

Kinetics and reaction mechanisms: selected examples from the experience of forty years

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Abstract - Kinetics of parallel reactions contribute to the elucidation of poly-step mechanisms. Competing pathways in the reaction of benzenediazonium ion with azide anion helped to establish the occurrence of phenylpentazole. Steady state kinetics clarified the competition between the interception of an intermediate and its return to the starting material. The Diels-Alder reactions of cyclooctatetraene and of diphenylbenzocyclobutenes, and the thermal equilibration of aziridines with azomethine ylides serve as examples. Kinetics and trapping experiments revealed a four-step sequence for the conversion of bromocyclooctatetraene to trans- β -bromostyrene.

INTRODUCTION

Physical organic chemistry is no longer the height of fashion as it has been 25 years ago. In the arsenal of methods and tools, chemical kinetics plays a kind of Cinderella role today. To the author's opinion, to this very day kinetics has been the most important instrument in the elucidation of reaction mechanisms.

Why rate measurements? In their pioneering work on cationic rearrangements and substitution mechanisms, Hans Meerwein and Christopher Ingold had demonstrated the power of the kinetic argument. At the time the author realized that many further reaction mechanisms required rate studies to be clarified beyond the stage of vagueness in which they were hovering. Unifying concepts, capable of bringing order into a chaos of facts, were expected to emerge from the exploration of reaction mechanisms. When foreign journals became accessible again in 1948/50, the author learned that many young scientists - world-wide - were directing their research activities toward mechanistic and physical organic chemistry.

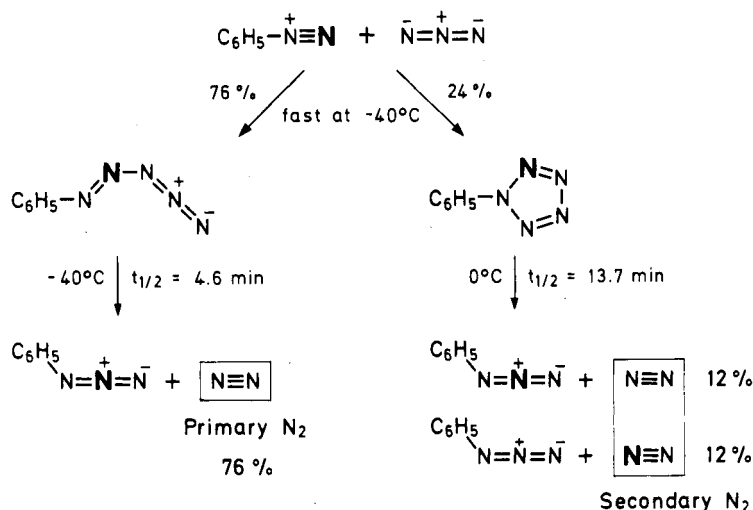
The application of chemical kinetics to mechanistic problems will be limited to selected examples of *competing pathways*. Competition belongs to the essence of life. Charles Darwin's "survival of the fittest" is evolution promoted by competition. In 1776 Adam Smith published his famous book on the wealth of nations. His dream is now reality: free enterprise, and *competition* have become the pillars of world economy and social structures. Competition pervades our individual life: at school, on the job, in sports, in scientific research.

This lecture is dedicated to Professor Paul D. Bartlett, one of the pioneers of physical organic chemistry, on the occasion of his 80th birthday.

We assumed the rapid formation of benzenediazoazide which enters at -40°C into competing pathways: 24% forms phenylpentazole by ring closure, and 76% breaks down into phenyl azide + nitrogen. The somewhat odd presentation in *Scheme 2* separates the upper -40°C region - here phenylpentazole is stable - from the 0°C part where its electrocyclic ring opening becomes noticeable. The half-life of 13.7 min refers to the 1,5-electrocyclic equilibration and the irreversible nitrogen loss (ref.4). There is hardly an intermediate other than phenylpentazole which satisfies the stringent symmetry conditions. The isolation of phenylpentazole by Ugi was no surprise (ref.5); neither was the X-ray analysis of 4-dimethylaminophenylpentazole by Dunitz et al. in 1983 (ref.6).

Kinetics can refute mechanistic schemes, but can never prove a proposed mechanism; *compatibility* is the optimal outcome. The combination with the distribution of the isotopic label solidified the evidence for the cyclic intermediate. Is the role of the second intermediate, benzenediazoazide, firmly established? It is not.

Scheme 3

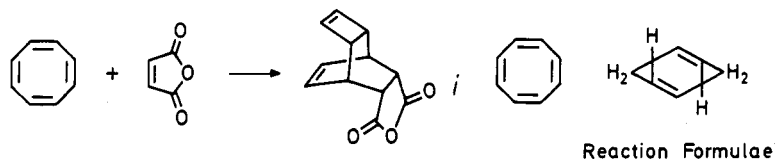


The alternative description of *Scheme 3* is likewise consistent with the kinetic data although we prefer the preceding scheme. Here the nucleophilic addition of azide ion to the benzenediazonium ion competes with a concerted 1,3 cycloaddition. Now benzenediazoazide is only the precursor of the primary nitrogen whereas the secondary comes from a 1,3-dipolar cycloreversion of phenylpentazole.

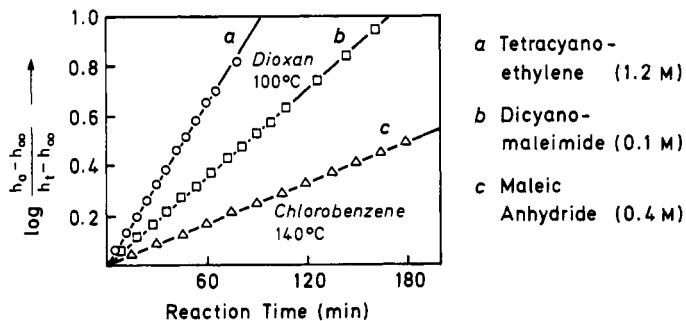
DIELS-ALDER REACTIONS OF CYCLOOCTATETRAENE

In the next kinetic system to be discussed, the interception of an intermediate competes with its return to the starting material. In the pioneering work of Walter Reppe et al., the Diels-Alder reactions of cyclooctatetraene (COT) were studied, and the structure of the maleic anhydride adduct was clarified (*Scheme 4*). However, the question of whether the skeletal rearrangement of COT takes place before, during, or after the reaction with the dienophile, was not answered by the BASF group. They used "reaction formulae" to code the colorful reactivity of this higher vinylog of benzene (ref.7).

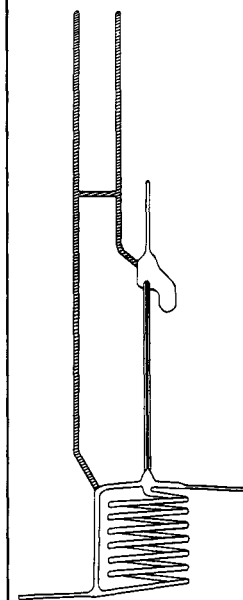
Scheme 4



Dilatometric Rate Measurements with Large Excess of Dienophile



Scheme 5



We expected to find a clue through a kinetic study. Many chemists are unaware of the precision and elegance of the dilatometric rate measurement (refs. 8,9); "contractometric" would be more fitting since the combination of two molecules is accompanied by volume shrinkage of the solution. The dilatometer (Scheme 5) is a sensitive liquid thermometer; it requires constancy of the temperature within a few thousands of a degree. The sinking of the meniscus in a capillary is measured by a cathetometer.

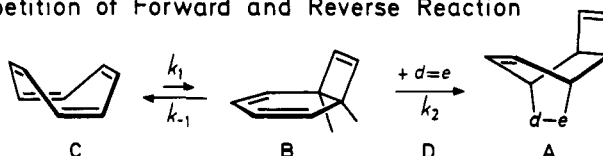
The near quantitative yields of Diels-Alder adducts allowed dilatometry which is only applicable to first-order reactions (Scheme 4). The combination of COT with large and variable excess concentrations of dienophiles provided first-order or pseudo-first-order rate constants. Maleic anhydride, tetracyanoethylene, and dicyanomaleimide are dienophiles of increasing reactivity.

The kinetic study carried out by Fritz Mietzsch in 1964 presented experimental evidence for an electrocyclic equilibrium of cyclooctatetraene with bicyclo[4.2.0]octatriene (Scheme 6, ref.10). This became textbook knowledge in the meantime. Yet not so much the phenomenon itself, but rather the kinetic approach to it shall be discussed here.

According to the electron diffraction data of cyclooctatetraene, the double bonds of the boat conformation are fixed in close to *orthogonal* arrangement (ref.11). However, a nearly planar 1,3-diene system is a prerequisite for the concerted Diels-Alder reaction. Bicyclooctatriene B contains such a planar system and is a plausible intermediate. The structure of the adduct A (ref.12) suggests that the dienophile approaches from below, i.e., the less hindered side.

How does the dilatometric rate constant depend on the excess concentration of increasingly active dienophiles? Steady state treatment of the system with a reversibly formed isomer of monocyclic C is based on $d(B)/dt = 0$, i.e., the change of the concentration of intermediate B is negligible compared with

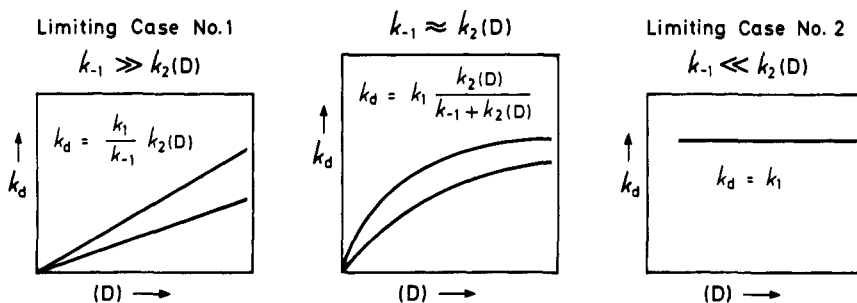
Scheme 6 Competition of Forward and Reverse Reaction



Steady State Kinetics

$$d(B)/dt = 0 = k_1(C) - k_{-1}(B) - k_2(B)(D); \quad (B) = k_1(C)/(k_2(D) + k_{-1})$$

$$\frac{d(A)}{dt} = k_2(B)(D) = k_1(C) \frac{k_2(D)}{k_{-1} + k_2(D)}; \quad k_d = k_1 \frac{k_2(D)}{k_{-1} + k_2(D)}$$



the changes of C and A. An expression is derived for the rate of adduct formation, $d(A)/dt$, which includes the isomerization constant k_1 multiplied by a coefficient which reflects partitioning of the intermediate B between second-order cycloaddition and first-order reversion to C. The dilatometric rate constant, called k_d , depends on k_1 , k_{-1} , and k_2 ; note that the dienophile concentration, (D), occurs in numerator and denominator of the fraction (ref.13). A large excess of the dienophile always guarantees overall first order.

As long as the reversion constant, k_{-1} , is large compared with $k_2(D)$, the latter can be neglected in the denominator and the expression simplifies to that of the lower left of Scheme 6.

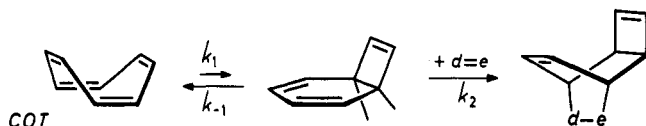
The intermediate B is captured from the established equilibrium with C. The proportionality of k_d and (D) forbids any conclusion on the electrocyclic ring closure which precedes the cycloaddition. This rate law is observed for less reactive dienophiles like maleic anhydride (ref.10).

For more reactive dienophiles, k_2 grows and $k_2(D)$ competes with k_{-1} . On plotting k_d versus the dienophile concentration, (D), one is led to anticipate curves approaching a plateau as illustrated by the diagram in the middle of Scheme 6. With increasing (D), $k_2(D)$ in the denominator will exceed k_{-1} ; finally, k_{-1} becomes negligible, and the plateau corresponding to $k_d = k_1$ is reached.

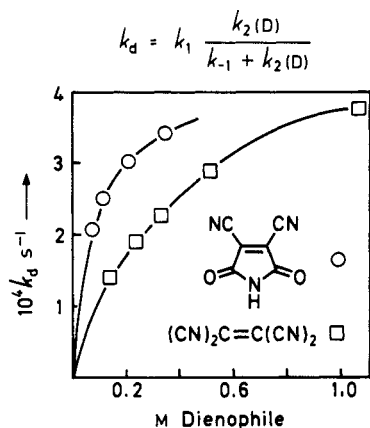
The limiting case no.2 at the lower right of Scheme 6 is verified when k_2 becomes so large that k_{-1} is dwarfed compared with $k_2(D)$. The dilatometric rate constant is now independent of the dienophile concentration; k_d becomes identical with k_1 , the first-order rate constant of tautomerization.

Tetracyanoethylene and dicyanomaleimide are dienophiles of high activity. Several dilatometric rate measurements were run with COT and increasing dienophile concentrations. Plotting of k_d versus (D) led to curves approaching a plateau (Scheme 7).

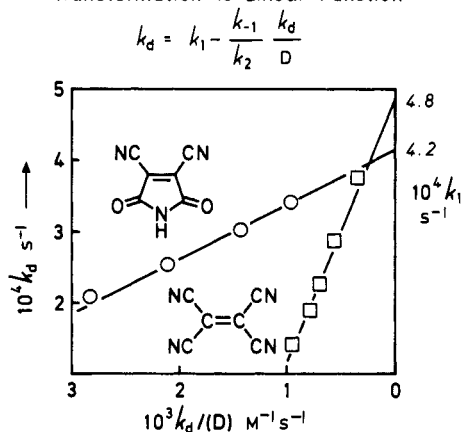
Scheme 7



Dicyanomaleimide and Tetracyanoethylene in Dioxan at 100°C



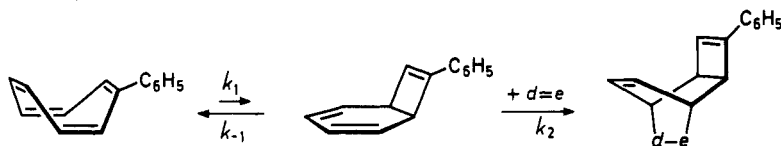
Transformation to Linear Function



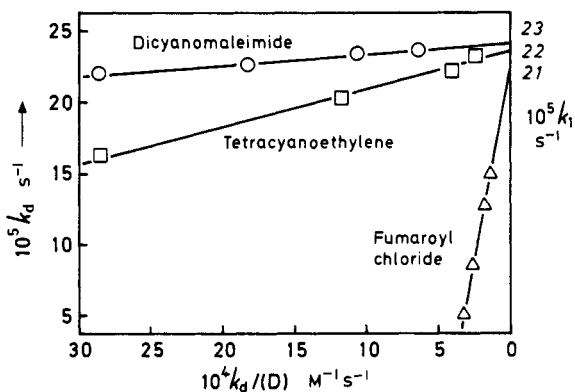
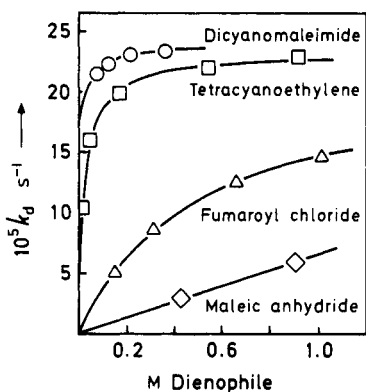
However, linear functions are superior for quantitative evaluation of kinetic data. Simple transformation of the left-hand equation yields a straight line when k_d is regarded as a function of $k_d/(D)$. The abscissa of the resulting diagram (Scheme 7, right-hand side) shows the origin on the right; it corresponds to a fictitious infinitely high concentration of D. The intercept equals k_1 and should be independent of the nature of the dienophile. This is satisfied within some generous error limits - $4.8 \cdot 10^{-4}$ versus $4.2 \cdot 10^{-4} \text{ s}^{-1}$ at 100°C. The slope is identical with k_{-1}/k_2 ; the values indicate that dicyanomaleimide is 5 times more potent than tetracyanoethylene as a dienophile (ref.10).

What does this experiment prove? The second-order Diels-Alder reaction must be preceded by a reversible first-order isomerization of cyclooctatetraene. It is acceptable that bicyclo[4.2.0]octatriene occurs as an intermediate

Scheme 8



Dicyanomaleimide (THF), Tetracyanoethylene (Ethyl Acetate), Fumaroyl Chloride (Ethyl Acetate) and Maleic Anhydride (THF) at 70°C



since orbital symmetry allows concertedness of the disrotatory ring closure of the triene system incorporated in COT. By the way, in 1964 we spoke of valence tautomerism. The terms "electrocyclic" and "disrotatory" had not yet been introduced.

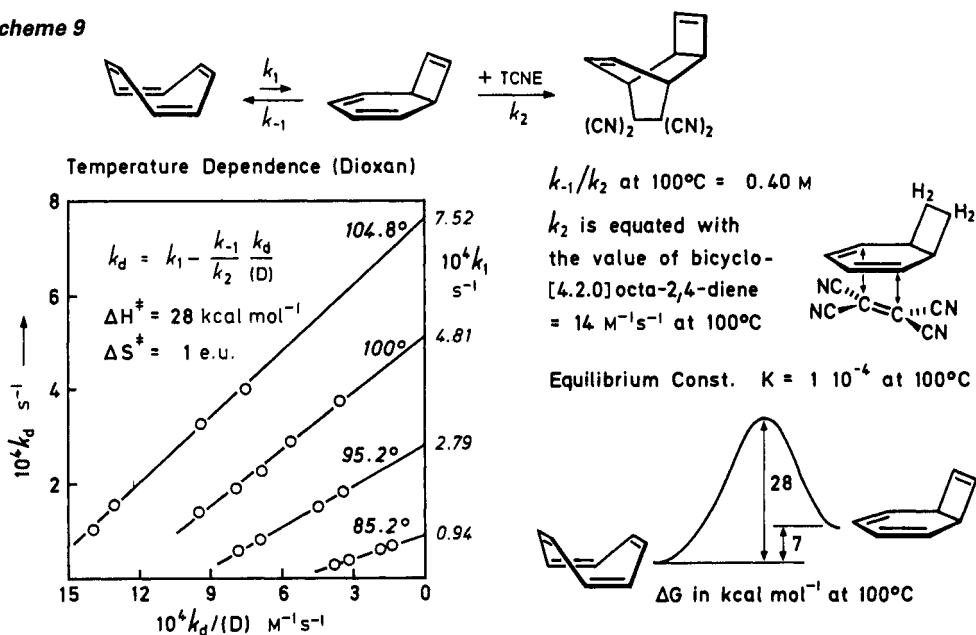
Phenylcyclooctatetraene combined with dienophiles furnishing virtually only one cycloadduct out of four conceivable positional isomers, the one with phenyl at the cyclobutene double bond. The Diels-Alder rates exceed those of the unsubstituted COT; they were measured at 70°C. The overall rate constant, k_d , depends linearly on the excess concentration of maleic anhydride, but non-linear functions occurred for three more active dienophiles. It may be noticed that the rate constants measured for dicyanomaleimide are close to the limiting value (*Scheme 8*, ref.10).

We call the function of k_d versus $k_d/(D)$ the "Bodenstein plot" in honor of Max Bodenstein, pioneer of the steady state principle in chemical kinetics (ref.14). The three dienophiles in the right-hand diagram of *Scheme 8* produce rather similar intercepts: $10^5 k_2 = 21, 22, \text{ and } 23$; they pertain to k_1 , the tautomerization constant. Relative k_2 values are calculated from the slopes of the straight lines: 1:20:60 for fumaroyl chloride, tetracyanoethylene, and dicyanomaleimide.

In the dilatometric experiments the concentration of tetracyanoethylene, as well as the temperature, has been varied by Fritz Mietzsch (ref.10). The slopes of the straight lines in the Bodenstein plot (*Scheme 9*) rise with the temperature as anticipated for k_{-1}/k_2 . The constant k_{-1} of unimolecular ring opening increases faster with rising temperature than the constant k_2 of bimolecular cycloaddition; the latter is burdened by a large negative entropy of activation.

The intercepts provided k_1 values over a temperature range of 20°C. The Eyring parameters calculated are reasonable. An activation entropy near zero for the conversion of one rigid molecule into another is no surprise (ref.15).

Scheme 9



The k_d measurements at 100°C afforded $k_{-1}/k_2 = 0.40$ M, but only the ratio is accessible. The determination of k_{-1} requires a dirty trick, namely the assumption that the Diels-Alder rate constants of bicyclo[4.2.0]octa-2,4,7-triene and bicyclo[4.2.0]octa-2,4-diene are the same. Since the dienophile approaches the diene from below, the k_2 values of the compounds containing the cyclobutene or the cyclobutane ring on top probably differ by less than factor 10. Bicyclooctadiene is isolable (ref.16) and its Diels-Alder rates with TCNE were measured by Gernot Boche (ref.17). Based on $k_2 = 14 \text{ M}^{-1}\text{s}^{-1}$, we obtained $k_{-1} = 5.6 \text{ s}^{-1}$ and an equilibrium constant of 10^{-4} . Thus, the concentration of bicyclooctatriene amounts to 0.01% at 100°C, and the small diagram at the lower right of *Scheme 9* displays the free energies involved (ref.18).

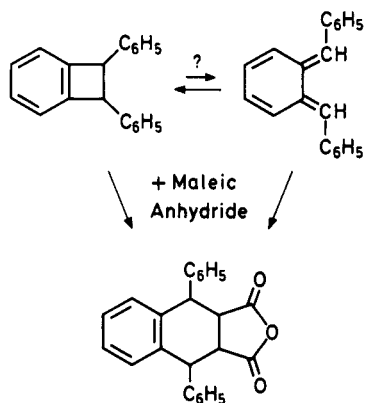
A concentration of 0.01% is insufficient for direct NMR analysis. Recently Squillacote et al. (ref.19) developed a flash technique for establishing the electrocyclic equilibrium in the gas phase at 400-700°C and 10^{-5} Torr. $^1\text{H-NMR}$ analysis of the frozen samples likewise furnished $\Delta G(100^\circ\text{C}) = 7 \text{ kcal mol}^{-1}$, which is in perfect agreement with our value obtained indirectly via Diels-Alder kinetics.

Having successfully dealt with one problem, the scientist immediately looks around for related phenomena. In particular, he tries to apply steady state kinetics in the hope that his investment into the dilatometric technique will pay off. In 1965 electrocyclic reactions - the term was introduced by Woodward and Hoffmann (ref.20) - became fashionable tests for the principle of conservation of orbital symmetry. Our work on diphenylbenzocyclobutene predated this achievement.

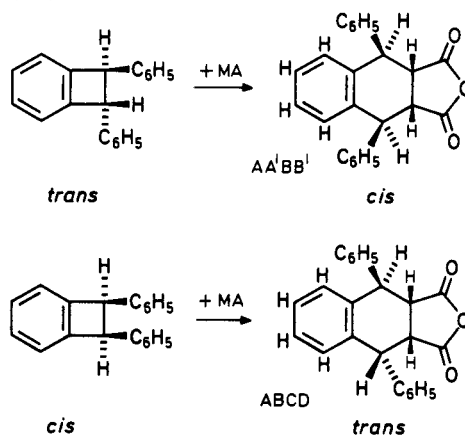
BENZOCYCLOBUTENES AND o-QUINODIMETHANES

Several authors had observed cycloadditions of benzocyclobutenes, and in 1958 Jensen and Coleman delineated the mechanistic alternatives (ref.21): Either the ring opening to o-quinodimethane precedes the cycloaddition, or a four-center reaction with maleic anhydride leads directly to the adduct (*Scheme 10*).

Scheme 10



Scheme 11



cis-Diphenylbenzocyclobutene at 50°C

TCNE M	0.162	0.188	0.473
$10^5 k_d \text{ s}^{-1}$	3.82	3.60	3.67

The interaction has a stereochemistry. *Trans*- and *cis*-1,2-diphenylbenzocyclobutene furnished diastereoisomeric adducts stereospecifically. Helmut Seidl scrutinized the NMR signals of the four benzo protons. The AA'BB' spectrum indicates a plane of symmetry in the first example; it is this *cis* adduct which comes from *trans*-diphenylbenzocyclobutene. Conversely, the lack of symmetry shown by an ABCD spectrum is consistent with a *trans*-diphenyl structure; in this case *cis*-diphenylbenzocyclobutene is the precursor (Scheme 11, ref.22).

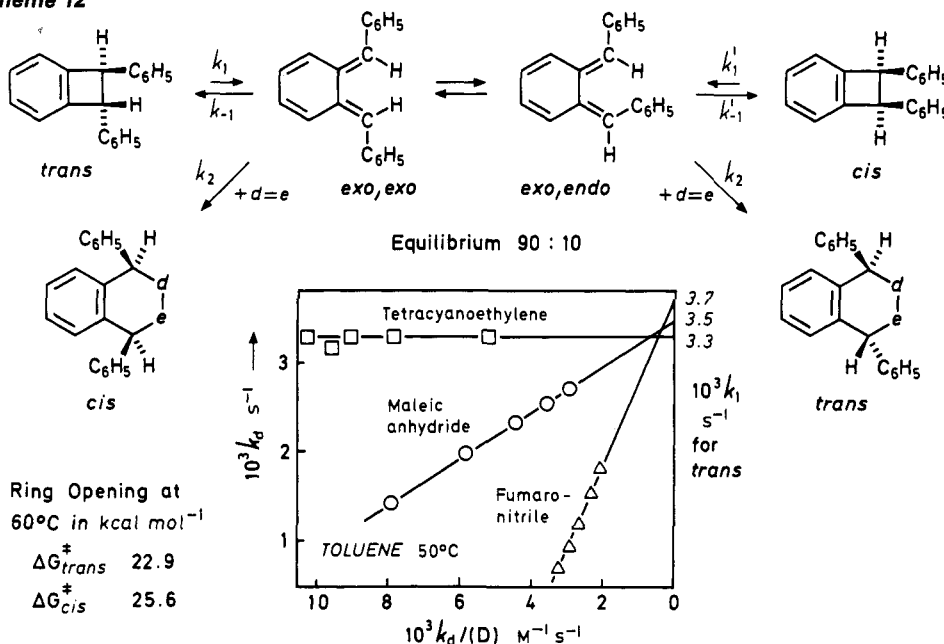
At first attempt, dilatometric rate measurements with excess of tetracyanoethylene revealed *cis*- and *trans*-diphenylbenzocyclobutenes to be candidates for the limiting case no. 2 of Scheme 6. The value of k_d for the *cis*-diphenyl compound remained the same after the molar TCNE concentration had been increased 2.5-fold (Scheme 11). Thus, k_d is a first-order and not a pseudo-first-order constant.

Trans- and *cis*-diphenylbenzocyclobutene are interconnected via the *exo*, *exo*- and *exo*,*endo*-diphenyl-*o*-quinodimethanes (Scheme 12). The configurations of the cycloadducts disclose conrotation for the electrocyclic reactions. A 90:10 equilibrium of *trans* and *cis* isomers is established at 50°C.

The cycloaddition onto active dienophiles is faster than equilibration. The Bodenstein plot in Scheme 12 shows two phenomena: that the return to *trans*-diphenylbenzocyclobutene (k_{-1}) competes with the cycloaddition of the dienophile for fumaronitrile and maleic anhydride on the one hand; and that TCNE completely suppresses the recyclization on the other. The k_1 values, obtained by extrapolation, do not depend on the nature of the intercepting dienophile within the usual limits (ref.22).

The electrocyclic ring opening of *trans*-diphenylbenzocyclobutene (ethyl acetate, 50°C) is 70 times faster than that of the *cis* isomer, corresponding to a difference of 2.7 kcal mol⁻¹ for the free activation energies. The reason is the loss of conjugation energy due to enforced twisting of the *endo* phenyl in the *exo*,*endo*-diphenyl-*o*-quinodimethane.

Scheme 12



The intermediacy of potent dienes was established for the first time by Helmut Seidl in this investigation of 1964 (ref.22). The steric course lends credence to the assignment of the *o*-quinodimethane structures. In the meantime, direct observation of quinodimethanes by flash photolysis (ref.23) or the matrix isolation technique (ref.24) has been achieved. Furthermore, *intramolecular* cycloadditions of benzocyclobutenes via quinodimethanes were used in natural product synthesis (ref.25).

Conrotatory ring openings of cyclobutenes to butadienes - here the open-chain species is the stable one - have been noticed by E. Vogel (ref.26) and by R. Criegee et al. (ref.27), and they became important in backing up the Woodward-Hoffmann rules. *Scheme 12* illustrates the first instance of the *benzo-fused* system rigidly obeying the same conrotatory course of ring opening and closure.

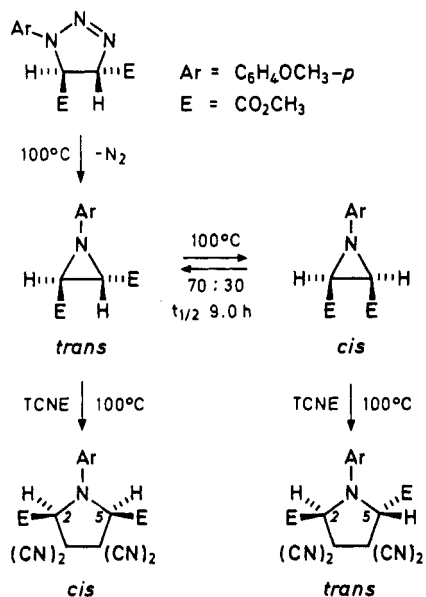
Like the 1,3-diene, the allyl anion is a 4π system. In their famous short communication of 1965, Woodward and Hoffmann predicted also conrotation for the ring opening of the cyclopropyl anion to yield the allyl anion (ref.20), a prediction which still lacks a stringent verification. Our first confirmation for an isoelectronic example was not the result of deliberate planning.

ELECTROCYCLIC RING OPENING OF AZIRIDINES

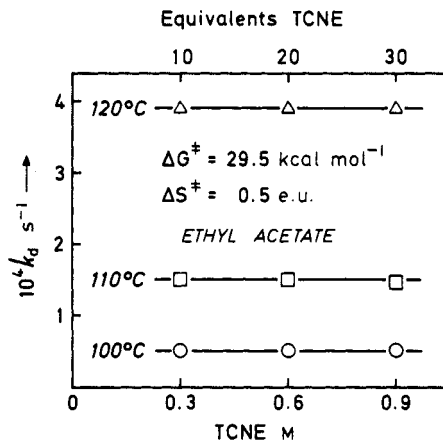
We dealt with 1,3-dipolar cycloadditions of azides. The adduct of 4-methoxyphenyl azide and dimethyl fumarate lost nitrogen on heating. The resulting aziridine-2,3-dicarboxylic ester showed an amazing behavior. *Trans,cis* equilibration took place at 100°C as a first-order reaction without base catalysis (*Scheme 13*). We concluded that the isomerization requires a ring-opened species (ref.28).

Dimethyl acetylenedicarboxylate or tetracyanoethylene suppressed the *trans,cis* isomerization by intercepting the open-chain intermediates in stereospecific cycloadditions as found by Wolfgang Scheer. Please, notice that the aziridine with *trans* ester groups afforded the pyrrolidine-2,5-*cis*-dicarboxylic ester and vice versa (ref.29).

Scheme 13



Dilatometric Rate Measurements
of *trans*-Aziridine + TCNE



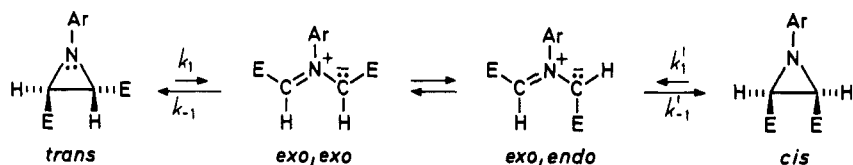
Our dilatometers and the steady state equation proved useful again. According to W. Scheer's measurements, the reactions of the aziridine-trans-diester with 10, 20, or 30 equivalents of TCNE proceeded with one and the same first-order rate constant k_d (Scheme 13). We deduced from the limiting case no.2 that trans,cis isomerization as well as regeneration of the aziridine is blocked by the cycloaddition. The conversion of the trans-aziridine to the active species has to overcome an activation enthalpy of $29.5 \text{ kcal mol}^{-1}$; the entropy change is negligible (ref.30).

In 1967 we reported the novel conrotatory ring opening of these aziridines furnishing azomethine ylides, this being an isoelectronic analogue of the conversion of cyclopropyl anion to allyl anion (ref.31). Conrotation carries the trans ester groups to the exo,exo positions of the azomethine ylide; similarly, the aziridine cis-diester correlates with the exo,endo configuration of the open-chain species (Scheme 14). By the way, the 1,3-cycloadditions of azomethine ylides provided the first examples for the complete retention of structure on the side of the 1,3-dipole (ref.32).

Another Bodenstein plot is presented in Scheme 14 dealing with the cycloadditions of the aziridine-cis-dicarboxylic ester; Hansjoachim Mäder measured the rate constants. Just like TCNE, dimethyl fumarate also traps every single molecule of the exo,endo azomethine ylide. Norbornene and ethylenetetracarboxylic ester are less active dipolarophiles and still allow some return to the original aziridine. The extrapolation to infinite concentration of D approximates the rate constant k_1' of ring cleavage (ref.33).

Photochemical ring opening of the aziridine-dicarboxylic esters was effected at room temperature, and it is even of aesthetic appeal that now disrotation rules the field (ref.31). This is in accordance with the quantum-chemical prediction for the first excited singlet state. The yellow azomethine ylides became visible, and their thermal conrotation was measured; the half-lives

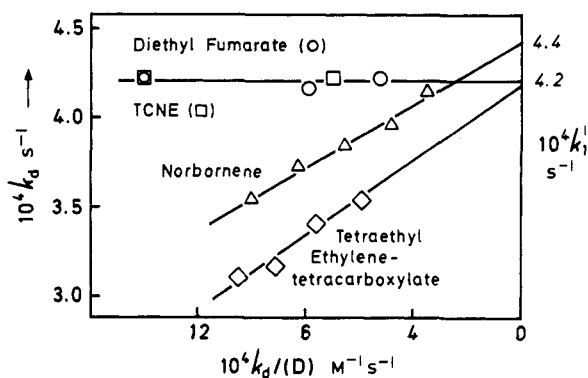
Scheme 14



Ar = $\text{C}_6\text{H}_4\text{OCH}_3\text{-}p$

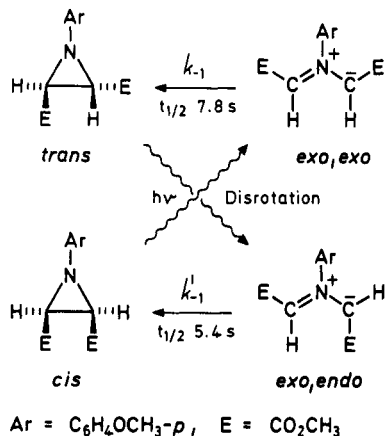
E = CO_2CH_3

Cycloadditions
of *cis*-Aziridine;
Dilatometric Rate
Measurements in
Ethyl Acetate at 119°C

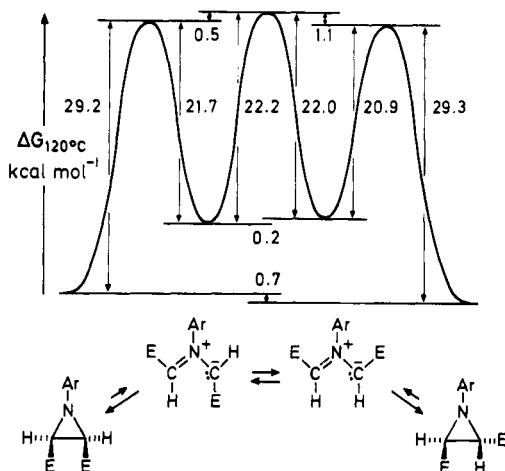


Scheme 15

Generation of Azomethine Ylides
by Flash Photolysis at 25°C



Free Energy Profile of Thermal
Isomerization of Aziridines



amount to 8 and 5 seconds at room temperature (Scheme 15, ref.34). The flash-photolytic studies were carried out by H. Mäder in cooperation with Horst Hermann at Mülheim/Ruhr.

In our isomerization scheme, the activation enthalpies of ring opening were supplemented by measurements of the net isomerization rates of the aziridines. The depths of the troughs were obtained from the temperature dependence of the recyclization rates of the 1,3-dipoles. This ensemble of kinetic data gave access to the complete energy profile of interconversions (Scheme 15). The measurements were not precise enough to justify the decimal in the free energy changes; its whole function is to preserve additivity of the contributions. The inaccuracy of the flash-photolytic measurements makes the depths of the troughs uncertain by a couple of kcal mol⁻¹ (ref.34).

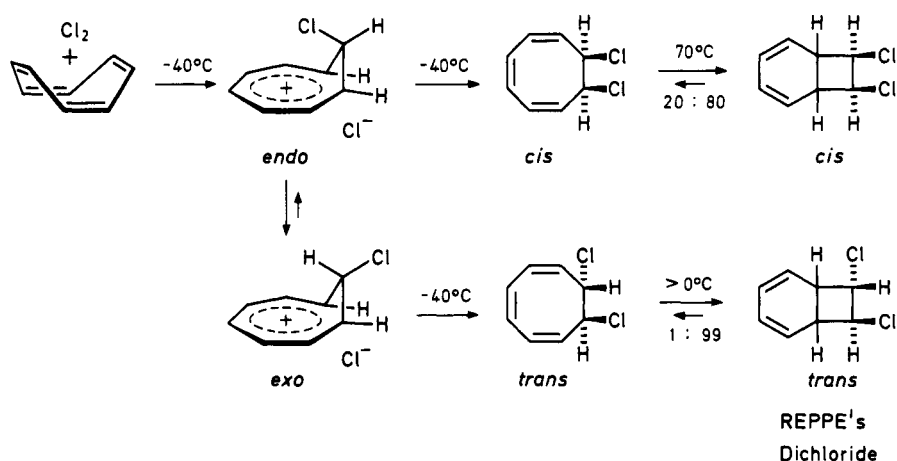
The energy level of the azomethine ylides lies 8 kcal mol⁻¹ above that of the cyclic tautomers. The recyclization requires two 90° rotations about the CN bond axes; the resonance energy of the 1,3-dipole is lost before the incipient σ -bonding starts to contribute. This is the reason for astonishingly high barriers to recyclization (22 and 21 kcal mol⁻¹ in Scheme 15). Intermolecular 1,3-dipolar cycloaddition easily comes out ahead in the competition with the electrocyclic ring closure.

REARRANGEMENTS OF HALOCYCLOOCTATETRAENES

Cyclooctatetraene is a molecular acrobat; we will bring it into focus again. The imaginative wiggles by which the nonaromatic 8 π system unerringly finds its way to benzenoid resonance, will be the last topic of the discussion.

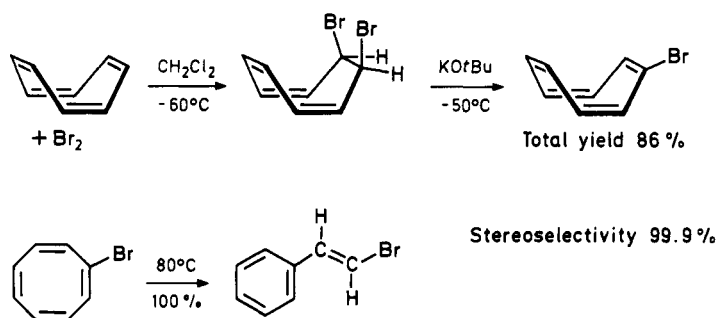
Reppe reported trans-7,8-dichlorobicyclo[4.2.0]octadiene to be the chlorination product of COT (ref.7). Gernot Boche, Wolfgang Hechtl, and Johann Gasteiger unveiled a drama in many acts (Scheme 16). All four covalent dichlorides were isolated, and their interconversions were clarified (ref.35); the

Scheme 16



8-chloro-homotropylium ions were crystallized as hexachloroantimonates (refs. 36, 37). Chlorination of COT in carbon tetrachloride at -40°C provided the monocyclic cis-dichloride. Bromination takes an analogous course as illustrated in Scheme 17 (ref.38).

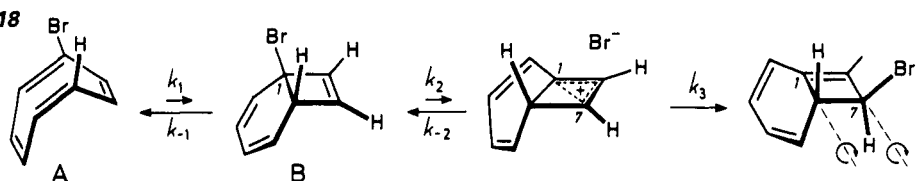
Scheme 17



Treatment of the cis dihalides with potassium tert-butoxide opened easy access to halocyclooctatetraenes (ref.39). In 1952 Cope and Burg reported the thermal conversion of halocyclooctatetraenes to β -halostyrenes (ref.40); the chloro compound required 200°C , the bromo compound 100°C . We observed a quantitative conversion of the bromocyclooctatetraene to trans- β -bromostyrene which was 99.9% stereoselective according to GC (Scheme 17). The rearrangement obeyed the first-order law, and no intermediate became visible during its course (refs.41, 42).

Will Elmar Konz established the four-step sequence of Scheme 18 by means of a combination of interception reactions and kinetic studies. The electrocyclic equilibration with 1-bromobicyclooctatriene is followed by an ionization to a homocyclopropenium salt. Ion recombination on the upper side and conrotatory ring opening of the 7-bromobicyclooctatriene give rise to trans- β -bromostyrene. This pathway was supported by a wealth of data (refs.41, 43); some people would call it an "overkill". The bromine in the product is no longer attached to the original C-atom, but has performed a 1,3 migration. This was confirmed by the rearrangement of 1,4-dibromocyclooctatetraene yielding 4, β -dibromostyrene; six C-atoms separate the bromine atoms in the product (Scheme 18, ref.44).

Scheme 18

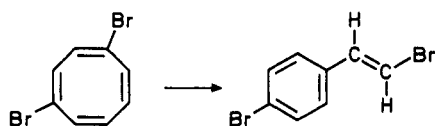


$$\text{Effective Ionization Constant } k_i = k_2 \frac{k_3}{k_{-2} + k_3}$$

$$\frac{d(B)}{dt} = k_1(A) - k_{-1}(B) - k_i(B) = 0; \quad (B) = \frac{k_1(A)}{k_{-1} + k_i}$$

$$\frac{d(C)}{dt} = k_{\text{exp}}(A) = k_i(B) = k_1(A) \frac{k_i}{k_{-1} + k_i}$$

$$k_{\text{exp}} = k_1 \frac{k_i}{k_{-1} + k_i}$$



We assume that the fast aromatization by conrotatory ring opening (k_4) renders the ion recombination step with k_3 irreversible. This permits us to define an effective ionization constant, k_i , as k_2 times the partition coefficient, $k_3/(k_{-2} + k_3)$. k_i is the first-order rate constant by which 1-bromobicyclooctatriene B is converted to bromostyrene C (Scheme 18).

Now the steady state treatment is applied to B, the 1-bromobicyclooctatriene. The concentration of B is a function of (A) and three rate constants. Finally, the rate of the bromostyrene formation is connected with the concentration of A by the overall experimental rate constant, k_{exp} ; the latter, in turn, is shown to be a function of k_1 , k_{-1} , and k_i .

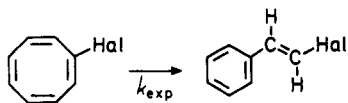
The logarithms of k_{exp} measured by W.E. Konz are plotted in Scheme 19 versus the Dimroth-Reichardt parameter of solvent polarity (ref.45). Bromocyclooctatetraene undergoes rearrangement in acetonitrile at 80°C nearly 600 times faster than in cyclohexane, and the relation is linear for solvents of intermediate polarity. Surprisingly, an increase of solvent polarity beyond acetonitrile and DMSO is no longer honored by an increase of k_{exp} .

Our partition coefficient explains this behavior. In nonpolar media the ionization constant k_i is small compared with k_{-1} , the rate of electrocyclic ring opening. As a consequence, k_{exp} is proportional to k_i and its logarithm depends linearly on solvent polarity. In highly ionizing solvents, however, k_i becomes larger than k_{-1} , i.e., no longer the ionization, but rather the preceding valence tautomerization controls the overall rate (ref.41).

Under the same conditions, iodocyclooctatetraene is converted to trans- β -iodostyrene. Allylic iodides ionize faster than allylic bromides. For iodocyclooctatetraene k_i is larger than for the bromo compound and responds more sensitively to solvent polarity (Scheme 19). The ratio of the k_{exp} values is 7 in cyclohexane and 44 in dioxan. The k_{exp} of iodocyclooctatetraene already reaches the plateau for bromobenzene as a solvent; the tautomerization constants, k_1 , are obviously similar for both halocyclooctatetraenes (U. Schnegg, ref.46).

Scheme 19

Solvent Dependence of Rearrangement Rate



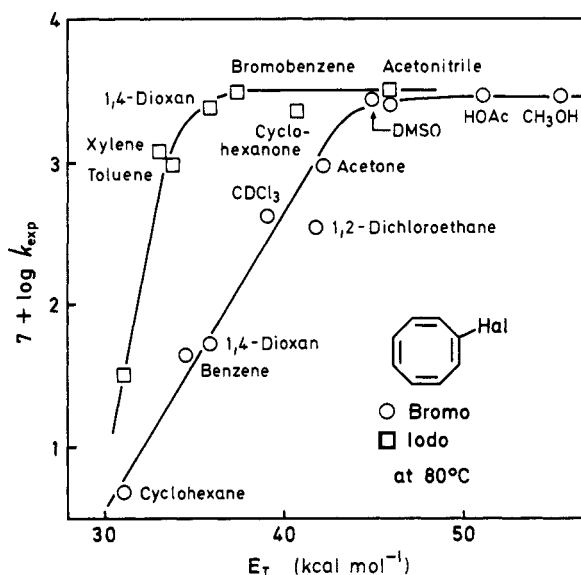
$$k_{\text{exp}} = k_1 \frac{k_i}{k_{-1} + k_i}$$

For nonpolar solvents

$$k_{\text{exp}} = \frac{k_1}{k_{-1}} k_i$$

For highly polar solvents

$$k_{\text{exp}} = k_1$$



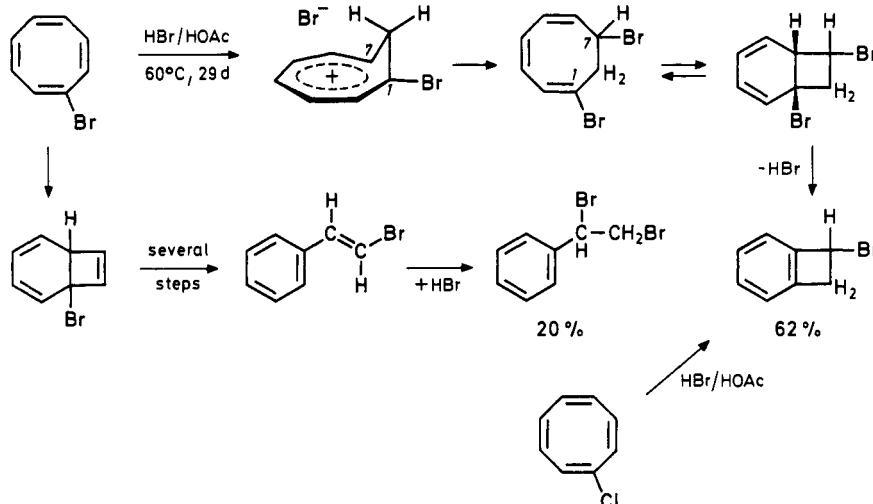
The eagerness to arrive at benzenoid aromaticity is obvious in the last contribution to cyclooctatetraene chemistry. It deals with a novel isomerization of bromocyclooctatetraene and is not yet published, although part of a Ph.D. Thesis of 1974. Ulrich Schnegg reacted bromocyclooctatetraene with hydrogen bromide in acetic acid at 60°C and obtained 62% of 1-bromobenzocyclobutene and 20% of α,β -dibromoethylbenzene (Scheme 20, ref.46).

The initiating step is the formation of the 1-bromohomotropylium bromide. This 1-bromo ion was dominant among positional isomers when bromocyclooctatetraene was dissolved in fluorosulfonic acid. Ion recombination furnishes 1,7-dibromocyclooctatriene which enters into the electrocyclic ring closure. Now the 6π aromatic system is in close reach and propels a *cis* elimination of HBr.

Notice that the bromine of the starting material is dropped along the way and that the bromine of the product comes from HBr. It is therefore no surprise that chlorocyclooctatetraene afforded the same 1-bromobenzocyclobutene on treatment with hydrogen bromide (ref.46).

In a competing pathway which was discussed above, bromocyclooctatetraene is converted to β -bromostyrene; here the HBr addition is the concluding step.

Scheme 20



This was the concluding step also in the list of examples. The author hopes to have demonstrated that studying chemical kinetics is not a complete waste of time, not even for the modern chemist. The modern chemist? The young generation will probably regard the examples as antiquities and will react with a slightly bored "d'jà vue".

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