

METHUEN'S MONOGRAPHS ON
CHEMICAL SUBJECTS

CHAIN REACTIONS

An Introduction

F. S. DAINTON



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*Professor of Physical Chemistry
at the University of Leeds*

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PREFACE

IN 1913 there appeared in the *Zeitschrift für Physikalische Chemie* the classic paper by BODENSTEIN in which the idea that reactions might proceed by a chain of subsidiary reactions was first proposed. Since that date the subject has developed rapidly and is now a well-established branch of reaction kinetics. Despite this, and despite the immense range of chemical reactions which proceed by a chain mechanism, only one book concerned exclusively with the subject has been written. This very useful book, by SEMENOV, was published as long ago as 1935 and for several years there has been a need for a shorter book in the English language in which the emphasis was on the underlying principles, rather than on the hypothetical reaction schemes currently in fashion to account for the detailed properties of individual reactions, and which would include some of the important advances made in the last twenty years. The present volume is an attempt to fill this gap and to provide an introduction to the subject for the university student, either undergraduate or postgraduate, who already has some acquaintance with the general principles of reaction kinetics.

It is the author's hope that the book will not only serve this purpose but also stimulate further reading in the rapidly expanding original literature in this fascinating field of study. For this and other reasons only a few reactions have been discussed as such (in the last two chapters) and these have been chosen solely to illustrate the principles and methods elaborated earlier. Accordingly, the accounts of these reactions are far from exhaustive and do not include all the recent findings. Instead it has been considered preferable to include in the bibliographies some references to review articles in which more recent work is described and which are convenient starting points for further reading.

It is impossible to write so brief a book, involving much compression and arbitrary selection without the inadvertent obtrusion of inaccurate or misleading statements and infelicitous expressions. The author has been saved from many of his original sins both of omission and commission by many friends who from

time to time have kindly read parts of the manuscript. These include Drs. P. G. Ashmore, E. Collinson, J. A. Davies, K. O. Kutschke, P. P. Manning and A. F. Trotman-Dickenson. To them he offers his grateful thanks; they should be dissociated from the many blemishes which the book doubtless still possesses. To his own pupils in the teaching of whom he has learnt much, he also gives grateful acknowledgement.

LIST OF IMPORTANT SYMBOLS

(In order of first appearance)

CHAPTER I

k	= velocity constant
k_{obs}	= observed velocity constant
k_{obs}^0	= the non-exponential term in the Arrhenius equation
E_A	= the observed Arrhenius activation energy
R	= gas constant in k. cal mole ⁻¹ deg. C ⁻¹
T	= temperature on absolute scale
α, β, \dots	= order of reaction with respect to reactants A, B, $\dots, n = \Sigma(\alpha + \beta \dots)$
$t_{\frac{1}{2}}$	= time for 50 per cent chemical reaction to occur
a	= initial concentration
ΔE	= increment in internal energy
Z	= collision rate
k	= Boltzmann constant, ergs deg ⁻¹
μ	= reduced mass in gm
σ	= collision diameter in cm
n	= concentration in molecules c.c. ⁻¹
m	= mass
c	= average velocity of translation
k_{coll}	= velocity constant calculated on collision theory
E	= activation energy defined by equation (1.5)
P	= probability factor defined by equation (1.6)
M	= any substance, usually acting as a 'third body'
R	= reactant molecule
A	= activated reactant molecule
Pr	= product molecule
s	= number of 'square terms'
E_c	= 'classical' activation energy = difference between potential energy of transition state and reactants at absolute zero neglecting zero point energy
$z.p.e.$	= 'zero point' or 'residual' energy = $\frac{1}{2}\Sigma h\nu$
h	= Planck's constant in erg sec.
ν	= vibration frequency (sec ⁻¹)
$+$	= subscript or superscript denoting transition state

CHAPTER I—(contd.)

D	= bond dissociation energy
$E_{\text{calc}}, A_{\text{calc}}$	= energy of activation and frequency factor as defined by equation (I.13)
v	= velocity
F	= partition function
$\prod_r x_R$	= product of r terms of the type x_R
κ	= transmission coefficient
A	= Helmholtz Free Energy
S	= Entropy
p_i	= degeneracy of the i th quantum level
ϵ_i	= energy of the i th quantum level
I	= moment of inertia, gm cm ²
ρ	= rotational symmetry factor

CHAPTER II

P_l	= lower pressure limit to ignition
P_u	= upper pressure limit to ignition
$S.R.$	= slow reaction
B	= energy of activation of branching reaction
π	= the third or 'thermal' explosion limit
n (as a subscript)	= number of monomeric segments in a given polymer molecule
$O.P.$	= osmotic pressure
\bar{M}	= number average molecular weight
c	= concentration
η	= viscosity

CHAPTER III

q	= heat of reaction
m_j^*	= polymer chain containing j monomeric segments and capable of further growth
m_1	= monomer
m_n	= polymer containing n units of monomer

CHAPTER IV

k_p	= rate constant of a propagation reaction
t	= average interval of time between the destruction of a reaction centre in a propagation step and its next reformation
I, F, G, W	= Rate and coefficients defined by equation (IV.5)

CHAPTER IV—(contd.)

τ	= average time between initiation and termination of a chain
$k.c.l.$	= kinetic chain length
k_t	= rate constant of a mutual or quadratic termination reaction
ϕ_1	= quantum yield of the primary act, in initial centres per quantum
I_{abs}	= intensity of actinic light absorbed in quanta per sec. per litre
γ	= quantum yield
D	= diffusion coefficient

CHAPTER V

n	= concentration of reaction centres
θ	= the rate of initiation of reaction chains
f	= the coefficient of linear branching = $f_0 e^{-\frac{B}{RT}}$
F	= the coefficient of quadratic branching
g	= the coefficient of homogeneous linear termination
δ	= the coefficient of homogeneous quadratic termination
x	= space coordinate
d	= diameter of a cylindrical or spherical reaction vessel
\bar{n}	= volume average concentration of centres
α	= average thermal velocity
λ	= average mean free path of centres
\bar{z}	= average number of collisions between propagation steps
$\bar{\Delta}$	= average displacement
$I.P.$	= induction period due solely to the time development of the chain
ϕ	= net linear branching factor
Γ	= the constant in the approximate wall termination rate expression
ϕ'	= net quadratic branching factor
\bar{R}	= average rate under intermittent irradiation
Pr_i, Pr_d	= amounts of product formed during t_i and t_d respectively
t_i	= period of illumination

CHAPTER V—(contd.)

t_d	= period of darkness
R_0	= rate without sector, i.e. continuous light
n_l	= centre concentration at end of light period
n_d	= centre concentration at end of dark period
x	= exponent in equation $R_0 \propto I_{abs}^x$
b	= $t_l/\tau_\delta = t_l(\theta\delta)^{1/2}$
f	= $(t_l + t_d)/t_l$

CHAPTER VI

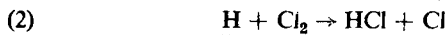
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CHAPTER VII

d (as a subscript)	= depropagation; thus k_d = velocity constant of depropagation
T_c	= ceiling temperature
r_α, r_β	= monomer reactivity ratios = $k_{\alpha\alpha}/k_{\alpha\beta}$ and $k_{\beta\beta}/k_{\beta\alpha}$ respectively

INTRODUCTION

WHEN a chemical reaction proceeds by a chain mechanism most of the reactants are transformed into the products by so-called *propagation* reactions with certain intermediates called chain centres. The essential feature of a propagation reaction is that the chain centre which is destroyed is replaced by a new chain centre. The new chain centre, which may differ chemically from the original centre, is, by definition, able to take part in another propagation reaction or a series of propagation reactions, in the course of which a centre of the first type is regenerated. A simple example of this behaviour is afforded by the two propagation reactions ((1) and (2) below) involved in the photosynthesis of hydrogen chloride gas.



In this reaction the chain centres are chlorine atoms and hydrogen atoms.* The power of chain centres to enter into reactions which result in their regeneration as well as in the conversion of reactants to products enables the propagation reactions to be repeated many times, and, under favourable conditions, thousands of product molecules may be formed from one initial centre which is produced in, or introduced into, the reactant mixture. Such a sequence of reactions is called a reaction chain. Occasionally a centre may be involved in an especially favourable encounter with a reactant and instead of only one new centre being formed, two or more centres may be produced, each of which is capable of propagating a reaction chain. Such a reaction is called a *branching* reaction and will cause the chains to proliferate, the number of centres to increase and the overall reaction to accelerate. Acting in opposition to the propagation and branching reactions are the chain *termination* processes in which centres are converted into species which are incapable of propagating the chain. This removal of centres may occur

* Throughout this book the chain centres in chemical reactions other than addition polymerization will be underlined.

heterogeneously or homogeneously and may involve one or two chain centres. It will be obvious that even when the conditions for chain propagation and branching are optimum, no chains will exist in the system and hence no reaction will occur unless there is some mechanism for the formation of centres which is independent of the propagation and branching reactions. The reactions in which the first centres of reaction chains are created are called the *initiation* reactions, and, as will be seen, may be very diverse in character. A very convenient classification is to call the initiation reaction the primary process or primary act, and to refer to the subsequent reactions of propagation, branching and termination as the secondary processes.

The interplay of the characteristic part processes of initiation, propagation, branching and termination determines the overall kinetic behaviour of a chain reaction. The identification of these constituent reactions, and the determination of their velocity constants are therefore of prime importance and are the major aims of most investigations in this field. The order of presentation of the material in this book has to a large extent been dictated by these facts. Since the individual chain steps are often simple homogeneous uni-, bi-, or ter-molecular processes it has been necessary to review briefly the kinetics of simple homogeneous reactions which may occur in gaseous or liquid systems. Chain reactions often display kinetic properties not shown by non-chain reactions and these differences are next discussed because they may be exploited as experimental criteria for the recognition of a chain mechanism. The same features often impose novel experimental methods of investigation, and a brief account of experimental methods therefore follows. The largest section is concerned with a discussion of the chemical nature of the various types of constituent chemical reactions which may be involved in chain reactions together with an outline of the kinetic consequences of combining these constituent steps in different ways. Finally, a few important groups of reactions are considered in a little greater detail, in order to illustrate the application of the experimental and theoretical methods. This order is not the historical one. No apology is made for this, since the historical approach is not necessarily the approach of greatest didactic value, and in the field of chain reactions the codification of the theoretical treatment achieved by HINSHELWOOD and SEMENOV and their co-workers just over twenty years

ago, has provided an intellectual framework for the student which will enable him to place in correct perspective the vast amount of kinetic data published both before and after this date. It will be clear that the debt of any worker in this subject to these two authors is very considerable.

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CHAPTER I

HOMOGENEOUS REACTIONS WHICH DO NOT INVOLVE CHAINS

THE observed rates of many chemical reactions may often be represented by an expression of the form

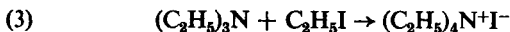
$$\text{rate} = k_{\text{obs}}^{\circ} \cdot e^{\frac{-E_A}{RT}} [A]^{\alpha} [B]^{\beta} \quad \dots \quad (\text{I.1})$$

in which α, β, \dots are the orders of reactions with respect to the reagents A, B, \dots . The individual orders are often small integers and the sum $\Sigma(\alpha + \beta + \dots) = n$ is referred to as the overall order of the reaction. The quantity

$$k_{\text{obs}}^{\circ} \cdot e^{\frac{-E_A}{RT}} = k_{\text{obs}}$$

is called the velocity constant, or specific rate constant and when k_{obs}° is constant over the temperature range of investigation, the reaction obeys the Arrhenius law for the variation of the rate with temperature. E_A is the Arrhenius activation energy in calories mole⁻¹ when R , the gas constant, is expressed in calories mole⁻¹ deg C⁻¹, and T is the absolute temperature.

The distinction between the order, which is an experimentally determined quantity, and the molecularity is important. A reaction is said to be uni-, bi-, or ter-molecular according as the 'activated complex' is constituted from one, two, or three reactant molecules respectively. The exact meaning of the term 'activated complex' will appear later; for the present it suffices to define it as the unstable entity formed from the appropriate number of reactant molecules, which it exceeds in energy content by an amount ΔE^{\ddagger} (see later) and capable of changing into the products without further acquisition of energy. Whilst the overall order and molecularity are often identical, as for example in the bimolecular, second order reaction



this is not always the case and there are many unimolecular processes which under certain conditions are second order. In general, for simple homogeneous reactions, the overall order may exceed but is never less than the molecularity.

The values of the order, k_{obs} and E_a are obtained from measurements of the change of reactant concentration with time, for different initial concentrations of reactants at each of several temperatures. The experimental means employed to determine instantaneous values of the reagent concentration are diverse, often involving titration for solution reactions, manometric and gas analysis measurements for gas reactions, and where more convenient, the measurement of some physical property (e.g. thermal conductivity, optical density, viscosity, volume etc.) of the reaction mixture which is related to its composition. In very fast reactions it may be desirable to use flow methods. Details of these methods may be found in references 1 and 2. The analysis of the data is carried out by three main methods.

(1) The half-life method in which the reciprocal of the time for 50 per cent change ($t_{1/2}$) is plotted against the initial concentration. When all the reactants are initially present in the same concentration (a) and the stoichiometry is suitable, $t_{1/2}$ is inversely proportional to a^{n-1} and hence n and k_{obs} may be evaluated.

(2) The reactant concentration against time curves are frequently linear in the first stages of the reaction and in these cases the tangents to these curves at the origin may be determined with accuracy. n and k can then be calculated from the relation that the initial slopes of these curves are equal to ka^n .

(3) The third main method is to plot an appropriate function of the initial and instantaneous reagent concentrations against time. In practice the order is often known before such plots are made, but this method removes the uncertainty often experienced in methods (1) and (2) of the precise time of starting the reaction.

A plot of $\log_{10} k_{obs}$ against T^{-1} should then give a straight line of slope $= -E_a/2.303R$. However, there are a considerable number of reactions for which the simple Arrhenius Law, i.e. k_{obs} independent of temperature, does not hold and there are a few cases for which the curve $\log_{10} k_{obs}$ against T^{-1} is neither linear nor of negative slope. In certain cases the explanation of such anomalous behaviour is simple, namely, that some of the reactants form an intermediate compound with evolution of heat and that this compound is really one of the reagents, and

combines with another reagent to form the activated complex. k_{obs} measured as the observed rate divided by (reactant concentra-

tion)² will then be proportional to $e^{\frac{-E_A - \Delta E}{RT}}$, in which $-\Delta E$ is the exothermicity of the reaction in which the intermediate compound is formed and E_A is the Arrhenius activation energy of the reaction between this intermediate and another reagent to form the observed product. It is perhaps not without significance that in the termolecular reactions which behave anomalously, two of the three molecules are identical, paramagnetic, and are known to form a dimer⁽³⁾ (and in one reaction, $2NO + O_2 \rightarrow 2NO_2$, all three are paramagnetic).

The Collision Theory. In all bimolecular reactions the rate of reaction cannot exceed the collision rate of the molecules which comprise the activated complex. The simple collision theory leads to the following values of the collision rates (Z) in collisions c.c.⁻¹ sec⁻¹:

(a) Between dissimilar molecules A and B

$${}_AZ_B = \left(\frac{8\pi kT}{\mu} \right)^{\frac{1}{2}} {}_A\sigma_B^2 n_A n_B \quad (1.2)$$

where n_A and n_B are the numbers of A and B molecules per cubic centimetre; μ is the reduced mass in grammes defined by $\mu = m_A m_B / (m_A + m_B)$; k is the Boltzmann constant in ergs deg⁻¹ molecule⁻¹; and ${}_A\sigma_B$ is the mean collision diameter = $(\sigma_A + \sigma_B)/2$ in centimetres, σ_A and σ_B being the collision diameters deduced from the study of transport phenomena in the gases A and B .

(b) Between the same molecules A

$${}_AZ_A = \left(\frac{16\pi kT}{m_A} \right)^{\frac{1}{2}} \sigma_A^2 n_A^2 \quad (1.3)$$

and since the average velocity, c_A of A molecules is $\left(\frac{8kT}{\pi m_A} \right)^{\frac{1}{2}}$ we may write

$${}_AZ_A = \sqrt{2} \pi \sigma_A^2 c_A n_A^2 \quad (1.4)$$

Collision rates calculated by means of equations (1.2) and (1.4) are usually far larger than the observed reaction rates, and this fact combined with the observation that Arrhenius' Law is

generally obeyed for these reactions whereas the collision rate is proportional to the square root of the temperature, leads to the conclusion that only those collisions result in reaction for which the energy of the pair of colliding molecules is at least equal to a value E/N where N is Avogadro's number. Provided only two square terms* are required to define this energy, the fraction of collisions which are fruitful is $e^{\frac{-E}{RT}}$ and hence for a bimolecular reaction showing second order kinetics the velocity constant on the collision theory, k_{coll} , is given by

$$k_{\text{coll}} = Z_0 e^{\frac{-E}{RT}} \quad (1.5)$$

where Z_0 is the collision rate at reactant concentrations of 1 mole litre⁻¹. At 27°C the value of Z_0 for a reaction between molecules of molecular weight = 30 and collision diameter = 3 Å would be 1.4×10^{11} moles litre⁻¹ sec⁻¹. The values of k_{obs} (in litre moles⁻¹ sec⁻¹ units) are frequently of this order of magnitude⁽⁴⁾, but many cases are known for which the agreement between theory and experiment is very poor. It has therefore become the practice to introduce a probability factor P defined by the equation (1.6).

$$k_{\text{obs}} = P \cdot Z_0 \cdot e^{\frac{-E}{RT}} \quad (1.6)$$

In applying this equation it must be remembered that $E = EA - \frac{1}{2}RT$.† The values of P which have been observed cover a wide range. For example $P \ll 1$ for many association reactions such as the dimerization of olefins, the Diels-Alder reaction and the reaction of organic halides with tertiary amines or disulphides to form quaternary ammonium halides or sulphonium halides. It is a weakness of the collision theory that a unified treatment

* For a given co-ordinate, potential and kinetic energy can often each be represented by a term in which the variable is squared, e.g. kinetic energy as $\frac{1}{2}mv^2$ (m = mass, v = velocity), potential energy in a system in which the force is proportional to the displacement, as $\frac{1}{2}fx^2$ (f = force constant, x = displacement). The total energy of molecules, both internal and external, is often the sum of terms of this kind and each such term is called a 'square term'. The number of such terms corresponds to the number of modes of storage of energy.

† From equation (1.1), $EA = RT^2 \frac{d \ln k_{\text{obs}}}{dT}$ and from equation (1.6) since $Z_0 \propto \sqrt{T}$, $E = \frac{RT^2 \frac{d \ln k_{\text{obs}}}{dT}}{\frac{1}{2}} - \frac{1}{2}RT$

of the wide range of the observed P values does not seem to be possible. Instead, additional hypotheses must be employed such as the necessity for the collisional process to satisfy special configurational or steric conditions often peculiar to individual reactions and not readily amenable to quantitative treatment.

Bimolecular reactions in solution present further problems. In order to apply the collision theory, a model of solutions must be assumed. A common assumption is that the dissolved reagents behave just as they would do in the gas phase at the same temperature and concentration. Some support for this view is provided by the fact that certain reactions proceed at the same rate in the gas phase as in solution in certain so-called 'inert' solvents, which are usually non-polar liquids like carbon tetrachloride and cyclohexane. The reactions mentioned in the previous paragraph are in this category. On the other hand, there are also some reactions of which the velocity constants are greatly different in the gas phase and in solution and many others which, although they cannot be investigated in the gas phase, proceed at very different rates in different solvents. Analysis of the data reveals that both E and Z may be influenced by the solvent, and some classification of these influences is possible. Generally speaking it is more convenient and illuminating to consider these reactions in the light of the transition state theory.

There are relatively few genuine third order reactions, and the first difficulty which is encountered in trying to give a satisfactory account of these reactions on the collision theory basis is the difficulty of deriving a satisfactory formula for the collision rate. It is usual to regard a ternary collision as occurring when the third molecule strikes a pair of molecules which may be deemed to be in binary collision. The ternary collision rate is then the binary collision rate between the collision pairs and single molecules. To complete the calculation the instantaneous concentration of the collision pairs must be known, which in turn requires a knowledge of the time during which two colliding molecules may be regarded as constituting a collision pair. A crude treatment is to equate this time to the period for which the two molecules of the collision pair are in such close proximity that a third molecule cannot pass freely between them; the time is then roughly equal to the mean collision diameter divided by the average relative velocity. More refined methods have been described, e.g. by TOLMAN, all leading to approximately the same