *(of product composition)*

The term characterizes conditions that lead to reaction products in a proportion governed by the equilibrium constant for their interconversion and/or for the interconversion of *reaction intermediates* formed in or after the *rate-limiting step*. (Some workers prefer to describe this phenomenon as "equilibrium control").

See also *kinetic control*.

THERMOLYSIS

The uncatalysed cleavage of one or more covalent *bonds* resulting from exposure of the compound to a raised temperature, or a process in which such cleavage is an essential part.

See also *pyrolysis*.

TIGHT ION PAIR

See *ion pair*.

TRANSFORMATION

The conversion of a *substrate* into a particular product as a consequence of *chemical reactions(s)*, irrespective of reagents or *mechanisms* involved. For example, the transformation of aniline ($C_6H_5NH_2$) into *N*-phenylacetamide ($C_6H_5NHCOCH_3$) may be effected by use of acetyl chloride or acetic anhydride or ketene, etc.

TRANSIENT (CHEMICAL SPECIES)

Relating to a short-lived *reaction intermediate*. It can be defined only in relation to a time scale fixed by the experimental conditions and the limitations of the technique employed in the detection of the intermediate. The term is a relative one: intermediates having a relatively longer mean-life are described as "persistent".

TRANSITION CO-ORDINATE

The normal co-ordinate (of an "activated complex") corresponding to a vibration with an imaginary frequency. Motion along it leads towards products.

See also *reaction co-ordinate, transition state.*

TRANSITION STATE

In theories describing *elementary reactions* it is usually assumed that there is a transition state of more positive molar Gibbs energy between the reactants and the products through which an assembly of atoms (initially composing the *molecular entities* of the reactants) must pass on going from reactants to products in either direction. In the formalism of "transition state theory" the transition state of an elementary reaction is that set of states (each characterized by its own geometry and energy) such that an assembly of atoms, when randomly placed there, would have an equal probability of forming the reactants or of forming the products of that elementary reaction. This set of states is characterized by $q_{\ddagger}$, the partition function for the transition state. The assembly of atoms at the transition state may be called an "activated complex". (It is not a *complex* according to the definition given in this Glossary.)

In a more qualitative fashion a transition state is sometimes described as an "early transition state" (reactant-like) or as a "late transition state" (product-like). The clearest application of the use of these terms is linked to the *Hammond principle*. The energy of an early transition state of an elementary reaction is close to that of the initial state, and only a small reorganization of molecular structure occurs between these two states. A late transition state, having an energy close to that of the final state, will require little reorganization of molecular structure between the transition state and the final state.

It may be noted that calculations of reaction rates by the transition state method and based on calculated *potential energy surfaces* refer to the potential energy maximum at the saddle point, as this is the only point for which the requisite separability of transition state co-ordinates may be assumed. The ratio of the number of assemblies of atoms that pass through to the products to the number of those that reach the saddle point from the reactants can be less than unity, and this fraction is the "transmission coefficient", κ. (There are also reactions, such as the gas-phase *colligation* of simple *radicals* that do not require "activation" and which therefore do not involve a transition state.)

See also *Gibbs energy of activation, potential-energy profile*.

TRANSMISSION COEFFICIENT

See *transition state*.

TRANSPORT CONTROL

See *microscopic diffusion control*.

TRAPPING

The interception of a *reactive* molecule or reactive *reaction intermediate* so that it is removed from the system or converted to a more *stable* form for study or identification.

See also *scavenger*.

UNIMOLECULAR

See *molecularity*.

UNREACTIVE

Failing to react with a specified *chemical species* under specified conditions. The term should not be used in place of *stable*, since a relatively more stable species may nevertheless be more *reactive* than some reference species towards a given reaction partner.

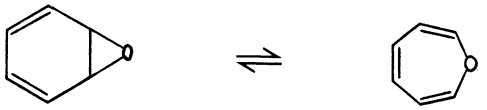
UNSTABLE

The opposite of *stable*, i.e. the *chemical species* concerned has a higher molar Gibbs energy than some assumed standard. The term should not be used in place of *reactive or transient*, although more reactive or transient species are frequently also more unstable.

(Very unstable chemical species tend to undergo exothermic *unimolecular* decompositions. Variations in the structure of related chemical species of this kind generally affect the energy of the *transition states* for these decompositions less than they affect the stability of the decomposing chemical species. In this context, low stability may therefore parallel a relatively high rate of unimolecular decomposition.)

VALENCE TAUTOMERISM

The term describes simple reversible and generally rapid *isomerizations* or *degenerate rearrangements* involving the formation and rupture of single and/or double *bonds*, without *migration* of atoms or *groups*; , e.g.



See also *fluxional, tautomerism*.

VAN DER WAALS FORCES

The attractive forces between *molecular entities* (or between groups within the same molecular entity) other than those due to *bond* formation or to the electrostatic interaction of ions or of ionic *groups* with one another or with neutral molecules.

VINYL CATION (or **Vinylic cation**)

The species $CH_2{=}\overset{+}{C}H$ or a substitution derivative thereof.

VOLUME OF ACTIVATION, ΔV_a

A quantity derived from the pressure dependence of the *rate constant* of a reaction (mainly used for reactions in solution), defined by the equation

$$\Delta V_a = -RT\left(\frac{\partial \ln k}{\partial p}\right)_T$$

providing that the rate constants of all reactions (except first-order reactions) are expressed in pressure-independent concentration units, such as mol dm^{3} at a fixed temperature and pressure.

The volume of activation is interpreted, according to *transition-state* theory as the difference between the partial molar volume of the transition state ($V^{\ddagger}$) and the sum of the partial molar volumes of the reactants at the same temperature and pressure, i.e.,

$$\Delta V_a = \Delta V^{\ddagger} = V^{\ddagger} - \Sigma r V_R$$

where r is the stoichiometric number of the reactant R in the reaction (see *order of reaction*) and V_R its partial molar volume.

WHELAND INTERMEDIATE

See *Meisenheimer adduct*.

YLIDE

A *chemical species* produced (actually or notionally) by loss of a proton from an atom directly attached to the central heteroatom of an *"oniom" ion*, e.g.

$$Ph_3\overset{+}{P}\text{-CHRR'} \xrightarrow{-H^+} (Ph_3\overset{+}{P}\text{-}\overset{-}{C}RR' \longleftrightarrow Ph_3P\text{=CRR'})$$

ylide

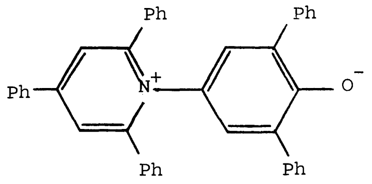
Z-VALUE

An index of the *ionizing power* of a solvent based on the frequency of the longest wavelength electronic absorption maximum of 1-ethyl-4-methoxycarbonyl pyridinium iodide in the solvent. The Z-value is given by

$$Z = (2.859 \times 10^4/\lambda \text{ nm}^{-1})\text{kcal mol}^{-1}$$

where λ is expressed in nanometres.

A similar scale is the E_T scale [called $E_T(30)$ by its originators] derived in an exactly analogous way from the visible spectrum of



E_T is given by

$$E_T = (1.1962 \times 10^5/\lambda \text{ nm}^{-1})\text{kJ mol}^{-1}$$

KOSOWER (1958)

DIMROTH, REICHARDT, SIEPMANN and BOHLMANN (1963).

ZAITSEV RULE

Dehydrohalogenation of secondary- and tertiary-alkyl halides proceeds by the preferential removal of the β-hydrogen from the carbon that has the smallest number of hydrogens. Originally formulated by A. Zaitsev to generalize the orientation in *β-elimination reactions* of alkyl halides, this rule has been extended and modified, as follows: When two or more alkenes can be produced in an elimination reaction, the thermodynamically most *stable* olefin will predominate. Exceptions to the Zaitsev rule are exemplified by the *Hofmann rule*.

SAYTZEFF (1875).

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