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SYSTEM FOR SYMBOLIC REPRESENTATION OF REACTION MECHANISMS

(Recommendations 1988)

Prepared for publication by

ROBERT D. GUTHRIE

University of Kentucky, Lexington, Kentucky, USA

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System for symbolic representation of reaction mechanisms (Recommendations 1988)

Abstract

This system is designed to provide simple descriptions of reaction mechanisms suitable for use in oral and written communication. The need arises because the system originally devised by Ingold is becoming increasingly overburdened with nonsystematic modifications.

The new system describes a mechanism in terms of bond making (symbolized A for "attachment") and breaking (D, "detachment"), with subscripts and other symbols to indicate the pattern of electron movement. For example, $A_N D_N$ describes a single concerted process involving nucleophilic bond making and nucleofugic bond breaking (such as the S_N2 Ingold mechanism), and $A_N + D_N$ represents a two-step process (such as S_N1). There is provision for describing homolytic and cyclic mechanisms, for diffusional control, and for electron transfer. Separate provision is made for symbolizing extra-mechanistic information, including the class of transformation, the nature of the substrate, and the occurrence of catalysis, using easily pronounced terms. Thus the symbol Em-AL-B describes an elimination from an alkyl substrate under general base catalysis.

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PREAMBLE

These rules constitute a system for the symbolic description of simple reaction mechanisms. The primary goal is to provide a simple but useful symbolic language for oral and written transmission of the details of reaction mechanism models. The mechanistic nomenclature devised by Ingold^{1,2} has been modified by extension and alteration for 30 years.³ The Ingold system is still widely used, but suffers from two problems.

1. It is over-concise by having to serve partly as a phenomenological description of the observed features of a reaction (substitution, elimination), and partly as a statement regarding the mechanism of the reaction (molecularity, concertedness, electronic characteristics).

2. It provides ambiguous interpretations of mechanisms, which are perhaps most noticeable for the S_N2 - S_N1 spectrum in solvolysis and other substitution reactions. In some cases quite different mechanisms come under the same designation. (See, for example, S_E2 . Table 2.)

It is desirable to separate descriptions of the observed properties of a reaction and of its mechanism. We propose here a system that is designed specifically to describe mechanisms of reactions. While most of the properties of a reaction may be deduced through a logical dissection of the mechanistic code, we also propose a modification of the Ingold nomenclature which may be useful to describe the observed properties of a reaction.

A system of nomenclature for reaction mechanisms should deal directly with the basic currency of molecular change: bond making and bond breaking. The most important properties of a reaction mechanism that should be described by such a system are:

1. The number of steps in the reaction.
2. The sequence of steps.
3. The nature of these steps, including significant diffusional steps.

The logic of naming mechanisms in terms of bond-making and bond-breaking steps was emphasized by Mathieu in 1960.⁴ A division of ligand substitution mechanisms based on bond-making/bond-breaking sequence was later suggested by Langford and Gray.⁵ In 1975 the proposals of Mathieu were modified somewhat by Guthrie⁶ and this document preserves the spirit and many of the details of the Mathieu and Guthrie systems. As pointed out by Guthrie and elaborated later by Roberts⁷ and by Littler,⁸ the symbolic representation of reaction mechanisms can be carried out at varying levels of completeness and with proportional complexity in the symbolization. The degree of completeness and type of information transmitted in a mechanistic designation will depend on its intended use. For the representation of an S_N2 reaction at the information level of the Ingold system we would wish to indicate that a bond is formed to a nucleophile, that a bond is broken with separation of a nucleofuge and that these two events occur in a single reaction. This document will be confined to names appropriate for use in speech/writing delineation of distinguishable bond-making and bond-breaking sequences.

In choosing examples to illustrate the system, we have emphasized mechanisms for which Ingold-type designations have been previously assigned. For historical reasons, most of these are of the heterolytic variety. We contend that the system is equally capable of handling homolytic and pericyclic mechanisms at the same level of information content. Our approach becomes unwieldy only when a mechanism involves a large number of separate reactions or bonding changes at many different atomic centers. However, even such complicated mechanisms may be viewed as sequences of easily symbolized component processes.

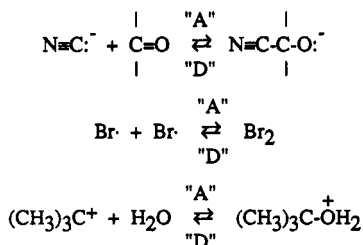
The main guideline is simplicity. The name should consist of the minimum number of symbols necessary to separate the categories but should not require a large number of different kinds of symbols. It should be possible for the user to either recognize or construct the symbolic representations without reference to tables or long lists of rules. The names should also be pronounceable in a few syllables. It will be impractical for variations which differ only in elemental composition to be distinguished at this level. Details of transition state structure and

stereochemistry or properties dependent on the presence of large collections of molecules will be temporarily ignored and dealt with in supplemental rules. It will be kept in mind, however, that extension of the simple system to one of greater completeness and precision should be a continuous change. Compatibility should therefore be maintained between these basic representations and those envisioned for the type of linear abbreviation eventually to be used in an information retrieval system.

RULES

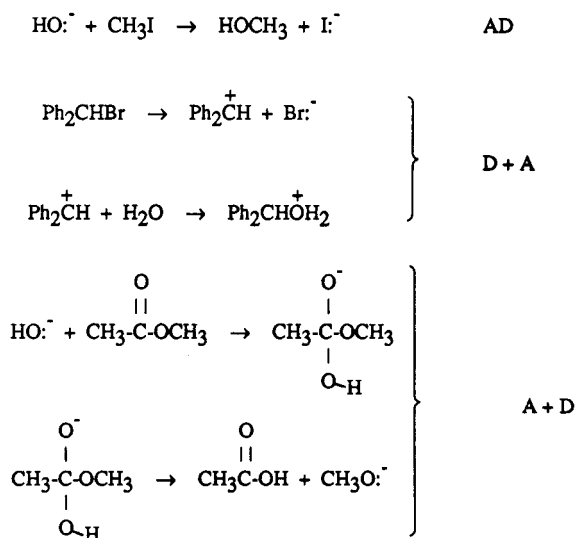
Rule 1. Bond Making and Breaking. When a new bond is formed during the transformation of one molecular structure to another, the mechanistic representation of the transformation will include the symbol "A" (association or attachment) to represent this bond-forming component. Similarly bond-breaking components will be symbolized by "D" (dissociation or detachment). There will be no explicit symbolic representation of changes in bond multiplicity. For example the name of an elimination will contain two "D" symbols for the separation of the leaving groups but no term for double bond formation because this *must* occur. These "A" and "D" symbols have been referred to as *primitive changes*.⁹ The formation of weak or partial bonds, as in hydrogen bonds and ion pairs, is not indicated by "A" or "D".

Events described by "A" and "D":



Rule 2. Concerted¹⁰ and Stepwise Multibond Processes. The "A" and "D" symbols or sets of "A" and "D" symbols representing the bonding changes occurring during a transformation will be normally punctuated by a "+" sign when the changes take place in separate reaction steps (nonconcerted). Sets of nonpunctuated "A" and/or "D" symbols correspond to *elementary reactions*.⁹

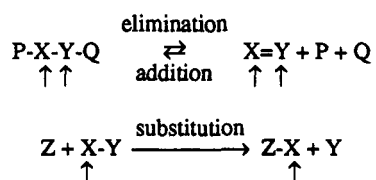
Combining "A"s and "D"s:



For those cases in which an intermediate is of such short life that it reacts in a step faster than diffusion but slower than a molecular vibration it may be useful to substitute the symbol "*" for "+". For reactions in solution this would normally correspond to a lifetime too short to permit diffusional equilibrium with the bulk solution (i.e., to permit exchange between nearest neighbors and other components of the solution). For the third example above, the borderline situation, A*D, would be that where the tetrahedral intermediate lies in an energy minimum but its lifetime is too short to allow exchange with low concentration hydron donors or acceptors.

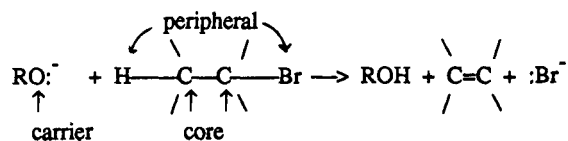
Rule 3. Direction of Electron Movement in the Mechanisms of Transformations¹¹. In order to allow specification of the direction of electron movement in bond formation and bond scission (primitive changes), it is necessary to designate one of the participating atoms as a reference atom relative to which the process is nucleophilic, electrophilic, nucleofugic or electrofugic. When molecular transformations are viewed as additions, eliminations, or substitutions¹¹ a set of reference atoms is implicitly established. We define as *core atoms* the two atoms involved in a transformed multiple bond (addition or elimination) or the single atom at which substitution occurs or is considered to occur (see note on rationale after rule 3.3). In some cases to be discussed later, a larger set of atoms may carry out the same function as these minimal sets and in such cases, all members will be considered core atoms. The reader should recognize that *the core atoms need not be carbon atoms* although in the most familiar cases they are.

Core Atoms (↑)



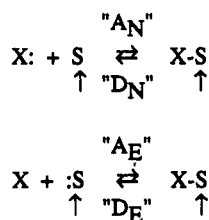
When an "A" or "D" term represents a primitive change involving a *core atom*, a subscript (E, N or R defined below) will be affixed.

Two other types of atoms participating in primitive changes are delineated for purposes to be described below. *Peripheral atoms* are non-core atoms which at some point in the mechanistic sequence are situated in the molecule containing the core atom(s). *Carrier atoms* are those participant atoms which are neither core atoms nor peripheral atoms. As implied by their name, these carry other atoms or groups of atoms to or from the molecule containing the core atoms but do not themselves become covalently attached to that molecule. An example illustrating the mechanistic function of the three different types of atoms follows:



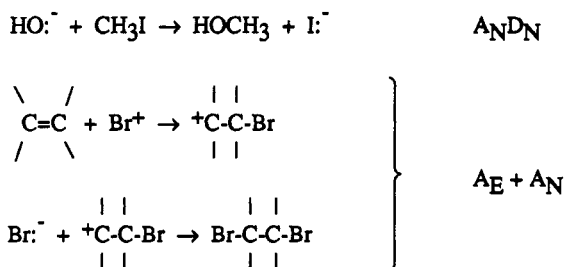
In selecting a reference atom for any primitive change, priority is given to core atoms over peripheral and carrier atoms and to peripheral atoms over carrier atoms. *If two peripheral atoms are involved in a primitive change, the one closest to a core atom (smallest number of intervening bonds) is chosen as the reference atom.* In the special case of a primitive change in a bond between two peripheral atoms which are equally distant from core atoms, a situation which arises in cyclic processes (rule 4.2), the subscript "n" will be arbitrarily chosen.

3.1. Direction of Electron Movement in Primitive Changes Involving Core Atoms. Primitive changes involving core atoms are identified by upper case subscripts. The subscript is "N" if the core atom is undergoing bond formation to a nucleophile (A_N) or bond scission with loss of a nucleofuge (D_N). The subscript is "E" when the core atom is involved in corresponding electrophilic or electrofugic processes (A_E or D_E).



The subscript "R" is used to designate homolytic primitive changes (A_R and D_R). Reactions of radicals with nucleophiles or electrophiles are discussed in the section on homolytic processes (3.4). If the primitive change does not involve a core atom, a lower case subscript is affixed as described in the following section.

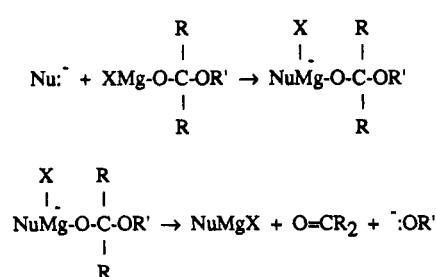
Use of Subscripts



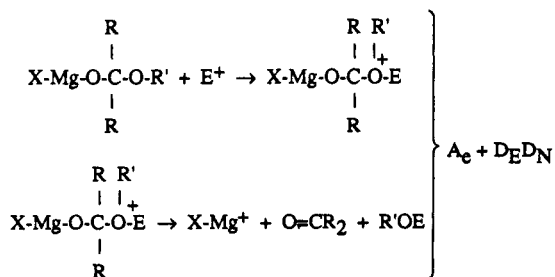
3.2. Primitive Changes Not Involving Core Atoms. The subscript "e" is used to indicate that a peripheral reference atom is being attacked by an electrophile or losing an electrofuge (A_e and D_e , respectively). The subscript "n" indicates the same phenomena with a nucleophile or nucleofuge (A_n and D_n). Homolytic primitive changes not involving core atoms are identified by the subscript "r" (A_r and D_r).

The use and importance of these lower case subscripts is illustrated by the following example. Consider two heterolytic elimination mechanisms of the general class, $D_E D_N$. Assume that in one case an electrophile bonds to the nucleofugal group in a separate step before the elimination process. This then becomes $A_e + D_E D_N$. In the other case, a nucleophile binds to the electrofugal group and the designation is $A_n + D_E D_N$. Bonding to an electrophile is the more common situation but both processes are conceptually possible. Consider two possible decomposition modes for the adduct of a Grignard reagent to an ester (clearly not a complete set nor necessarily a realistic one).

Promotion by a nucleophile



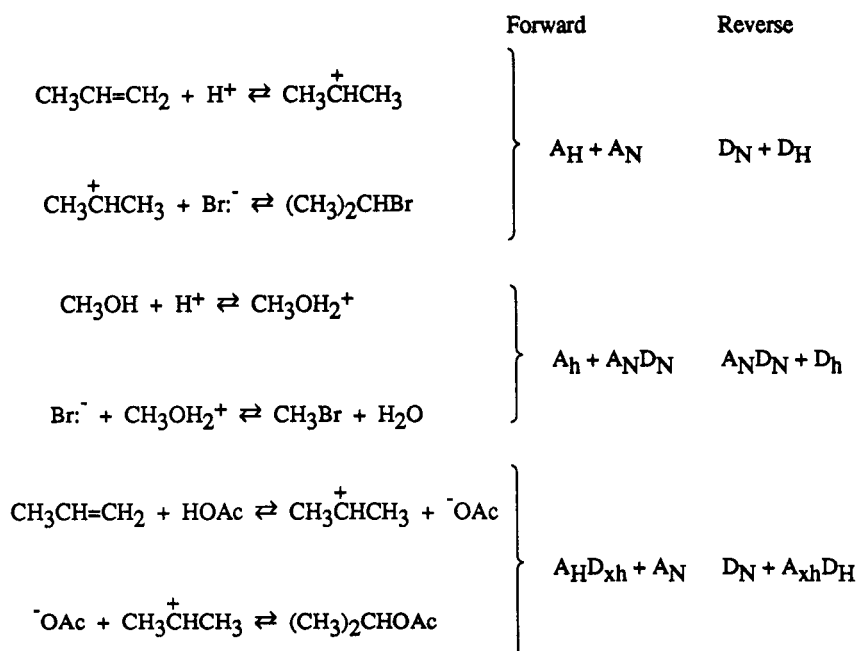
Promotion by an electrophile



Without any identifying notation for the isolated "A" term, these two mechanisms would be represented by identical sets of symbols. With an upper case subscript the capacity to emphasize the eliminative character of the transformation would be lost. Note that in both examples the attacking atom (Nu or E) and the atom attacked (Mg or O) must be considered peripheral atoms because at the intermediate stage, both are part of the same molecular unit as the core atoms. However, Mg is closer to the core atom than Nu, and O is closer than E. Therefore Mg and O become reference atoms for the isolated primitive change in the first and second examples respectively.

The lower case modifiers could be omitted in speech or prefaced by "peri". The nucleophile-promoted mechanism above would then be expressed "A peri n plus D E D N". If the symbol "*" is employed it may be represented in speech by the word "star".

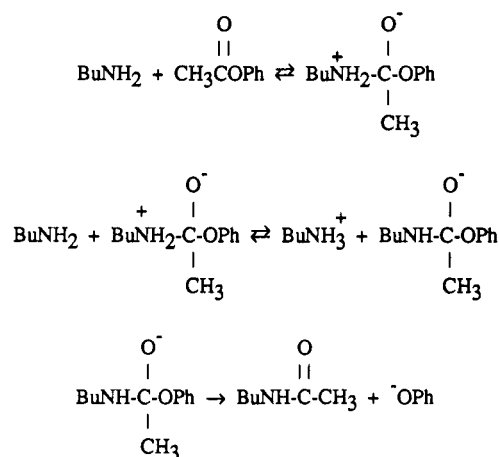
3.3. The Hydron* as a Special Case. Because of the special role of the hydron and in the interest of increased clarity, A_h , D_h , A_H and D_H may be used where the electrophile involved in a primitive change is the hydron. Appearance of "h" or "H" as a subscript effectively identifies hydrogen as the electrophilic or electrofugal partner in the primitive change regardless of whether hydrogen or its partner should be the reference atom according to the preceding rules. If a core atom is involved in the primitive change, the subscript is "H", if not it is "h". If a carrier atom is the partner in a primitive change involving the hydron the subscript "xh" will be used to denote a primitive change involving a generalized carrier atom, x, and the hydron, h. (Note that "xH" is an undefined subscript because use of "H" specifies either hydrogen or its partner as a core atom. In either case the primitive change partner of hydrogen is not a carrier atom.) Some illustrative examples follow.



Note that for the proton transfer component of the first two examples the companion primitive changes, breaking of a bond to solvent in the forward reaction and formation of a bond to solvent in the reverse reaction, are not specified. Thus the appearance of only one H-subscripted or h-subscripted term in the symbol string representing a mechanism indicates that solvent, or possibly lyate ion, is the probable solution partner for the hydron. (This is not necessarily an indication of specific acid or specific base catalysis in the observed rate law.)

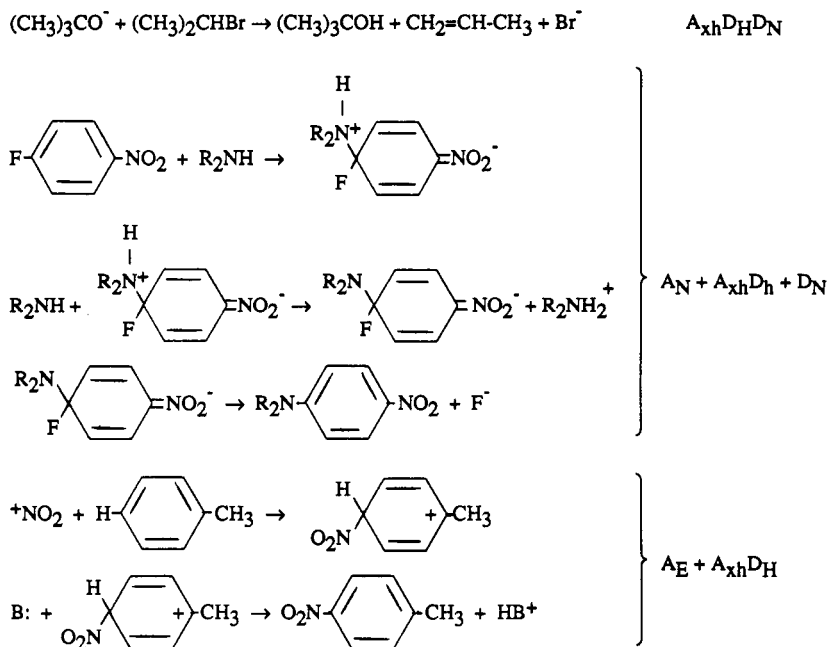
*The Commission on Physical Organic Chemistry recommends^{11a} the use of the term "hydron" for the positive ion of hydrogen in general, without regard to nuclear mass. Thus the proton, the deuteron and the triton are all hydrons.

The "xh" subscript is particularly useful when describing proton transfers to and from peripheral atoms. Consider the following substitution mechanism:



This is now represented as $A_N + A_{xh}D_h + D_N$. Without the "x", the second step would be represented as A_hD_h . This would signify a proton transfer but would leave unclear which of several possible proton transfers was intended. Protonation at $-\text{O}^-$ or intramolecular proton transfer from $-\text{NH}_2^+$ to $-\text{O}^-$ would be alternative interpretations. With "xh" used to identify the primitive change involving the carrier atom, however, protonation at oxygen becomes A_hD_{xh} , whereas intramolecular transfer is A_hD_h (no carrier atom involved). The prefix "intra" is recommended in the latter case to emphasize the intramolecular aspect of the change. (See rule 4.2.)

Other Examples:

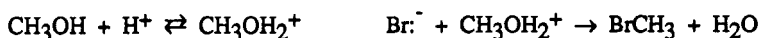


When a hydron is transferred to or from oxygen and nitrogen it may be acceptable to omit the hydron-transfer terms. This is illustrated in example 1.8 (see below under Simple Examples and in Table 2) wherein the mechanism designated as $A_{AC}2$ by Ingold can be described as $A_h + A_N + A_hD_h + D_N + D_h$ or as $A_h + A_N + D_N$ or simply as $A_N + D_N$. The choice depends on the context of the usage. As pointed out earlier, the transmission of more detailed information will require more complex strings of symbols.

Rationale for Rules 3.1-3.3.

It is of considerable importance to be able to specify which atom is providing the electron pair when a chemical bond is formed. The terms "A" and "D" specify that a bond is made or broken but are incapable of transmitting information about electron flow. Adding a modifier to "A" or "D" does not solve the problem unless there is some method of distinguishing and assigning priorities to the two atoms involved. There are a variety of ways in which this could be done, but the least disruptive to established practice is the traditional one of viewing simple reactions as substitutions, additions or eliminations. Once this is done, certain atoms are automatically distinguished from others and can serve as reference points which allow the direction of electron movement to be specified.

If a reaction is viewed as a substitution,^{10,11} the viewer has decided, perhaps for reasons of commonality with stored information, to assign priority to a specific atom and to emphasize the changes that occur relative to this atom. Consider the reaction of methanol with hydrogen bromide:



An organic chemist would normally see this as a substitution reaction at carbon. To adopt this viewpoint establishes a priority for carbon. The reaction then becomes a nucleophilic substitution reaction in which carbon loses an electron pair to oxygen and gains a pair from bromine. With adoption of this viewpoint, the rules outlined above demand designation as $A_{\text{H}} + A_{\text{N}}D_{\text{N}}$. An equally valid though nontraditional viewpoint could be that the reaction is a substitution at oxygen. This would then be a case where the core atom is not carbon and the designation would then be $A_{\text{H}} + A_{\text{O}}D_{\text{E}}$. The choice of viewpoints is of course entirely arbitrary and subjective but properly so. We see no problem with the fact that this system may not specify a unique name for a particular mechanistic model. Unique names are prescribed in more elaborate systems^{6,7,8} which are better suited to complete information retrieval. The choice of emphasis that is provided in this simple version would be sorely missed if removed from the working language of chemistry.

When reactions are viewed as addition or elimination transformations,^{10,11} two atoms are selected between which bond multiplicity is decreased or increased respectively. These atoms can now be used as reference points in a manner completely parallel to that employed with the single core atom in substitution.

It will be noticed that in addition to encoding the sequence of bond-making and bond-breaking steps, this procedure allows rapid recognition of the transformation type from the mechanistic symbols. One locates the two terms having upper-case subscripts: *two subscripted "A" terms signal addition; two subscripted "D" terms indicate elimination; while an "A" and a "D" term (each subscripted) denote substitution.* The examples given following section 3.3 are thus readily identified as an elimination and two substitutions. Mechanisms requiring symbol strings containing more than two upper-case-subscripted terms are generally regarded as lying outside of the domain of this simple system. An exception is made in the case of simple rearrangements. (See Simple Examples 4.1-4.4.)

Some of the better-known examples of the Ingold system are translated in Table 1 for comparison. These translations are necessarily approximate because, as stated in the preamble, the Ingold System names are by nature less specific than those being set forth in these rules.

3.4. Homolytic Processes. If a bond is made by the coupling of two radicals or broken by the reverse of such a process, it is normally considered that each atom contributes one electron to the bond. When the terms representing such processes are to be subscripted, a simple "R" or "r" is used:



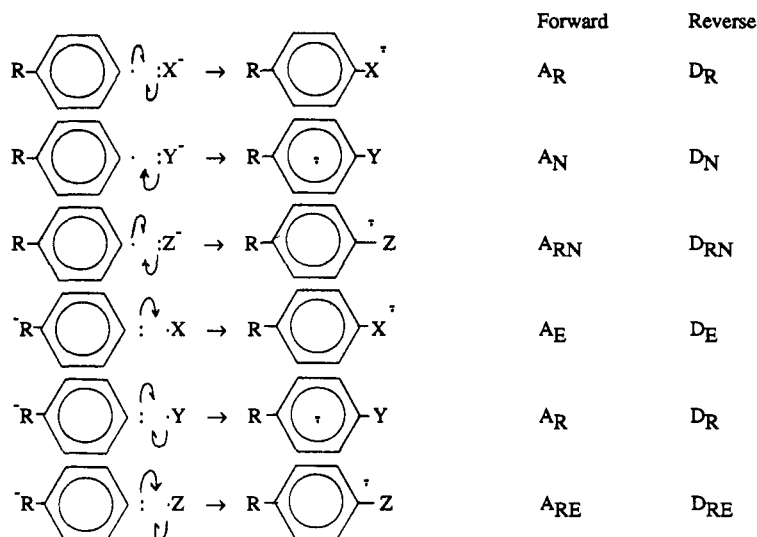
Table 1. Comparison of Selected Ingold-System Names with those Proposed in this Document.

Ingold Name	Proposed Name
S_N2	$A_N D_N$
S_N1 (limiting)	$D_N + A_N$
S_E1	$D_E + A_E$
E1	$D_N + D_H$ (or $D_N + D_E$)
E2	$A_{xh} D_H D_N$
ElcB ^a	$A_n D_E + D_N$ (or $A_{xh} D_H + D_N$)

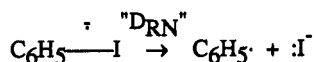
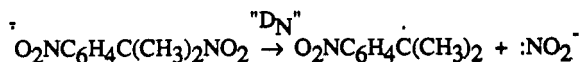
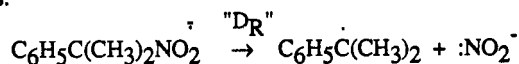
a. See also section on subcategories following Rules.

When an unpaired electron is associated with one of the bonding partners but not with the other, the process is sometimes viewed as a coupling in which the electrons in the non-radical member become unpaired and sometimes as analogous to a heterolytic process in which the bonding pair remains paired before, during and after the elementary reaction.

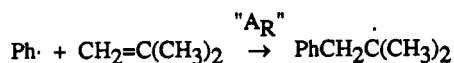
In the latter situation, the odd electron may be viewed as ending up in a π orbital of the product or in an antibonding σ orbital (σ^*) associated with the two atoms between which bond formation is taking place. To further complicate matters, either the partner carrying the odd electron or the partner carrying the electron pair could be designated as the core atom in a given case. A complete set of hypothetical models and the symbols assigned to each are listed below. The phenyl carbon is assigned the role of core atom in each example.



Note: The name is dependent, in part, on the namer's perception regarding the most representative canonical form of the product radical anion. In the third and sixth examples the symbol "·" is placed over the σ bond, indicating residence of the odd electron in the antibonding σ orbital associated with that bond.

Specific Examples:**Rationale for Section 3.4**

It is not the function of this document to deal with the relative validities of the models presented above. We have simply provided symbols to distinguish formally different representations of the primitive changes. It might be noted that the customary representation for addition of radicals to double bonds would qualify these as A_R processes regardless of which bonding partner contained the core atom:



3.5. Unsubscripted "A" and "D" Terms. Unsubscripted "A" and "D" terms are used when the preceding rules do not provide a basis for determining a subscript. The two most common situations where this applies are:

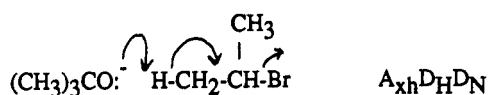
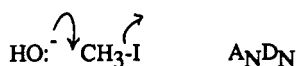
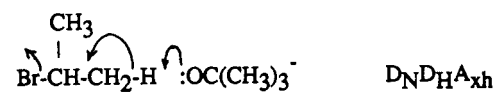
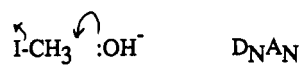
1. a primitive change is part of a cyclic process and the direction of electron movement is not known, examples appear in section 4.2;
2. a mechanistically relevant, isolated primitive change takes place in a molecule that does not contain the core atom(s), see example 1.15.

Rule 4. Sequence of Primitive Changes within an Elementary Reaction. If more than one primitive change occurs in an elementary reaction (a nonpunctuated set of "A" symbols, "D" symbols or combination thereof is present), rules are needed to provide consistency in order of presentation.

4.1. Left-to-Right Convention for Electron Movement. If possible, the structural formula(e) of the reactant(s) should be drawn so that the bonds to be made or broken form a linear array. The symbols representing each primitive change (bond-making or bond-breaking process) can then be arranged in a corresponding order. In general, there will be two such arrangements possible, one in which the electrons move from left to right and one in which they move from right to left. *The left-to-right order will be given preference.*

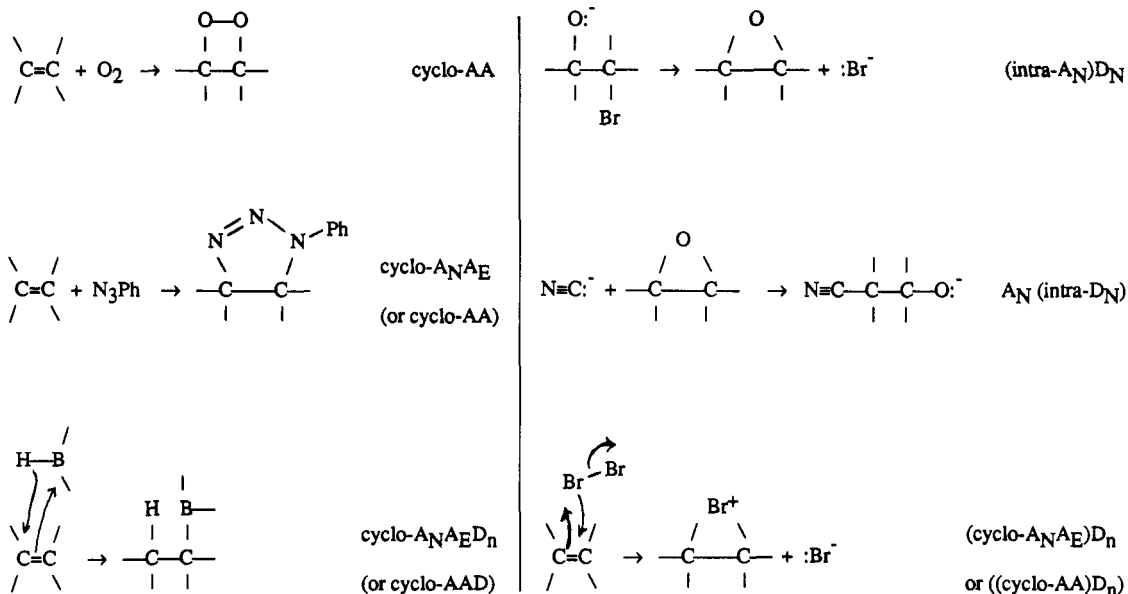
A unique name for any given noncyclic reaction mechanism will be generated by following these simple rules:

1. If the reaction is bimolecular, place the nucleophilic reactant on the left.
2. If the reaction is unimolecular, place the nucleofugic group on the right.
3. List processes according to the order in which they are encountered when proceeding from left to right across the structures.

Preferred form**Nonpreferred form**

4.2. Cyclic Processes. For a pericyclic reaction,⁹ the primitive changes which are components of the pericyclic reaction are identified by the prefix "cyclo-". Other ring-forming or ring-opening primitive changes are identified by the prefix "intra-". Where only part of an elementary reaction is "cyclo-" or "intra-", the prefix and the modified primitive change(s) are enclosed in parentheses.

Examples:



It will be noted from these examples that polar character of the transition states for cycloaddition and cycloelimination reactions may be emphasized by inclusion of subscripts or deemphasized by leaving terms for intra-ring primitive changes unsubscripted. This choice of emphasis is left to the discretion of the namer.

When subscripts are employed, the application of rule 4.1 to produce a unique name may be complicated by the requirement for arranging the bonds to be made or broken in a linear array. If these bonds form part of a ring, the choice of linear arrays is no longer unique, thus requiring the following supplemental rule. For the cyclic part of an elementary reaction, the two core-atom primitive changes are listed first followed by the non-core changes. If the core-atom primitive change terms are subscripted, their sequence is arranged to conform with the left-to-right electron movement convention of rule 4.1. In particular, this requires A_N before A_E in addition mechanisms and D_E before D_N in elimination mechanisms. Nucleophilic substitution will be A_ND_N (rather than D_NA_N) and electrophilic substitution will be D_EA_E (rather than A_ED_E). The non-core primitive changes follow the core atom changes in a sequence determined by their molecular proximity to the last-listed primitive change. Placing the two core-atom terms at the beginning of the string when representing cyclic processes, allows ready distinction of addition, elimination and substitution reactions even when no subscripts are employed. Thus the third example above is recognized as cycloaddition (cyclo-AAD). Its reverse (cyclo-DDA) is clearly cycloelimination.

The last three examples given above illustrate situations where only part of the elementary reaction symbol string represents primitive changes that involve ring bonds. The position of the terminal parenthesis may be expressed through the word "with" if such sequences are described orally. Thus the fourth example above would be described as intra A_N with D_N. Several general examples of cyclic processes are treated later including examples of rearrangement processes.

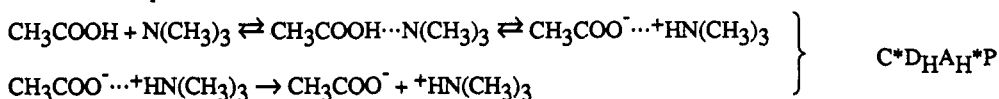
4.3. Other Cases. For any cases not covered by rules 4.1 and 4.2, we have arbitrarily decided to place "A" terms before "D" terms. This is particularly relevant to homolytic reactions. If the decision is between two "A" terms or between two "D" terms, we have placed the "N" subscripted term first.

4.4. Numbering of Primitive Changes. The domain of this simple system can be extended to somewhat more complex mechanisms by using numerical prefixes to specify non-obvious positional relationships between reference atoms. This approach has been used, for example, to differentiate allylic substitution mechanisms such as the Ingold S_N2' mechanism - see Simple Example 1.1 - from the normal S_N2 mechanism. S_N2' thus becomes $3/1/A_N D_N$ as distinct from normal $A_N D_N$ which is understood to be $1/1/A_N D_N$ by default. Note the use of post-slash arabic numerals to indicate *relative* sites of primitive changes. This approach follows soon to be published IUPAC recommendations on naming organic chemical transformations.¹¹ Symbol strings for mechanisms of addition transformations (two upper-case-subscripted "A" terms) and elimination transformations (two upper-case-subscripted "D" terms) presume a 1/2/-relationship between the two core atoms unless otherwise specified. If an elementary reaction symbol string contains both core-atom and peripheral-atom primitive changes, it is usually sufficient to attach only two prefixes which are understood to refer to the core-atom primitive changes - see Simple Example 1.6. If more than two core-atom primitive changes are specified it becomes essential to use a numerical prefix for each to avoid ambiguity. Although coding and decoding of mechanistic models requiring this degree of specification becomes somewhat laborious, the scope of applicability is extended significantly. A class of reactions which is viewed as sufficiently important to justify the effort is that of simple rearrangements - see Simple Examples 4.1-4.4.

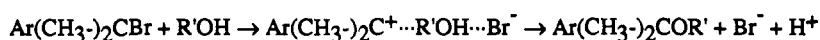
Rule 5. Diffusional Combination "C" and Separation "P". The diffusional assembly and separation of reactants and products is usually understood and need not be identified. However, in some cases it is useful to designate these steps, as in reactions in which they are rate limiting. *They may be designated as "C", for assembly or combination of reactants into an encounter complex, and "P", for separation or parting of a product.* These terms may be used for the formation or scission of weakly interacting complexes that do not warrant the designation "A" or "D", such as hydrogen-bonded complexes or ion pairs. Note that in order for diffusional processes to be kinetically significant, associated elementary processes will have comparable rates. This will normally make use of the "*" symbol (Rule 2) more appropriate than use of the "+" symbol.

The subscripts "int" or "ss" may be added to designate ion pairs or other weak complexes in which the reagents are known to be in contact (int = intimate) or separated by one or more solvent molecules (ss = solvent-separated). These subscripts should be added to the step in which the complex is formed.

Examples:



(For the purpose of illustrating their use, both "C" and "P" have been included in the example above. Normally either "C" or "P" but not both would appear. See the discussion of rate-limiting step in rule 7.1.)

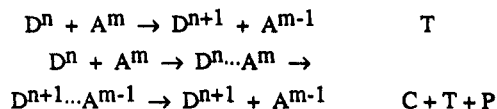


$\text{D}_{\text{Nss}}^* \text{A}_\text{N}$ Formation and solvolysis of a solvent-separated ion pair.

$\text{D}_{\text{Nss}}^* \text{P} + \text{A}_\text{N}$ The ion pair dissociates to a free ion before reaction with solvent.

$\text{D}_\text{N}^* \text{P} + \text{A}_\text{N}$ Same, nature of the ion pair is not known.

Rule 6. Electron Transfer. The process of transferring electrons between molecules or between groups in the same molecule need not involve strong bond formation and therefore cannot always be represented in terms of bond-making and bond-breaking steps. *For this reason a separate symbol is required for electron transfer. We use the symbol "T".* This descriptor may be employed to denote an overall one-electron-transfer transformation with or without additional mechanistic detail:



(D and A are used here in their traditional meaning of donor and acceptor). An attachment reaction of a potential nucleophile-electrophile pair proceeding by prior electron transfer would be distinguished as shown below.



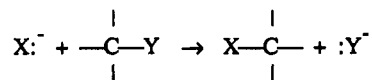
SIMPLE EXAMPLES

The following sections show how frequently encountered substitution, addition and elimination mechanisms may be delineated using the rules set forth above. The relationship to Ingold categories will also be discussed. Homolytic processes are dealt with separately from similar heterolytic types.

For each mechanism a prototype example is given with carbon core atoms and generalized entering and leaving groups. The choice of carbon "substrates" is intended to facilitate reference to textbook examples and is in no way restrictive. In the examples given, we have used negatively-charged nucleophiles and positively-charged electrophiles. This is done to avoid the appearance of reactions with unbalanced charges. We intend no implication of restrictions predicated on charge type. Nucleophilic and nucleofugal electron pairs are represented by the conventional "dots" and the absence of such "dots" identifies an electrophilic or electrofugal group. As an added convenience to the reader we have adopted the convention, X:, nucleophile; Y:, nucleofuge; Q, electrophile; Z, electrofuge; M, migrating group; U, utility group. Radical species carry a single, mid-line "dot".

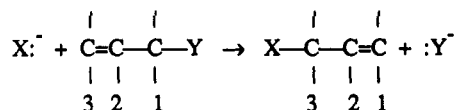
Common Substitution Mechanisms

1.1. One of the most common substitution mechanisms is that of *one-step, concerted nucleophilic displacement at a single atom*:



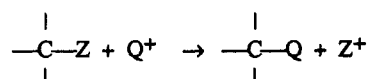
known in the Ingold System as the S_N2 mechanism. The new name is $A_N D_N$.

The vinylog of the S_N2 process, previously called the S_N2' mechanism in which *one-step, concerted nucleophilic displacement occurs by attachment of the nucleophile at the 3-position of a system having the nucleofugal atom or group in the 1-position and a multiple bond between the 2- and 3-positions*:



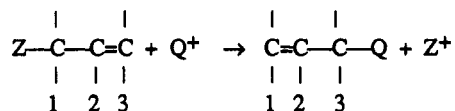
is called $3/1 A_N D_N$.

1.2. *One-step, concerted electrophilic displacement at a single atom*:



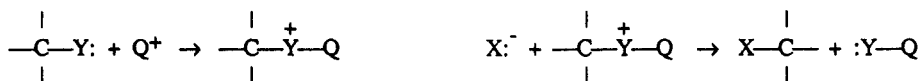
is termed the $D_E A_E$ mechanism. This has usually been referred to as the S_E2 mechanism in Ingold System nomenclature.

The vinylog of the S_E2 process, previously called the S_E2' mechanism, in which *one-step, concerted electrophilic displacement occurs by attachment of the electrophile at the 3-position of a system having the electrofugic atom or group in the 1-position and a multiple bond between the 2- and 3-positions:*



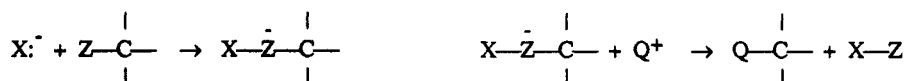
is called $1/3/D_EA_E$.

1.3. A common variant of the A_ND_N process is a *concerted nucleophilic displacement preceded by coordination of the incipient nucleofugic atom or group to an electrophilic reagent:*



This mechanism has been called the S_N2cA or the A_2 mechanism.¹² In the present system it becomes $A_e + A_ND_N$ (or $A_h + A_ND_N$ if the electrophile is the hydron).

1.4. An analogous variant of the A_ED_E mechanism is *concerted electrophilic displacement preceded by coordination of a nucleophile with the incipient electrofugic atom or group:*



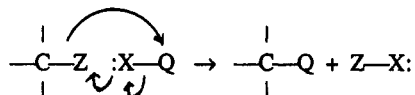
This is termed the $A_n + D_EA_E$ mechanism. This mechanism does not seem to have been given a special category using the Ingold System although a subclass in which X and Q are linked before reaction has been named and is covered below.

1.5. A rather common D_EA_E type mechanism is designated as S_EC or S_E2 coord in the Ingold System.^{13,14} This refers to a *mechanism in which electrophilic displacement occurs at a single atom preceded by coordination of a nucleophile to the electrofugic atom or group. This differs from the $A_n + D_EA_E$ mechanism in that the nucleophile and electrophile are linked together before the substitution step and this linkage is broken in concert with bonding to the electrophile and loss of the electrofuge:*



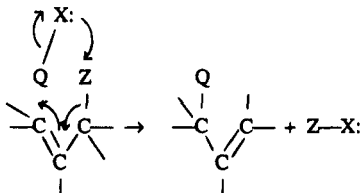
This mechanism is called $A_n + \text{cyclo-}D_EA_ED_n$. It will be noted that four bonding changes are involved making this one of the more unwieldy names in this document. However, the name quickly identifies the process as an electrophilic substitution and this is preceded by nucleophilic attack on a peripheral atom. The prefix "cyclo" signals the cyclic nature of the process. Thus the complexity created by the presence of four terms dissolves in the modular logic of the system.

1.6. Another variant of the D_EA_E process is *identical to the $A_n + \text{cyclo-}D_EA_ED_n$ mechanism defined in 1.5 except that all four bonding changes are concerted:*



This is called the $\text{cyclo-}D_EA_ED_nA_n$ mechanism. In decoding this name, it is recognized immediately that the process is an electrophilic substitution at a single core atom. The two additional primitive changes must take place in a ring connecting the electrophilic and electrofugic atoms. The selection of the lower case subscripts is described in rule 4.2. This mechanism has previously been called the S_{Ei} and the S_{F2} mechanism.^{15,16}

The vinylog of the cyclo- $D_E A_E D_N A_N$ process, known previously as the $S_E i$ mechanism:¹⁷



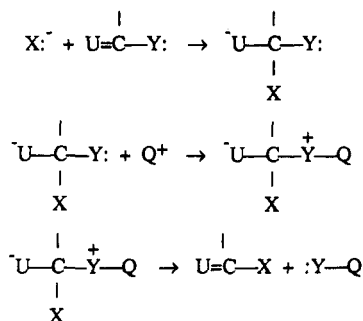
becomes the cyclo-1/3/ $D_E A_E D_N A_N$ process.

1.7. A nonconcerted substitution mechanism in which a nucleophile becomes attached followed by the loss of a nucleofuge in a separate step:



is termed the $A_N + D_N$ (or $A_N^*D_N$) mechanism. The documented examples where this mechanism leads to substitution at carbon all involve unsaturated carbon. The mechanism has been called $B_{AC}2$ for substitution of alkoxide by hydroxide at an ester carbonyl carbon,¹⁸ $S_N Ar$ when the site of substitution is aromatic carbon¹⁹ and Ad_N-E when the site is olefinic carbon.²⁰ As the variations in terminology are entirely dependent on substrate structure rather than mechanism *per se*, it is beyond the intent of the present system to distinguish them. A method for distinguishing substrate types is described in Appendix A.

1.8. A specialized version of the $A_N + D_N$ type mechanism which seems to warrant separate categorization is distinguished when the incipient nucleofugic atom or group forms a bond to an electrophile in a step before its departure. Complete definition includes the $A_N + D_N$ description given in example 1.7:



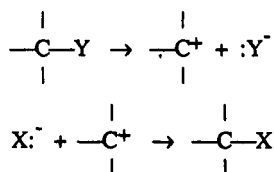
Following the usual guidelines, we designate this to be the $A_N + A_e + D_N$ mechanism. A subclass in this category has been previously designated $A_{AC}2$ and is specifically restricted to ester hydrolysis.²¹ It fits within the general definition of the $A_N + A_e + D_N$ class but includes a preliminary transfer step wherein a hydron binds to the carbonyl oxygen and a balancing final transfer step in which the hydron is lost. This becomes $A_H + A_N + A_H D_H + D_N + D_H$. Another frequent variation is that in which the nucleophile represented above as $:X$ arrives as $:X-Q$, with Q being lost in a subsequent step. These electrophile-mediation steps could be included in order to define subclasses of the $A_N + A_e + D_N$ category if such subdivision were to prove valuable.

1.9. Nonconcerted substitution in which an electrophile becomes attached followed by loss of an electrofuge in a separate step:



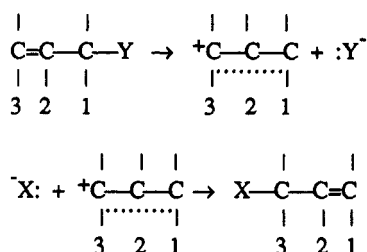
is called the $A_E + D_E$ mechanism. The most common modification is that of electrophilic aromatic substitution. (An example is discussed in connection with rule 3.3.) This mechanism has been labeled $S_E 2$ by Ingold.²²

1.10. Substitution reactions in which dissociation precedes association are also observed. The best-known version is probably the case in which *loss of a nucleofuge is followed in a separate step by attack of a nucleophile*:



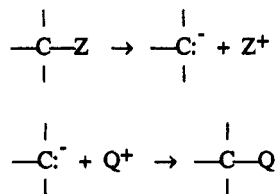
This sequence is usually taken to define the $\text{S}_{\text{N}}1$ mechanism provided that the first step is rate limiting. The present system now makes this the $\text{D}_{\text{N}} + \text{A}_{\text{N}}$ process. The special case in which :Y^- is carboxylate has also been called the $\text{B}_{\text{AL}}1$ mechanism.

The vinylog of this mechanism, previously delineated by the prime notation occurs when *detachment of a nucleofuge from the 1-position is followed in a separate step by attachment of a nucleophile at the 3-position*. The substrate for this reaction must have a multiple bond between the 2- and 3-positions:



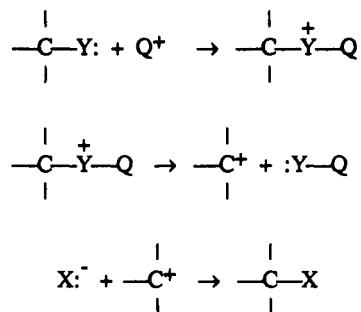
and the intermediate is usually an allylic carbocation. This mechanism is named $1/\text{D}_{\text{N}} + 3/\text{A}_{\text{N}}$.

1.11. Substitution mechanisms in which *an electrofuge is lost followed by attack of an electrophile in a separate step*:



which have previously been called $\text{S}_{\text{E}}1$ reactions now become $\text{D}_{\text{E}} + \text{A}_{\text{E}}$.

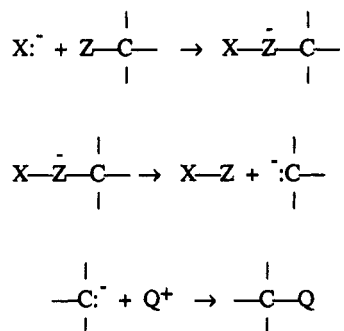
1.12. The $\text{D}_{\text{N}} + \text{A}_{\text{N}}$ mechanism has been observed to show an electrophile-assisted version, sometimes called the $\text{S}_{\text{N}}1\text{cA}$ or A_{I} mechanism.^{23,24} These are cases in which *the incipient nucleofugic atom or group coordinates to an electrophile in a step preceding the loss of the nucleofuge, the mechanism otherwise falling within the sequence discussed in example 1.10 as $\text{D}_{\text{N}} + \text{A}_{\text{N}}$* :



This mechanism is termed $\text{A}_{\text{e}} + \text{D}_{\text{N}} + \text{A}_{\text{N}}$ (or $\text{A}_{\text{h}} + \text{D}_{\text{N}} + \text{A}_{\text{N}}$).

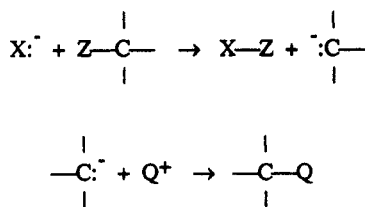
Two reactions which fall within this general definition are the so-called $A_{AC}1$ and $A_{AL}1$ reactions.²⁵ These are $A_h + D_N + A_N$ processes occurring at the carbonyl carbon of an ester or the alkyl group of an ester respectively. The related mechanism in which hydron transfer to the substrate is concerted with leaving group expulsion in the first step is designated $D_N A_h + A_N$. The general form of this reaction with unspecified electrophile is $D_N A_e + A_N$.

1.13. When a reaction fitting the definition of $D_E + A_E$ (1.11) is preceded by attack of a nucleophile at the incipient electrofugic group:



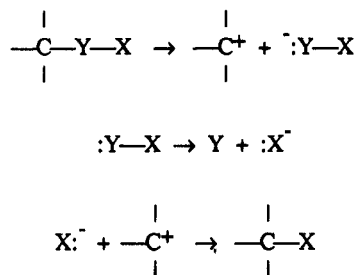
the mechanism becomes $A_n + D_E + A_E$.

1.14. A common type of electrophilic substitution mechanism is that in which *attack of a nucleophile on an incipient electrofugic atom or group occurs in concert with its departure. This is followed by attack of an electrophile in a separate step:*



This is called the $A_n D_E + A_E$ mechanism. A common reaction believed to follow this mechanism is the base-catalyzed hydrogen-deuterium exchange of carbon acids. A more specific name for this version is $A_{xh} D_H + A_H D_{xh}$. This has previously been called the $S_{E1}(N)$ or $S_{E1}-X$ mechanism.²⁶

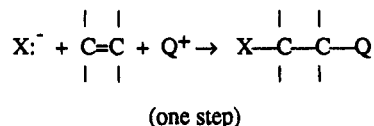
1.15. A somewhat more complex substitution mechanism is the non-concerted version of the S_N1 process.²⁷ *If loss of a nucleofugic group is followed in a separate step by bond rupture within the nucleofugic group, this process serving to generate a nucleophile which then attacks the substitution site in a separate step:*



the process is known as $D_N + D + A_N$. The isolated "D" symbol is left unsubscripted here because the use of "e" or "n" would imply that the bond-breaking was occurring within the molecule containing the core atoms (see Rule 3.5). If the internal return of the cleavage-generated nucleophile is to be emphasized, this might become $D_{Nint}^* D^* A_N$.

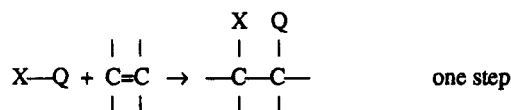
Common Addition Mechanisms

2.1. The class AA contains few well-documented examples. It has been termed Ad3 in the Ingold type nomenclature²⁸ and may be illustrated as follows:



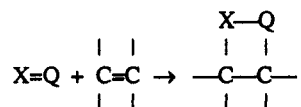
The complete designation of this mechanistic category is $\text{A}_\text{N}\text{A}_\text{E}$. It is used for all additions in which *two independent reagents add to an unsaturated system in a concerted manner*. It may be noted that this is the reverse of an E2 type elimination ($\text{D}_\text{E}\text{D}_\text{N}$ or $\text{A}_\text{n}\text{D}_\text{E}\text{D}_\text{N}$).

2.2. A closely related type of AA mechanism is illustrated as follows:



This is designated $\text{cyclo-A}_\text{N}\text{A}_\text{E}\text{D}_\text{n}$. This name is applied to *any process in which two linked groups become attached to an unsaturated system in concert with breaking of the linkage*. Note that the sequence of primitive change designations is dictated by rule 4.2. Although the use of $\text{cyclo-A}_\text{N}\text{A}_\text{E}\text{D}_\text{n}$ implies polarization of bonds at the transition state, the direction of the polarization is effectively unspecified. The name would be the same regardless of which direction electrons were polarized at the transition state. If it is felt that little or no polarization is present, the alternative cyclo-AA is recommended. Note also that all three primitive changes are part of the cyclic assembly in this mechanism. Mechanisms where this was not so would have the cyclic components set off by parentheses in the manner described in Section 4.

2.3. Another type of AA mechanism is concerted cycloaddition. This is designated cyclo-AA .



At the namer's discretion, the "N" and "E" subscripts may be inserted following the "A" symbols. However, in the most common examples of this mechanistic type, no polarity is implied. The designation will apply to *all processes in which two bonds are formed between a reagent and an unsaturated system, in concert, with no other bonds being made or broken*.

It should be noted that there is no intent to supplant the well established nomenclature originally suggested by Woodward and Hoffmann²⁹ for describing the observed characteristics of cycloaddition reactions and other pericyclic processes. Our system deals only with mechanism in the sense of bond-making sequence. To illustrate the distinction, it is possible to debate whether a $[\pi^4_\text{s} + \pi^2_\text{s}]$ reaction proceeds by an AA or an $\text{A}_\text{R} + \text{A}_\text{R}$ mechanism.

2.4. A nonconcerted addition mechanism in which a nucleophile adds first followed in a separate step by an electrophile:



is termed an $\text{A}_\text{N} + \text{A}_\text{E}$ (or $\text{A}_\text{N} + \text{A}_\text{H}$) mechanism.

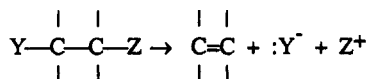
2.5. A nonconcerted addition mechanism in which an electrophile adds first followed in a separate step by a nucleophile:



is termed $\text{A}_{\text{E}} + \text{A}_{\text{N}}$ (or $\text{A}_{\text{H}} + \text{A}_{\text{N}}$).

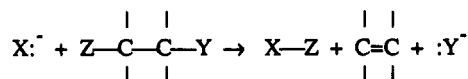
Common Elimination Mechanisms

3.1. An elimination reaction in which the two dissociation components are concerted:



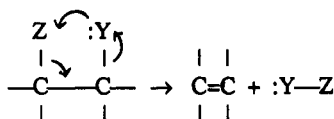
is termed a $\text{D}_{\text{E}}\text{D}_{\text{N}}$ process. There are relatively few examples where this basic mechanistic type occurs in isolation, although it is a component of several more elaborate mechanisms.

3.2. A commonly encountered concerted elimination process previously termed the E2 or E2H mechanism^{30,31} may be defined as an elimination reaction in which the electrofugic group bonds to a nucleophile in concert with separation of both the nucleofugic atom or group and the electrofugic atom or group from the substrate:



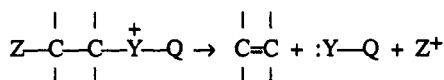
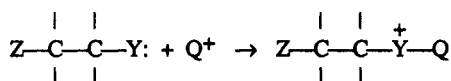
This process is called the $\text{A}_{\text{n}}\text{D}_{\text{E}}\text{D}_{\text{N}}$. The most common variation of this mechanism is more specifically symbolized by $\text{A}_{\text{xh}}\text{D}_{\text{H}}\text{D}_{\text{N}}$.

3.3. Another variation is that in which the nucleofugic group forms a bond to the electrofugic group in concert with the separation of these two groups from the substrate:

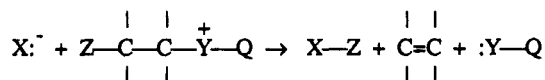


This process is termed the cyclo- $\text{D}_{\text{E}}\text{D}_{\text{N}}\text{A}_{\text{n}}$ mechanism. This mechanism has been called Ei in the Ingold system.³² It is often observed in pyrolytic eliminations.

3.4. An elimination mechanism analogous to the $\text{A}_{\text{e}} + \text{A}_{\text{N}}\text{D}_{\text{N}}$ substitution occurs when the nucleofugic group coordinates to an electrophile in a step preceding concerted processes $\text{D}_{\text{E}}\text{D}_{\text{N}}$ (3.1) or $\text{A}_{\text{n}}\text{D}_{\text{E}}\text{D}_{\text{N}}$ (3.2):

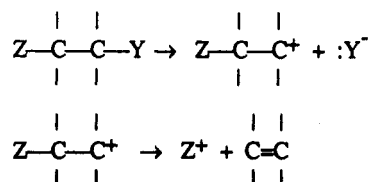


or, as an alternative second step:



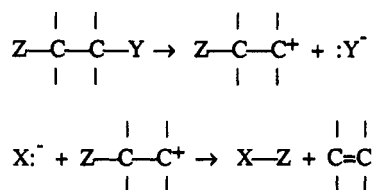
These mechanisms are named $\text{A}_{\text{e}} + \text{D}_{\text{E}}\text{D}_{\text{N}}$ and $\text{A}_{\text{e}} + \text{A}_{\text{n}}\text{D}_{\text{E}}\text{D}_{\text{N}}$ respectively.

3.5. The most commonly encountered D + D mechanism is the so called EI process in which a nucleofugic atom or group departs, followed by an electrofugic group in a separate step:



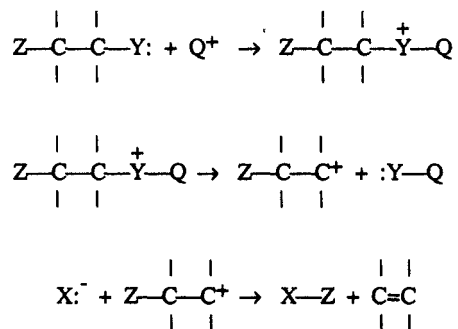
This is named the $\text{D}_\text{N} + \text{D}_\text{E}$ mechanism (or $\text{D}_\text{N} + \text{D}_\text{H}$).

3.6. As the electrofugic atom or group in a $\text{D}_\text{N} + \text{D}_\text{E}$ mechanism usually departs in association with a nucleophile, it seems advisable to distinguish this case where in a step following loss of a nucleofugic atom or group, an electrofugic atom or group bonds to a nucleophile in concert with its loss from the substrate:



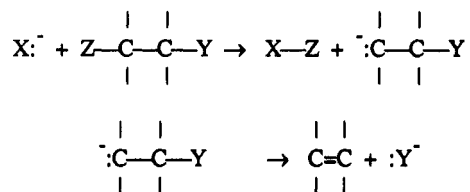
This process is called the $\text{D}_\text{N} + \text{A}_\text{n}\text{D}_\text{E}$ (or $\text{D}_\text{N} + \text{A}_\text{xh}\text{D}_\text{H}$) mechanism. This is probably a more accurate description of most reactions which are called EI processes than that provided by the simple $\text{D}_\text{N} + \text{D}_\text{E}$ name.

3.7. A mechanism which has been called ElcA^{33} occurs when the nucleofugic group coordinates to an electrophile followed by the two steps previously used to define the $\text{D}_\text{N} + \text{A}_\text{n}\text{D}_\text{E}$ process:



This is called $\text{A}_\text{e} + \text{D}_\text{N} + \text{A}_\text{n}\text{D}_\text{E}$ (or $\text{A}_\text{h} + \text{D}_\text{N} + \text{A}_\text{xh}\text{D}_\text{H}$).

3.8. Nonconcerted eliminations in which the electrofugic group leaves first have generally been termed ElcB processes.³⁴ The most commonly encountered modification in this class is that in which a nucleophile bonds to the electrofugic atom or group in concert with its separation from the substrate and this is followed in a separate step by loss of a nucleofugic atom or group:

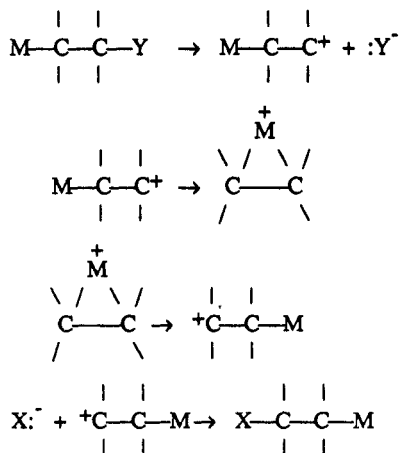


This is called the $\text{A}_\text{n}\text{D}_\text{E} + \text{D}_\text{N}$ mechanism (or $\text{A}_\text{xh}\text{D}_\text{H} + \text{D}_\text{N}$).

Common Rearrangement Mechanisms

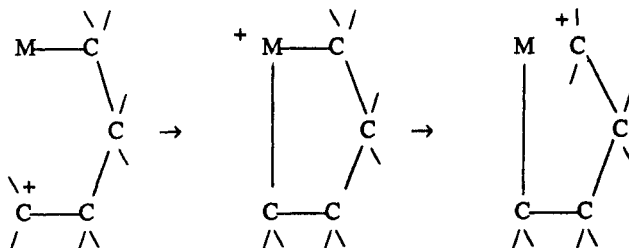
The simplest process which qualifies as a rearrangement involves the migration of an atom or group of atoms from one site in a molecule to another. A variety of events may precede or follow the actual migration. For purposes of illustrating how the system deals with rearrangements, we have chosen migration-interrupted nucleophilic substitution processes. It should be recognized that simply changing the "N" subscripts to "R" or to "E" generates a corresponding set of radical or electrophilic counterparts which are at least conceptually possible. For electrophilic and homolytic analogues of processes such as 4.2-4.4 where elementary processes contain more than one primitive change, the order of the primitive changes would be changed in accordance with rules 4.1 and 4.3.

4.1. In a sense, the simplest version is that for which *each primitive change constitutes a separate reaction step*:



This mechanism is named $1/D_N + \text{intra-}1/A_N + \text{intra-}2/D_N + 2/A_N$. It will be noted that we have chosen to view both the migration origin and terminus as core atoms. Thus the reaction becomes a $1/D_N + 2/A_N$ remote substitution reaction in much the same sense that the reaction mechanism formerly designated S_N1' is named $1/D_N + 3/A_N$. (See Simple Example 1.10.) The reaction can also be viewed a substitution at the 1/atom (looking only at the terms with "1/" prefixes) and is simultaneously a substitution at the 2/atom. Were it not for the modifying intra designations attached to one "A" term and one "D" term, the reaction might be mistaken for an elimination (two N-subscripted "D" terms) plus an addition (two N-subscripted "A" terms), which of course, is a possible mechanism for the overall transformation. These simple rearrangements thus become the only cases for which we recommend the use of more than two upper-case-subscripted primitive change components in describing a single mechanism. Of course multiple substitutions, eliminations, additions and combinations thereof are viable mechanistic models for other types of reactions but treatment of these using the simple system described in the present document is carried out at the user's risk.

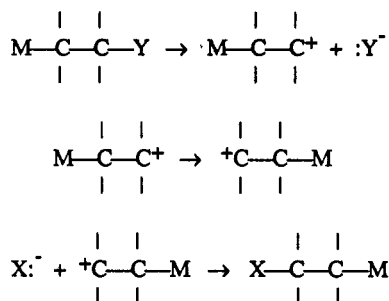
The basic approach described above can be used to treat rearrangement reactions wherein the migration origin and terminus are separated by additional atoms. Thus, for example, the sequence below:



would be described as $\text{intra-}1/A_N + \text{intra-}4/D_N$. The entire mechanism analogous to the 1,2-rearrangement

described above would then become $1/D_N + \text{intra-}1/A_N + \text{intra-}4/D_N + 4/A_N$. It is implicit in using this simple numbering system that the atom in the migrating group, M, which is connected to the migration origin ends attached to the migration terminus. It is possible to handle rearrangements for which this is not the case using a more complete numbering method proposed to handle attachment and detachment transformations which involve ring closing and ring opening.¹¹ The examples to follow are depicted as 1,2-rearrangements but in each case larger-ring homologues are nameable as described above.

4.2. As mentioned in section 4.1, a variation is that wherein the *migration takes place in a single elementary reaction and there is no cyclic intermediate*. If the attack of the entering group and the loss of the leaving group occur in separate reactions the mechanism is:



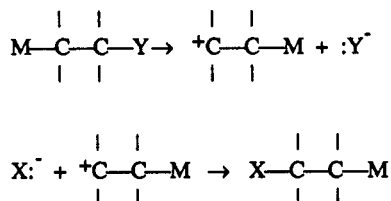
and is named $1/D_N + \text{intra-}1/2/A_N D_N + 2/A_N$.

4.3. In many cases, *loss of the leaving group and cyclization are described as taking place in a single elementary reaction, followed by nucleophile-promoted opening of the cyclic intermediate*:



This mechanism is termed $(\text{intra-}1/A_N)1/D_N + 2/A_N(\text{intra-}2/D_N)$. Note that procedures described in rule 4.2 are used to make it clear that "intra" applies to only part of the elementary reaction. To avoid confusion where the "intra" designation refers to only part of an elementary reaction, the prefix and all associated characters are enclosed in parentheses.

4.4. *Migration and loss of the leaving group occur in a single elementary reaction, followed by attack of the entering group in a separate step*:

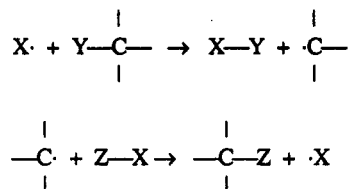


This mechanism is $(\text{intra-}2/1/D_N A_N)1/D_N + 1/A_N$.

The examples described, 4.1-4.4, clearly do not constitute an all-inclusive set of mechanisms, even for simple aliphatic rearrangement reactions. They do, however, represent a set of historically significant variations. The new nomenclature by clearly expressing the subtle differences between these variations should clarify communication and expedite discussion.

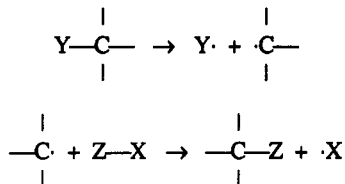
Common Homolytic Mechanisms

5.1. Most radical substitution mechanisms that have been studied proceed by kinetic chain processes. Although the chain nature of the mechanisms is not explicitly stated for purposes of basic categorization, it is implied by the generation of a radical in the final step of the mechanism. For example, a process sometimes called the $S_{\text{H}}2$ mechanism³⁵ is that in which a radical species attacks the leaving atom or group in concert with its separation from the atom or system at which substitution is to occur. The substrate radical thus generated then, in a separate step, bonds to a reagent in concert with homolysis of a bond in the reagent:



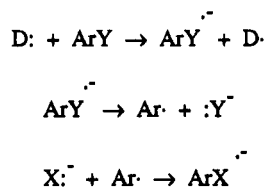
This is called the $A_{\text{r}}D_{\text{R}} + A_{\text{R}}D_{\text{r}}$ mechanism. It will be noted that, viewed from the perspective of the Y or Z atoms, the reaction consists of two consecutive $A_{\text{R}}D_{\text{R}}$ type substitutions. The $A_{\text{R}}D_{\text{R}}$ mechanism does not appear to be common for substitution at carbon and it has therefore not been formally delineated in these examples. It is, of course, also a bimolecular homolytic substitution and would also be called $S_{\text{H}}2$ in the Ingold system.³⁵

5.2. The so-called³⁵ $S_{\text{H}}1$ substitution mechanism is very similar to the $A_{\text{r}}D_{\text{R}} + A_{\text{R}}D_{\text{r}}$ type except for the initial "A_r" term. This is a substitution mechanism in which the leaving substituent separates homolytically from the substrate followed in a separate step by bonding of the resultant substrate radical to a reagent in concert with homolysis of a bond in the reagent:



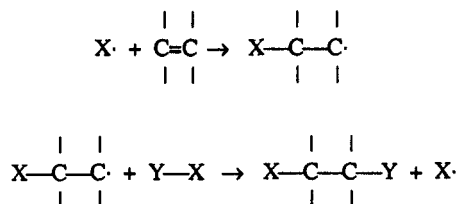
This mechanism is called $D_{\text{R}} + A_{\text{R}}D_{\text{r}}$. In general such mechanisms are not chain processes and the fate of X· is incidental to the process of interest. It would be logical to expect the occasional occurrence of $D_{\text{R}} + A_{\text{R}}$ mechanisms, and they are in fact observed. They are relatively uncommon, however, and examples are not given in this document.

5.3. A substitution mechanism which is being observed with increasing frequency³⁶ is that presently referred to as $S_{\text{RN}}1$. One commonly encountered modification of this mechanism involves loss of a nucleofugic atom or group from a radical anion followed by attack of a nucleophile on the resultant radical species in a separate step. The radical ion precursor is generated when the substrate gains an electron from some donor species:



This mechanism is called $T + D_{\text{N}} + A_{\text{N}}$. It will be noted that another electron transfer is necessary to produce the final product (Ar-X) but this is not made a part of the name. It seems likely that in some cases the first two steps are concerted, TD_{N} , but an example of this variation is not given in this document. In some cases the subscript N may be replaced by R or RN as described in Rule 3.4.

5.4. The most common free radical addition mechanism is probably that in which a radical species bonds to the substrate followed by attachment of the resultant radical species to a reagent molecule in concert with homolysis of a bond within the reagent molecule:



This is called the $\text{A}_\text{R} + \text{A}_\text{R}\text{D}_\text{r}$ mechanism. This pair of steps of course constitutes the propagation sequence in a radical chain reaction, the existence of the chain being viewed as extramechanistic information in the present system. (See Rule 7.2.)

Table 2. Comparison of Names Proposed in this Document with Corresponding Ingold-System Names.

Example Number	Ingold System Name	Proposed Name	Example Number	Ingold System Name	Proposed Name
SUBSTITUTION MECHANISMS			ADDITION MECHANISMS		
1.1a	$\text{S}_\text{N}2$	$\text{A}_\text{N}\text{D}_\text{N}$	2.1	Ad3	$\text{A}_\text{N}\text{A}_\text{E}$
1.1b	$\text{S}_\text{N}2'$	$3/1/\text{A}_\text{N}\text{D}_\text{N}$	2.2	none	cyclo- $\text{A}_\text{N}\text{A}_\text{E}\text{D}_\text{n}$
1.2a	$\text{S}_\text{E}2$	$\text{D}_\text{E}\text{A}_\text{E}$	2.3	none	cyclo-AA
1.2b	$\text{S}_\text{E}2'$	$1/3/\text{A}_\text{E}\text{D}_\text{E}$	2.4	none	$\text{A}_\text{N} + \text{A}_\text{E}$
1.3	$\text{S}_\text{N}2\text{cA}$ or A2	$\text{A}_\text{e} + \text{A}_\text{N}\text{D}_\text{N}$	2.5	none	$\text{A}_\text{E} + \text{A}_\text{N}$
1.4	none	$\text{A}_\text{n} + \text{D}_\text{E}\text{A}_\text{E}$	5.4	none	$\text{A}_\text{R} + \text{A}_\text{R}\text{D}_\text{r}$
1.5	$\text{S}_\text{E}2$ or $\text{S}_\text{E}2$ coord	$\text{A}_\text{n} + \text{cyclo-}\text{D}_\text{E}\text{A}_\text{E}\text{D}_\text{n}$	ELIMINATION MECHANISMS		
1.6a	$\text{S}_\text{E}i$ or $\text{S}_\text{F}2$	cyclo- $\text{D}_\text{E}\text{A}_\text{E}\text{D}_\text{n}\text{A}_\text{n}$	3.1	none	$\text{D}_\text{E}\text{D}_\text{N}$
1.6b	$\text{S}_\text{E}i'$	cyclo- $1/3/\text{D}_\text{E}\text{A}_\text{E}\text{D}_\text{n}\text{A}_\text{n}$	3.2	E2 or E2H	$\text{A}_\text{n}\text{D}_\text{E}\text{D}_\text{N}$ or $\text{A}_\text{xh}\text{D}_\text{H}\text{D}_\text{N}$
1.7	$\text{S}_\text{N}\text{Ar}$ or $\text{Ad}_\text{N-E}$ or $\text{B}_{\text{AC}}2$	$\text{A}_\text{N} + \text{D}_\text{N}$	3.3	E_i	cyclo- $\text{D}_\text{E}\text{D}_\text{N}\text{A}_\text{n}$
1.8a	none	$\text{A}_\text{N} + \text{A}_\text{e} + \text{D}_\text{N}$	3.4	$\text{E}_2\text{cA}?$	$\text{A}_\text{e} + \text{D}_\text{E}\text{D}_\text{N}$ and $\text{A}_\text{e} + \text{A}_\text{n}\text{D}_\text{E}\text{D}_\text{N}$
1.8b	$\text{A}_{\text{AC}}2$	$\text{A}_\text{h} + \text{A}_\text{N} + \text{A}_\text{h}\text{D}_\text{h} + \text{D}_\text{N} + \text{D}_\text{h}$	3.5	E1	$\text{D}_\text{N} + \text{D}_\text{E}$
1.9	$\text{S}_\text{E}2$	$\text{A}_\text{E} + \text{D}_\text{E}$	3.6	E1	$\text{D}_\text{N} + \text{A}_\text{n}\text{D}_\text{E}$ (or $\text{D}_\text{N} + \text{A}_\text{xh}\text{D}_\text{H}$)
1.10a	$\text{S}_\text{N}1$ or $\text{B}_{\text{AL}}1$	$\text{D}_\text{N} + \text{A}_\text{N}$	3.7	E1cA	$\text{A}_\text{e} + \text{D}_\text{N} + \text{A}_\text{n}\text{D}_\text{E}$ (or $\text{A}_\text{h} + \text{D}_\text{N} + \text{A}_\text{xh}\text{D}_\text{H}$)
1.10b	$\text{S}_\text{N}1'$	$1/\text{D}_\text{N} + 3/\text{A}_\text{N}$	3.8	E1cB	$\text{A}_\text{n}\text{D}_\text{E} + \text{D}_\text{N}$ (or $\text{A}_\text{xh}\text{D}_\text{H} + \text{D}_\text{N}$)
1.11	$\text{S}_\text{E}1$	$\text{D}_\text{E} + \text{A}_\text{E}$	REARRANGEMENT MECHANISMS		
1.12	$\text{S}_\text{N}1\text{cA}$ or A1	$\text{A}_\text{e} + \text{D}_\text{N} + \text{A}_\text{N}$	4.1	none	$1/\text{D}_\text{N} + \text{intra-}1/\text{A}_\text{N} + \text{intra-}2/\text{D}_\text{N} + 2/\text{A}_\text{N}$
1.13	none	$\text{A}_\text{n} + \text{D}_\text{E} + \text{A}_\text{E}$	4.2	none	$1/\text{D}_\text{N} + \text{intra-}1/2/\text{A}_\text{N}\text{D}_\text{N} + 2/\text{A}_\text{N}$
1.14	$\text{S}_\text{E}1(\text{N})$ or $\text{S}_\text{E}1-\text{X}^+$	$\text{A}_\text{n}\text{D}_\text{E} + \text{A}_\text{E}$	4.3	none	(intra- $1/\text{A}_\text{N}$) $1/\text{D}_\text{N} + 2/\text{A}_\text{N}$ (intra- $2/\text{D}_\text{N}$)
1.15	$\text{S}_\text{N}i$	$\text{D}_\text{N} + \text{D} + \text{A}_\text{N}$	4.4	none	(intra- $2/1/\text{D}_\text{N}\text{A}_\text{N}$) $1/\text{D}_\text{N} + 2/\text{A}_\text{N}$
5.1	$\text{S}_\text{H}2$	$\text{A}_\text{r}\text{D}_\text{R} + \text{A}_\text{R}\text{D}_\text{r}$			
5.2	$\text{S}_\text{H}1$	$\text{D}_\text{R} + \text{A}_\text{R}\text{D}_\text{r}$			
5.3	$\text{S}_\text{RN}1$	$\text{T} + \text{D}_\text{N} + \text{A}_\text{N}$			

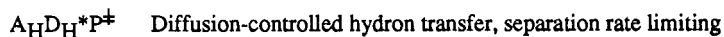
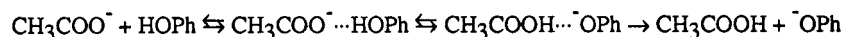
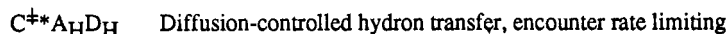
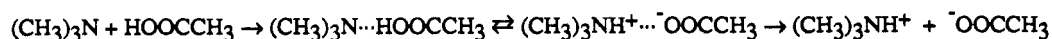
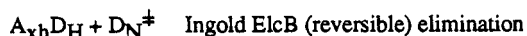
EXTENDED RULES FOR INCORPORATION OF EXTRAMECHANISTIC INFORMATION

To this point we have described a system which is purely mechanistic in the sense that only the sequence of bond-making and bond-breaking steps is described. For some purposes it may be desirable to transmit other kinds of information. Symbolic or abbreviated notations for some of these are recommended below.

Rule 7. Description of the Observed Properties of a Reaction. Certain experimentally observable characteristics of chemical reactions such as rate-limiting step, repetitive sequences (chain processes), etc. are statistical properties of large collections of molecules. These may be indicated along with structural information as described below.

7.1. Rate-Limiting Step. A superscript symbol, ‡, which somewhat resembles the "double dagger", used to symbolize transition states, may be appended to the term representing the rate-limiting step in a mechanistic sequence.

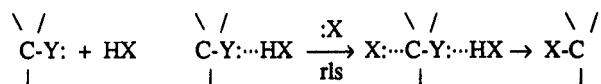
Examples:



(It will be noted that the hydron is the core atom in the two examples above.)

The use of "*" instead of "+" in these examples reflects the fact that an encounter complex is too short-lived to equilibrate with species in the external solvent before undergoing reaction. Note that there is often no purpose served by including "C" or "P" in a designation unless they are rate-limiting. Thus the "P" step in the first example and the "C" step in the second example have been omitted. The processes represented by these symbols are understood to be operative in all bimolecular reactions.

Exceptions to this rule signal the occurrence of nonobvious steps. For example "C^{‡*}A_N" indicates that diffusion to the reaction site by the nucleophile to be used in the subsequent bond forming step is rate-limiting. If two reactants were to diffuse together and nucleophilic association were then provoked by the rate-limiting arrival of a third reactant as shown in the following example:



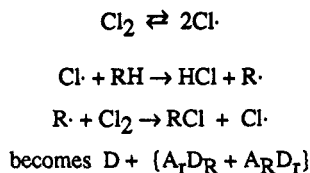
This sequence of events would have to be symbolized as "C^{‡*}C^{‡*}A_N".

It should be remembered that the concept of "rate-limiting step" is an oversimplification in many kinetic systems. The effective rate-limiting step as a factor affecting the form of the observed rate equation is often determined by variables unrelated to the inherent facility of the various elementary reactions taking place. In particular, a reaction controlled by a particular rate-limiting step in one concentration range may have a different

rate-limiting step in another concentration range. The mechanism (sequence of steps leading to product) will stay the same but the rate expression and the term to which "‡" is affixed will change.

7.2. Kinetic Chain Reactions. *If a subset of steps in a mechanistic sequence occurs repetitively, the repeated sequence may be placed in braces ({ }).*

Example:



The unsubscripted "D" term signifies a bond being broken in a reagent molecule. The homolytic character of this process may be inferred from the context.

APPENDIX A: SUPPLEMENTARY RULES FOR DESCRIPTION OF STRUCTURE CHANGE

A.1. Class of a Transformation. Although the class of the reaction (substitution, elimination, etc.) may be derived from the mechanistic symbols it is useful to have a more explicit method for stating this. *The following symbols are suggested:*

- Su - substitution
- Em - elimination
- Ad - addition
- De - detachment
- At - attachment
- Re - rearrangement
- Tt - tautomerization

These terms have been defined elsewhere.^{10,11}

A.2. Substrate Types. One of the valuable features of the nomenclature described in this document is that the mechanistic characteristics of a reaction are separated from its structural characteristics. For example, the simple $A_{\text{N}} + D_{\text{N}}$ mechanism has previously been assigned at least three different Ingold-System names, distinguished only by structural characteristics (see Simple Example 1.7). It is suggested that *common structural abbreviations or atomic symbols be appended to the class designation when transmission of structural detail is important.*

Examples:

- Su - AL (substitution at alkyl carbon)
- Su - AR (substitution at aryl carbon)
- Su - AC (substitution at acyl carbon)
- Su - P (substitution at phosphorus)
- Su - Ni (substitution at nickel).

APPENDIX B: SUPPLEMENTARY RULES FOR REPRESENTING ACID-BASE CATALYSIS

Observed properties of acid-base catalysis may be indicated by inclusion of one of the following notations after the terms indicating class and substrate type:

H⁺ - catalysis by the solvated proton

(observed catalysis by H⁺ may be either specific or general acid catalysis)

HO⁻, RO⁻ - catalysis by the lyate ion

(observed catalysis by HO⁻ or RO⁻ may be either specific or general base catalysis)

AH - general acid catalysis

(observed kinetic general acid catalysis can actually represent two cases, rate-limiting hydron transfer from AH or the kinetically equivalent, pre-equilibrium hydration followed by rate-limiting hydron removal by a base [specific acid - general base catalysis])

B - general base catalysis

(observed kinetic general base catalysis can represent two cases, rate-limiting hydron removal by B or the kinetically equivalent, pre-equilibrium dissociation of a hydron from the substrate followed by rate-limiting hydration by an acid [specific base - general acid catalysis])

Examples:

Ad-CO-AH addition to carbonyl, general acid catalysis.

Em-AL-B elimination in alkyl system, general base catalysis.

It should be noted that these additional symbols are not intended for use as part of the mechanistic designation but rather as categories of observed reaction characteristics. Each category describes a process which could occur by several different mechanisms. We envision the use of these supplementary symbols in modifying phrases. For example: "The Su-AL transformation may occur by either an A_ND_N or an D_N + A_N mechanism." or "The Em-AL-B reaction may proceed by a variety of mechanistic paths including A_{xh}D_HD_N and variations of A_{xh}D_H*D_N." The following section describes some of the more subtle ways in which symbolic representation can facilitate logical analysis of experimentally distinguishable mechanistic categories.

APPENDIX C: ADDITIONAL EXAMPLES SHOWING SUBCATEGORIES THAT MAY BE KINETICALLY DISTINGUISHABLE

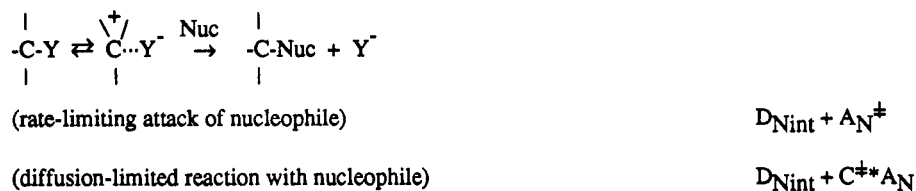
SUBSTITUTION

Variations of the Su-AL type

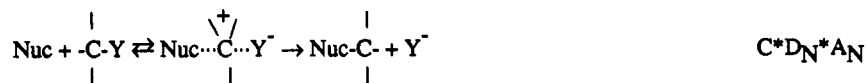
Ion formation rate limiting

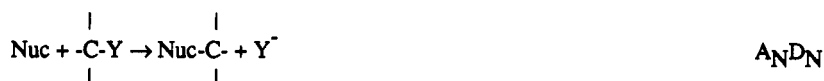


Substitution on an ion pair (or ion-dipole pair)



The "ion sandwich" or "S_N2-intermediate" mechanism.



Concerted (Ingold: S_N2)

Ligand exchange on metals:

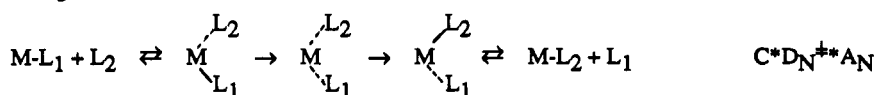
Dissociative:



Associative:

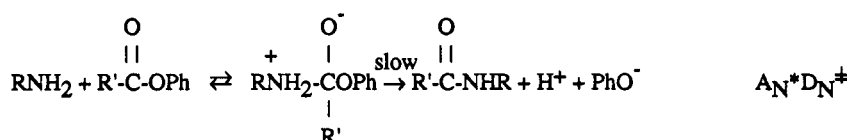


Interchange

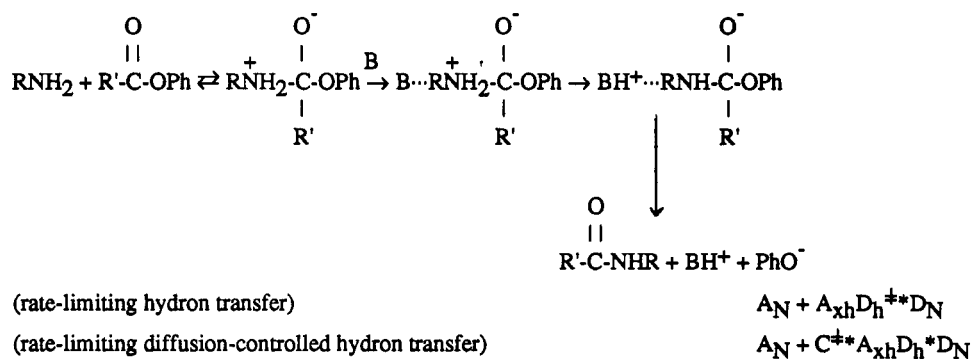


Variation of the Su-AC type

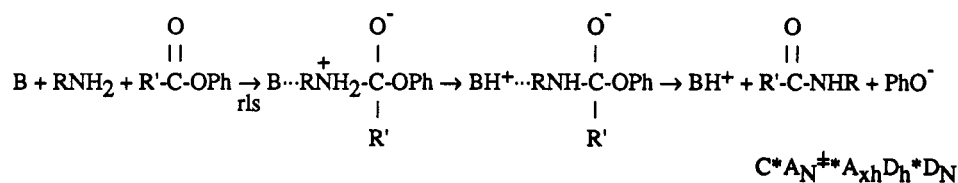
Second-order type



General base catalyzed (Su-AC-B)



Catalysis by hydrogen bonding in a preassociation mechanism

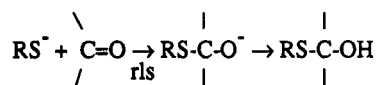


Note that the symbols "C" and "C[‡]" are used in different ways as discussed in rule 7.1. "C[‡]A_{xh}D_h[‡]D_N" indicates that diffusion of the base required for proton removal is rate-limiting. "C*A_N[‡]" indicates that a third reagent, in this case, B, arrives before nucleophilic attack. Note that no order of assembly of the three reagents is implied by this, only that the three reagents must be assembled before bond formation.

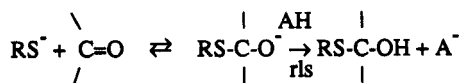
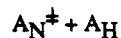
ADDITION

Variations of the Ad-CO type

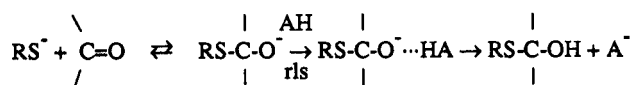
Second-order type



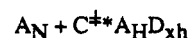
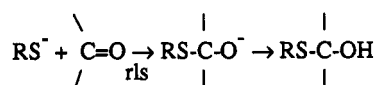
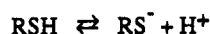
(rate-limiting attack by nucleophile)



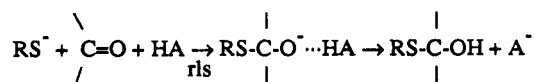
(rate-limiting hydron transfer)



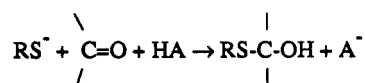
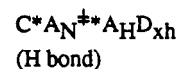
(rate-limiting diffusion-controlled hydron transfer)

Specific Base Catalyzed (Ad-CO-HO⁻)

General Acid Catalyzed (Ad-CO-AH)



(catalysis by hydrogen bonding in a preassociation mechanism)



(concerted general acid catalysis)



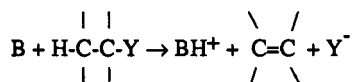
Note that the positioning of the D_{xh} and the absence of a modifying "cyclo-" shows that the carrier atom for H is not the nucleophile.

$\text{RSH} + \text{C}=\text{O} \rightarrow \text{R}-\text{S}-\text{C}-\text{OH}$, albeit possibly unrealistic, would be represented as $A_N(\text{intra-}D_{xh}A_H)$. Symbolized as $A_N A_H D_{xh}$, the mechanism would be interpreted as termolecular. Termolecular processes are usually understood to involve assembly of two of the reagents before concerted adduct formation. These processes could be emphasized by $C^* A_N A_H D_{xh}$.

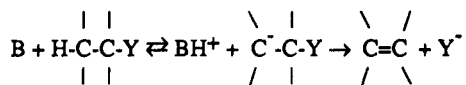
ELIMINATION

Variations of the Em-AL-B types

Ingold: E2

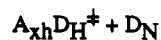
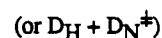
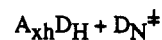


Ingold: ElcB

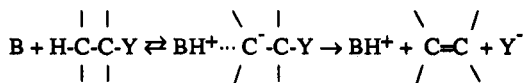


(reversible)

(irreversible)

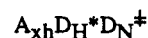
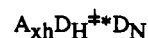


ElcB, Ion Pair

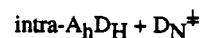
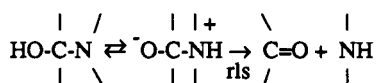
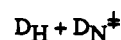
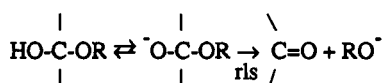


(rate-limiting hydron transfer)

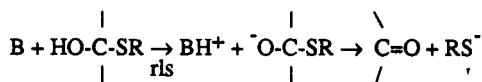
(rate-limiting expulsion of the leaving group)



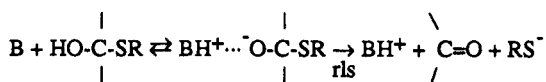
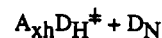
Variations of the Em-CO type

Specific base catalyzed (Em-CO-HO⁻)

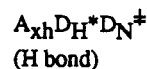
General base catalyzed (Em-CO-B)



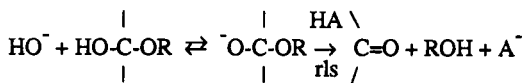
(rate-limiting hydron removal)



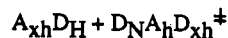
(kinetic general base catalysis, catalysis by hydrogen bonding after hydron transfer)



(H bond)

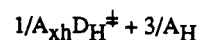
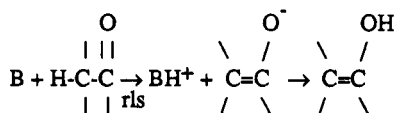


(Cleavage of the conjugate base of the substrate with concerted general acid catalysis. This is kinetically equivalent to general base catalysis with the uncharged substrate).

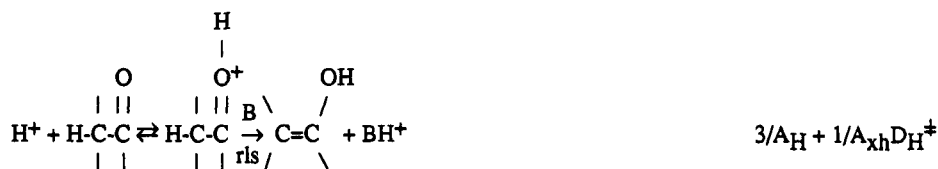


ENOLIZATION (Tt type)

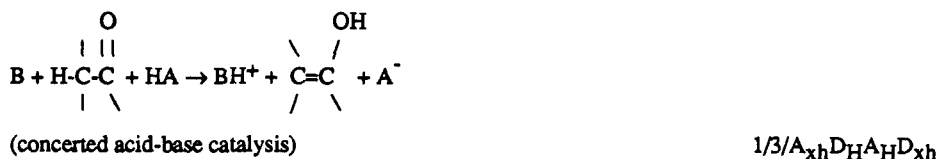
General base catalyzed (Tt-B)



General acid catalyzed (Tt-AH)



General base - general acid (Tt-B,AH)



GLOSSARY OF SYMBOLS AND TERMS

<i>Symbol</i>	<i>Placement</i>	<i>Meaning</i>	<i>Page</i>	
A	On the Line	Bond making (association)	26	
D	On the Line	Bond breaking (dissociation)	26	
+	On the Line	Stepwise processes	26	
*	On the Line	Same as "+", but intermediate short-lived	27	
E	{	Subscript	Electrophilic (bond making to a "core atom")	28
		Subscript	Electrofugic** (bond breaking from a "core atom")	
N	{	Subscript	Nucleophilic (bond making to a "core atom")	28
		Subscript	Nucleofugic** (bond breaking from a "core atom")	
R	Subscript	Homolytic (bond making or breaking)	32	
e	Subscript	Same as E but involving a "peripheral atom"	28	
n	Subscript	Same as N but involving a "peripheral atom"	28	
r	Subscript	Same as R but involving a "peripheral atom"	32	
H	Subscript	Designation for primitive change in which electrophile is the hydron	29	
h	Subscript	Same as H at a "peripheral" atom	29	
xh	Subscript	Designates bond making or bond breaking between the hydron and a hydron carrier reagent atom	29	
C	On the Line	Diffusional combination	35	
P	On the Line	Diffusional separation	35	
int	Subscript	Molecules or ions weakly complexed - intimate ion pairs or equivalent pairs of uncharged molecules	37	
ss	Subscript	Molecules or ions weakly complexed - solvent separated ion pairs or equivalent pairs of uncharged molecules	37	
‡	Superscript	The preceding step is rate-limiting	51	
{}	On the Line	Repeated Sequence	52	

**The terms electrofugal and nucleofugal are synonymous with electrofugic and nucleofugic respectively.

GLOSSARY OF CATEGORY DESIGNATIONS

Su	Substitution	50
Em	Elimination	52
Ad	Addition	52
De	Detachment	51
At	Attachment	51
Tt	Tautomerization	51
Re	Rearrangement	51
AL	Alkyl	51
AR	Aryl	51
AC	Acyl	51
H ⁺	Appearance of [H ⁺] in the rate equation	51
HO [·] , RO [·]	Appearance of [HO [·]] or [RO [·]] in the rate equation	52
AH	General acid catalysis	52
B	General base catalysis	52

GLOSSARY OF NEW TERMS

<i>Term</i>	<i>Definition</i>
carrier atom	Participant atoms which are neither core nor peripheral. Carry other atoms or groups to and from the molecule containing the core atom(s). Used to define subscript xh. See pages 27 and 29.
core atom	The primary reference atoms in mechanistic change. Usually either of the two atoms of a transformed multiple bond or the single atom at which substitution occurs. See section 3. Used to define subscripts "N", "E", "R" and "H". See pp. 27-28.
cyclo-	Prefix for an elementary reaction or some part thereof indicating that the bonds undergoing primitive changes form part of a ring in the transition state of a pericyclic process. See page 34.
elementary reaction	This is defined in reference 9 as: "A one-step reaction or a reaction step that has no intermediate." For present purposes it is represented by an unpunctuated string of "A" and/or "D" symbols. See page 26.
intra-	Prefix for an elementary reaction or some part thereof indicating that the bond(s) undergoing primitive changes form part of a ring in the transition state of the elementary reaction. This prefix is used for nonpericyclic processes only and is replaced by "cyclo" for pericyclic processes (see above).
peripheral atom	A secondary reference atom located in the same molecule as the core atom(s). See section 3. Used to define subscripts "n", "e", "r" and "h". See page 27.
primitive change	This is defined in reference 9 as a conceptually simple molecular change into which an elementary reaction can be notationally dissected. For present purposes, primitive changes are bond-making (A) and bond breaking (D) components of multibond reactions. See page 26.
reference atom	Atom relative to which a primitive change is nucleophilic, electrophilic, nucleofugal, electrofugal, or homolytic. See page 27.

NOTES AND REFERENCES

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2. C. K. Ingold, "Structure and Mechanism in Organic Chemistry", second edition Cornell University Press, Ithaca, NY, 1969.
3. J. March, "Advanced Organic Chemistry", third edition, John Wiley and Sons, Inc., New York, NY, 1985, has been used as the main source for determining the mechanisms to be covered in this initial document.
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9. This term is defined by V. Gold in "Glossary of Terms used in Physical Organic Chemistry" IUPAC, and utilized by Littler.⁸
10. See V. Gold (ed.), "Glossary of Terms used in Physical Organic Chemistry", *Pure & Appl. Chem.*, **55**, 1281(1983).
11. Terms used in this document are consistent, so far as possible, with R. A. Y. Jones and J. F. Bunnett, "Nomenclature for Organic Chemical Transformations", to be published shortly in *Pure & Appl. Chem.*
- 11a. J. F. Bunnett and R. A. Y. Jones, *Pure & Appl. Chem.*, **60**, 1115(1988).
12. See reference 3 pg. 311.
13. M. H. Abraham and J. A. Hill, *J. Organometal. Chem.*, **7**, 11 (1967).
14. M. H. Abraham "Comprehensive Chemical Kinetics", Eds. C. H. Bamford and C. F. H. Tipper, vol. 12, Elsevier, New York, NY, 1973, p. 15.
15. See H. B. Charman and C. K. Ingold, *J. Chem. Soc.*, 2523 (1959).
16. R. E. Dessy, W. L. Budder, *J. Am. Chem. Soc.*, **84**, 1172 (1962).
17. See ref. 2, p. 565.
18. See ref. 2, pg. 1128.
19. See ref. 3, pg. 576.
20. See ref. 3, p. 295. The "Ad" symbol for addition was proposed by Ingold, ref. 2, p. 247.
21. See ref. 2, p. 1128.
22. See ref. 1, p. 280.
23. See ref. 2, p. 447.
24. See ref. 3, p. 311.
25. See ref. 2, p. 1128.
26. I. P. Beletskaya, K. P. Butin and O. A. Reutov, *Organometal. Chem. Rev., Sect. A7*, 51 (1971).
27. See ref. 3, p. 286.
28. R. C. Fahey and D-J. Lee, *J. Am. Chem. Soc.*, **90**, 2124 (1968).
29. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Academic Press, 1970, p. 65.
30. See ref. 2, p. 651.
31. See ref. 3, p. 887.
32. See ref. 3, p. 897.
33. J. March, "Advanced Organic Chemistry", second edition, McGraw-Hill Book Company, New York, N.Y., 1978, p. 924.
34. See ref. 2, pp. 403, 653.
35. See ref. 3, p. 610.
36. J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463 (1970).