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SOME PROBLEMS OF CHEMICAL KINETICS AND REACTIVITY

VOLUME 1

外文书库

Revised and expanded by the author

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Volume 1

PUBLISHER'S NOTE

Since Volume 1 was printed a second Russian edition of the book has been published which contains a number of corrections and additions to the first edition. In order to bring this volume completely up to date, a list of these errata and addenda has been inserted at the end of Volume 2.

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INTRODUCTION

This book was first published in 1954 by the U.S.S.R. Academy of Sciences, its history being as follows: The Chemistry Division of the Academy had arranged an All-Union Conference on Chemical Kinetics and Reactivity, to be held in 1955, and I was requested to present the opening paper; while working on this I came to the conclusion that it would be of value to produce a small book in which the published data and my personal views on the topics to be discussed could be presented. The book appeared in 1954, and a collection of 69 papers presented at the Conference by various Soviet workers was published by the Academy in the first half of 1955; the Conference was held on 20–25 June, 1955, being a general discussion on my book and on the papers in the collection. A number of important topics, touching on the development of studies in chemical kinetics and reactivity, were considered.

The book was produced only in small numbers, and the edition was soon sold out; I was requested by the Academy to prepare a second edition. Immediately afterwards I was requested to grant my permission for the book to be translated into English and German, by Pergamon Press and Princeton University, and by the Academy of Sciences of the German Democratic Republic, respectively. The book has been substantially enlarged for the second edition, fresh data appearing in the world literature or obtained at the Institute of Chemical Physics being incorporated. The book consists of various views and calculations developed by myself and certain colleagues at the Institute of Chemical Physics during the last 10–15 years from our experiments and from the published data on chemical kinetics. The book therefore presents a particular viewpoint, does not cover all work done on reaction mechanisms, and does not pretend to be a treatise or work of reference. The main topics considered are radical and radical-chain reactions. More than 20 years have passed since my previous book *Chain Reactions* appeared; meanwhile studies in chemical kinetics and chain reactions have developed enormously, vast numbers of papers have appeared, but it still seems as though the main problems are as yet not completely solved; the situation is very different from that in the physics of nuclear reactions, particularly chain fission, which was discovered in 1939 and since then has been so completely elucidated. The unsatisfactory situation in relation to reaction mechanisms has arisen, in my opinion, because the world's scientists have been occupied with isolated observations on particular reactions and have not undertaken a general all-round study. Such isolated observations are now quite inadequate in most cases, and can even be useless in developing the theory, either in relation to particular types of reaction, or to general problems in kinetics and reactivity. To undertake isolated studies unrelated to general problems is like determining particular points on a surface of which we wish to define the form; if the surface is complicated, knowledge about a few points tells us nothing about the form, and only enables us to reject unfounded hypotheses. Only the organized efforts of physical, organic and inorganic chemists directed to elucidating the general problems of mechanism, in relation to basic types of reaction and related reactivity problems, can lead to a decisive advance in chemistry.

Here, as in all other problems, from the fundamental political problems of the struggle for peace onwards, the united forces of the world's scientists are required. I shall be happy if this book is of interest to chemists, even if only slightly so, and if it directs attention to the solution of problems in chemical kinetics and reactivity.

I record my thanks to S. S. Polyak, A. B. Nalbandyan, N. S. Enikolopyan, D. G. Knorre, A. E. Shilov and several others of my colleagues at the Institute of Chemical Physics, and also to A. M. Pravednikov, who have all participated in writing the new chapters and in supplementing the previous chapters for the second edition.

N. SEMENOV.

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PART I

RADICAL REACTIONS

(PROPAGATION AND BRANCHING OF CHAIN REACTIONS)

Chapter 1

UNIRADICAL REACTIVITIES

1. RADICAL REACTIONS: BASIC TYPES

The reactions of univalent free radicals may be divided into three basic classes:

(1) Substitution:

$$\dot{R}_1 + R_2R_3 \rightarrow R_1R_2 + \dot{R}_3$$

where R_1, R_2, and R_3 are atoms or radicals. R_2 is a single atom in the majority of substitution reactions which have so far been studied.

(2) Addition at multiple bonds, or reaction with atoms which have unpaired electrons:

(*a*) $$\dot{R} + A_1{=}A_2 \rightarrow RA_1{-}\dot{A}_2$$

(*b*) $$CO + \dot{C}l \rightarrow O{=}\dot{C}{-}Cl$$

A particular case of (*a*) is a polymerization, initiated by the radical $\dot{R}$:

$$\dot{R} + A_1{=}A_2 \rightarrow RA_1{-}\dot{A}_2$$
$$RA_1{-}\dot{A}_2 + A_1{=}A_2 \rightarrow RA_1{-}A_2{-}A_1{-}\dot{A}_2$$
$$RA_1{-}A_2{-}A_1{-}\dot{A}_2 + A_1{=}A_2 \rightarrow RA_1{-}A_2{-}A_1{-}A_2{-}A_1{-}\dot{A}_2, \text{ etc.}$$

(2′) Decomposition reactions (i.e. the inverse of addition):

(*a*) $$RA_1{-}\dot{A}_2 \rightarrow \dot{R} + A_1{=}A_2$$

(*b*) $$\dot{C}OCl \rightarrow CO + \dot{C}l$$

(3) Isomerization, e.g.:

$$H_2\dot{C}{-}CH_2{-}CH_3 \rightarrow H_3C{-}\dot{C}H{-}CH_3$$

All these elementary reactions, except those of types 2(*b*) and 2′(*b*), involve breaking one of the bonds of the initial molecules, and result in the formation of a new bond.

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The rates of all these processes are given by the formulae:

$$w_1 = a_1 \exp(-\varepsilon_1/RT)[\mathrm{R}] \tag{1}$$

(unimolecular decomposition; isomerization), and

$$w_2 = a_2 \exp(-\varepsilon_2/RT)[\mathrm{R}][\mathrm{M}] \tag{2}$$

(bimolecular reactions; e.g. of radicals with molecules, either by substitution or addition).

The rate constant is a numerical expression of the reactivity of a molecule when its various bonds are subjected to attack by a radical.

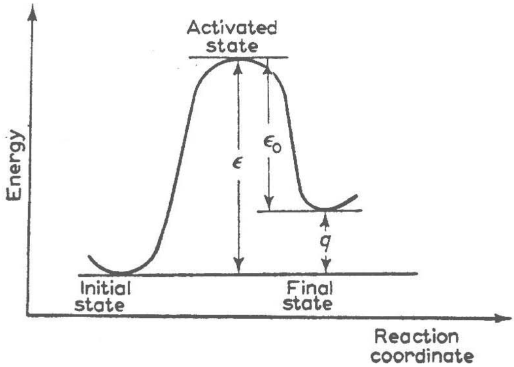


Fig. 1

The value of ε—the activation energy of the elementary process—indicates the minimum energy which the reacting system must possess in order that the reaction may take place. (The system may be a molecule or radical in unimolecular processes, or both the reacting particles in bimolecular processes.)

The state of the system may be represented graphically, taking the "reaction co-ordinate" as abcissa, and the potential energy of the reacting system as ordinate. Then the activation energy will be dependent on the height of the potential barrier that has to be surmounted during the reaction.

If, as is shown in Fig. 1, the reaction is endothermic, then the activation energy ε will be composed of two terms: firstly, ε_0, which is strictly the height of the potential barrier; and, secondly, the difference in energy between the final and initial states, i.e. the absolute value of the heat of reaction, $|q|$:

$$\varepsilon = \varepsilon_0 + |q| \tag{3}$$

If the process is exothermic (such as the reverse reaction to that of Fig. 1), then the activation energy will simply be equal to the height of the potential barrier ε_0. The difference in activation energy between the forward and back reactions is equal to the heat of the forward reaction. The factor a_1 is about 10^{13} sec^{-1} in many unimolecular reactions; this is of the order of molecular vibrational frequencies.

The values of a_1 for molecules and radicals are frequently assumed not to differ widely. In support of this assumption, we have the direct experiments of BUTLER and POLANYI [1], on the initial decomposition of iodides into two free radicals, and also the results of LADACKI and SZWARC [2] on the decomposition of a range of organic compounds; in these reactions, a_1 was found to be about 10^{13} sec^{-1}.

In bimolecular reactions a_2 is often close to the collisional frequency z (between molecules and radicals), i.e. about 10^{-10} cm^3/sec (or 10^{14} cm^3/mole-sec, depending on the unit of concentration used).

In fact, however, not every collision between a radical and a molecule leads to reaction, even if the energy of the colliding particles is sufficient; consequently, $a_2 = fz$, where f is the so-called steric factor ($f < 1$ normally). In most reactions $0{\cdot}1 < f < 1$. Latterly, it has been shown (mainly by STEACIE *et al.* [3, 4, 5]) that f falls to 10^{-3}–10^{-4} in some reactions of hydrocarbon radicals and hydrogen atoms with alkanes. The problem of the f-values in these reactions cannot yet be considered as definitely decided, however. Extensive experimental data on free radicals were presented at the Faraday Society Discussion in September, 1952. The results of different workers were sometimes inconsistent; e.g. according to BERLIE and LE ROY [6], ε is 6·8 kcal*, and $f = 4{\cdot}8 \times 10^{-3}$, in the reaction between atomic hydrogen and ethane. For the same reaction ($D + C_2H_6$) DARWENT and ROBERTS [7] found $\varepsilon = 9$ kcal, and $f = 0{\cdot}6$. We propose to use the latter values, since we can see no special theoretical reason for the occurrence of very small f-values in substitution reactions.†

Addition reactions (radicals or atoms) at double bonds would seem always to have low f-values (10^{-3}–10^{-5}). Numerous experimental results, both direct and indirect, bear this out. Theoretical reasons may be advanced for the small f-values in reactions of this type; these are based on the statistical theory of the activated complex. It is found that, in this case, the activated complex, unlike in substitution reactions, does not decompose and its entropy is lower than that of the initial state. The smallness of f thus follows by analogy with corresponding data for the equilibrium constant in addition reactions: the equilibrium constant can be expressed with a degree of accuracy which is sufficient for this purpose, in the form: $K = A \exp(-Q/RT)$. In equilibria of the type $C_2H_4 + HBr \leftrightharpoons C_2H_5Br$, A is about 10^{27}, being equal to the ratio a_1/a_2 (the a-values for decomposition and addition respectively): $A = 10^{27} = a_1/a_2$. In many reactions, $a \simeq 10^{13}$, so $a_2 \simeq 10^{-14}$; consequently, $f \simeq 10^{-4}$.

---

* For brevity, we use "kcal" to indicate "kilocalories per mole" throughout this book.

† More recently, some further results on substitution reactions have appeared, in which the authors stress the importance of steric factors of 10^{-3}–10^{-4}. The experimental data serve only to determine the a-factors, however, and these may be the product of the steric factors for a number of two-body collisions. The collisional frequency for a radical is calculated from gas-kinetic diameters of similar molecules: this may result in large errors. No theoretical basis for expecting small f-values in substitution reactions has been put forward, except by STEPUKHOVICH [8]: the arguments he uses do not appear very convincing to us, since a number of assumptions, for which there is little justification, are made in calculating the steric factors.

By analogy with molecular additions, the steric factors in radical additions are supposed small.

In the gas phase, at pressures $\simeq$ 1 atm, unimolecular reactions (decomposition or isomerization) proceed considerably more rapidly than bimolecular reactions (substitution or addition), temperature and activation energy being equal. The rates of unimolecular reactions are given by:

$$w_1 \simeq 10^{13} \exp(-\varepsilon_1/RT)c$$

where c is the number of molecules per cubic centimetre; c being about 10^{19} at atmospheric pressure. The rates of bimolecular reactions are given by:

$$w_2 \simeq 10^{-10} \exp(-\varepsilon_2/RT)c^2$$

Then, if $\varepsilon_1 = \varepsilon_2$ $\quad \dfrac{w_1}{w_2} = \dfrac{10^{13}}{10^{-10}c} = \dfrac{10^{13}}{10^{-10} \times 10^{19}} = 10^4$

i.e. under the same conditions, unimolecular reactions are about 10^4 times more rapid than bimolecular ones.

2. EXPERIMENTAL DETERMINATION OF ACTIVATION ENERGIES

The quantity $\exp(-\varepsilon/RT)$ in the expression for the rate constant will now be examined. The magnitude of this factor is determined by the value of ε. The latter quantity is, as we have seen above, equal to the potential barrier height ε_0 in exothermic reactions. When radicals react with molecules, or when radicals decompose, $\varepsilon_0 < 10$ kcal usually; most frequently, it lies in the range 3–6 kcal. Strongly endothermic radical reactions may have much larger activation energies. For instance, the decomposition of alkyl radicals to olefin + H (e.g. $CH_3—CH_2 \rightarrow C_2H_4 + H$) may involve an activation energy of about 40 kcal. These reactions are endothermic, the energy absorbed in the forward reaction being about 38 kcal. Now, according to (3), $\varepsilon_0 = \varepsilon - |q|$, so ε_0 is not great in these reactions, being only about 2 kcal. The reverse (exothermic) reaction—addition of a hydrogen atom at the double bond in olefins—has been found by direct experiment to have a very small activation energy, about 2–4 kcal [7, 9, 10].

The endothermic reaction $Br + H_2 \rightarrow HBr + H$ has an ε of 17·6 kcal: since we have, from (3), $\varepsilon = \varepsilon_0 + |q|$ and $q = -16{\cdot}4$ kcal, $\varepsilon_0 = 1{\cdot}2$ kcal.

Table 1 gives values of ε_0 determined for exothermic reactions of hydrogen atoms with various molecules. In Tables 2, 3, 4, and 5

Table 1. *Heat of reaction and activation energy for some elementary reactions involving hydrogen atoms*

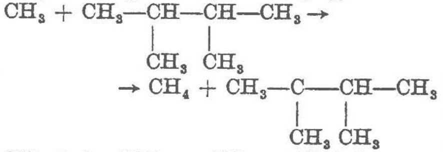
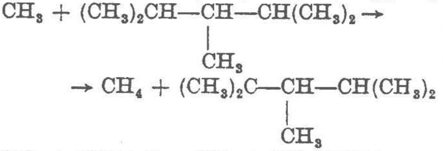
Reaction	q* (kcal)	ε_0 (kcal)	Reference
$H + CH_4 \rightarrow H_2 + CH_3$	+ 2	13	[11]
$H + C_2H_6 \rightarrow H_2 + C_2H_5$	+ 5	9·5	[5]
$H + C_3H_8 \rightarrow H_2 + iso\text{-}C_3H_7$	+ 13	8·5	[5]
$H + C(CH_3)_4 \rightarrow H_2 + CH_2C(CH_3)_3$	+ 4	9·3	[5]
$H + CH_3CHO \rightarrow H_2 + CH_3CO$	+ 18	6	[12]
$H + CCl_4 \rightarrow HCl + CCl_3$	+ 33·5	3·5	[10]
$H + CHCl_3 \rightarrow HCl + CHCl_2$	+ 28	4·5	[10]
$H + CH_2Cl_2 \rightarrow HCl + \dot{C}H_2Cl$	+ 24	6	[10]
$H + CH_3Cl \rightarrow HCl + CH_3$	+ 22	8	[10]
$H + C_2H_5Cl \rightarrow HCl + C_2H_5$	+ 22	8	[10]
$H + C_2H_5Br \rightarrow HBr + C_2H_5$	+ 20	6	[10]
$H + CH_3Br \rightarrow HBr + CH_3$	+ 18	3–7	[10]
$D + CH_4 \rightarrow HD + CH_3$	+ 2	11	[10]
$D + C_2H_6 \rightarrow HD + C_2H_5$	+ 5	9	[7]
$D + C_3H_8 \rightarrow HD + iso\text{-}C_3H_7$	+ 13	7·2	[7]
$D + iso\text{-}C_4H_{10} \rightarrow HD + tert\text{-}C_4H_9$	+ 18	6·3	[7]
$H + D_2 \rightarrow HD + D$	0	6·5	[13]
$D + H_2 \rightarrow HD + H$	0	5	[14]
$H + Cl_2 \rightarrow HCl + Cl$	+ 45	2	[13]
$H + Br_2 \rightarrow HBr + Br$	+ 40	1·2	[13]
$H + I_2 \rightarrow HI + I$	+ 35	0	[13]
$H + HCl \rightarrow H_2 + Cl$	+ 1·1	4·5	[13]
$H + HBr \rightarrow H_2 + Br$	+ 18	1·2	[13]
$H + HI \rightarrow H_2 + I$	+ 33	1·5	[13]

* q is an expression of the thermochemical value of the reaction: for exothermic reactions it will therefore be positive.

Table 2. Heat of reaction and activation energy for some elementary reactions with hydroxyl radicals

Reaction	q (kcal)	ε_0 (kcal)	Reference
$OH + CH_4 \rightarrow H_2O + CH_3$	+ 16	8·5	[15]
$OH + C_2H_6 \rightarrow H_2O + C_2H_5$	+ 19	5·5	[15]
$OH + HCHO \rightarrow H_2O + HCO$	+ 38	0·5	[16]
$OH + CH_3CHO \rightarrow H_2O + CH_3CO$	+ 32	4·0	[16]
$OH + CO \rightarrow CO_2 + H$	+ 26	7·0	[17]

Table 3. Heat of reaction and activation energy for some elementary radical reactions

Reaction	q (kcal)	ε_0 (kcal)	Reference
$CH_3 + CH_4 \rightarrow CH_4 + CH_3$	0	11·2	[3]
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	+ 4	10·4	[3]
$CH_3 + C_4H_{10} \rightarrow CH_4 + \textit{iso}\text{-}C_4H_9$	+ 11·5	8·3	[3]
$CH_3 + C_5H_{12} \rightarrow CH_4 + \textit{iso}\text{-}C_5H_{11}$	+ 13	8·1	[3]
$CH_3 + C_6H_{14} \rightarrow CH_4 + \textit{iso}\text{-}C_6H_{13}$	+ 14	8·1	[3]
 $CH_3 + CH_3\text{—}\underset{CH_3}{\underset{\mid}{CH}}\text{—}\underset{CH_3}{\underset{\mid}{CH}}\text{—}CH_3 \rightarrow CH_4 + CH_3\text{—}\underset{CH_3}{\underset{\mid}{C}}\text{—}\underset{CH_3}{\underset{\mid}{CH}}\text{—}CH_3$	+ 16	6·9–7·8	[3]
$CH_3 + \textit{iso}\text{-}C_4H_{10} \rightarrow CH_4 + (CH_3)_3C$	+ 16	7·6	[3]
$CH_3 + (CH_3)_3CC(CH_3)_3 \rightarrow$ $CH_4 + (CH_3)_3CC(CH_3)_2CH_2$	+ 4	9·5	[3]
 $CH_3 + (CH_3)_2CH\text{—}\underset{CH_3}{\underset{\mid}{CH}}\text{—}CH(CH_3)_2 \rightarrow CH_4 + (CH_3)_2C\text{—}\underset{CH_3}{\underset{\mid}{CH}}\text{—}CH(CH_3)_2$	+ 16	7·9	[3]
$CH_3 + (CH_3)_4C \rightarrow CH_4 + CH_2C(CH_3)_3$	+ 4·0	10·0	[3]
$CH_3 + C_3H_8 \rightarrow CH_4 + \textit{iso}\text{-}C_3H_7$	+ 11·5	8	[10]
$CH_3 + CH_3Cl \rightarrow CH_4 + CH_2Cl$	+ 3·6	9·4	[18]
$CH_3 + CH_2Cl_2 \rightarrow CH_4 + CHCl_2$	+ 7·8	7·2	[18]
$CH_3 + CHCl_3 \rightarrow CH_4 + CCl_3$	+ 12	5·8	[18]
$CH_3 + CH_3Br \rightarrow CH_4 + CH_2Br$	+ 6	10·1	[18]
$CH_3 + CH_2Br_2 \rightarrow CH_4 + CHBr_2$	+ 13·3	8·7	[18]
$CF_3 + CH_4 \rightarrow CF_3H + CH_3$	+ 2	10·3–9·5	[19]
$CF_3 + C_2H_6 \rightarrow CF_3H + C_2H_5$	+ 5	7·5	[19]
$CF_3 + C_3H_8 \rightarrow CF_3H + \textit{iso}\text{-}C_3H_7$	+ 14	6·5	[19]
$CF_3 + n\text{-}C_4H_{10} \rightarrow CF_3H + \textit{iso}\text{-}C_4H_9$	+ 14	5·1	[19]
$CF_3 + \textit{iso}\text{-}C_4H_{10} \rightarrow CF_3H + C(CH_3)_3$	+ 18	4·7	[19]
$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3$	+ 16	6·8	[20]

the activation energies which have been determined for some other radical substitution reactions are given, together with the calculated values for the heats of reaction q.

Table 4. Heat of reaction and activation energy for some elementary reactions with hydrogen or halogen atoms

Reaction	q (kcal)	ε_0 (kcal)	ε (kcal)	Reference
$H + H_2 \rightarrow H_2 + H$ . .	0	6·2 ± 1	—	[13]
$D + D_2 \rightarrow D_2 + D$. . .	0	6·0	—	[13]
$Cl + H_2 \rightarrow HCl + H$ . .	− 1·1	5·6	—	[13]
$Br + H_2 \rightarrow HBr + H$ . .	− 16·4	1·2	17·6	[13]
$F + H_2 \rightarrow HF + H$ . .	+ 31	7·5	—	[13]
$Br + CCl_3Br \rightarrow Br_2 + CCl_3$.	− 4	2·0	(6·0)	[10]
$I + C_2H_4I_2 \rightarrow I_2 + C_2H_4I$.	− 11	*	(12·0)	[21]
$Cl + CHCl_3 \rightarrow HCl + CCl_3$.	+ 13	8·0	—	[10]
$Cl + CH_4 \rightarrow HCl + CH_3$. .	+ 1	6·2	—	[10]
$Cl + C_7H_{16} \rightarrow HCl + C_7H_{15}$.	+ 8	6·0	—	[10]
$Br + CHCl_3 \rightarrow HBr + CCl_3$.	− 6*	4*	10·0	[10]
$Br + CH_3Br \rightarrow HBr + CH_2Br$.	− 12*	3·6*	15·6	[22]
$Br + CH_4 \rightarrow HBr + CH_3$.	− 18*	0* (1·4)	17·8	[22]
$Cl + Br_2 \rightarrow BrCl + Br$ . .	+ 6	0	—	[13]
$Cl + BrCl \rightarrow Cl_2 + Br$ . .	+ 5·7	0	—	[13]

* Indicates that the value given was derived by indirect methods. Unreliable values are indicated by parentheses.

It is very difficult to measure the activation energies of elementary free radical reactions; much more so than for reactions between molecules. Free radicals are unstable, and disappear rapidly by combination, either on the walls of the vessel, or by homogeneous reaction. In consequence, it is very difficult to maintain a constant concentration of free radicals, and to measure it especially in the gas phase.

Free radicals are commonly obtained from electrical discharges in gases, by the action of ultra-violet light, or by pyrolysis of compounds that decompose to give free radicals (such as peroxides). Direct quantitative determination of the free radical concentration is usually extremely difficult, particularly as the concentrations normally encountered are very small indeed. For this reason, the concentrations and rates of reaction are usually deduced from the rates of formation of stable intermediates, or of final products. In addition to the primary reaction between the radical and molecule in question, secondary reactions (between the radicals

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