

E.F.CALDIN

**FAST
REACTIONS
IN
SOLUTION**

Fast Reactions in Solution

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Preface

Research on fast reactions in solution has developed enormously in the last fifteen years; novel techniques have been developed, and numerous reactions which would once have been called 'instantaneous' have been investigated in detail. In writing this survey, I have had in mind both the general reader who wants an outline of the field, and the research worker seeking a solution to a particular problem. I have tried to give a readable account, intelligible to senior undergraduates, of the principles and main achievements of the various methods, and also to give the researcher the information he wants on the scope and peculiarities of each technique.

Chapter 1 includes a preliminary survey of the methods, which are summarized in a table on pages 8-9. Chapters 2 to 11 outline the methods in turn and summarize their applications; these chapters are self-contained as far as possible, and cross-referenced. Chapter 12 takes up some general problems in the mechanisms and energetics of reaction.

The text was written in the main by January 1963, except the last chapter which was written six months later; the whole was revised up to August 1963. References have been included to the chapters on fast reactions in the second edition of *Investigation of Rates and Mechanisms of Reactions*, part II, edited by Friess, Lewis and Weissberger (Interscience, 1963); but this book appeared too late for me to make use of it in preparing my own.

My warmest thanks are due to the colleagues and friends who have helped me by commenting on the several chapters and in other ways; in alphabetical order they are Messrs J. Albery (chapter 9), J. Andrae (4, 5), N. Atherton (10), P. Ayscough (10), R. P. Bell (1, 2, 9, 12), E. J. Bowen (8), T. M. Connor (11), M. Fleischmann (9),

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Leeds
September 1963

E. F. C.

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CHAPTER 1

Introduction

Historical and general introduction

For many years after the earliest investigation in 1850^[1] the rates of chemical reactions in solution were studied by simple methods. The reaction was initiated by mixing the reagent solutions, and its progress was followed by titrating samples, or making measurements of some physical property, after various intervals of time. The time required for mixing and for observation had to be short compared with the half-time of the reaction. Consequently, the fastest reactions that could be measured had half-times of minutes, or at least seconds. Many reactions, especially those of ions, were immeasurably fast, and their mechanisms could not be kinetically investigated.

The situation is now entirely altered. The first major advance was the introduction of the continuous-flow method by Hartridge and Roughton in 1923.^[2] This made possible the study of reactions with half-times of a few milliseconds—a reduction of the order of 10^3 or 10^4 compared with conventional methods. The limiting factor was the rate of mixing. In the years that followed, the method was steadily developed, and was applied to reactions of haemoglobin and enzymes, but it was not at once widely taken up. During the 1930's several papers appeared on fluorescence quenching, and on the photostationary state, by which very high rates could be measured; there were also some investigations at low temperatures. These were the only special techniques that had been developed by 1939 for fast reactions in solution.

By 1954, however, when the Faraday Society held a discussion on the study of fast reactions, a whole range of techniques had

[1] *Wilhelmy, Pogg. Ann.* 1850, 81, 413.

[2] Hartridge and Roughton, *Proc. Roy. Soc., A*, 1923, 104, 376; cf. p. 29.

emerged.^[3] Some of these were developments of flow methods which made them simpler and more widely applicable. Others were radically different, in that the reaction was not initiated by mixing. Some, such as the temperature-jump and flash techniques, made use of oscillographic fast-recording gear. In others, such as the fluorescence and ultrasonic-absorption methods, a steady state was achieved, which could be observed at leisure. Others exploited the special properties of electron-spin resonance and nuclear magnetic resonance. In 1959 an international conference on fast reactions in solution held at Hahnenklee in Germany^[4] showed that these new methods were being systematically used and had produced results of great interest. Rate constants can now be measured over the whole range from those accessible to conventional techniques right up to the highest values conceivable on current theories, when every encounter between reactant molecules is effective. The accessible time-range has been extended by something like ten powers of ten.

New fields of research have been opened up by these advances in technique. On the one hand, the mechanisms of reactions formerly labelled 'instantaneous', whether organic or inorganic, can be investigated, and a rich diversity of behaviour has been revealed. There is a mass of new information, on a great variety of reaction types, including proton-transfers, hydrogen-bonding, electron-transfers, complex-formations, enzyme reactions, inversions of configuration, and reactions of free radicals and of triplet states. On the other hand, the physicochemical study of rate processes in general and their energetics has been promoted, especially by studies of reactions that have low activation energies and are subject to diffusion control.

The meaning of 'fast'. The term 'fast reaction' is relative, imprecise, and ambiguous, but it is none the less serviceable. In its primary sense, it means a reaction that is fast relative to the time

[3] Papers on most of these techniques are to be found in *Discuss. Faraday Soc.* 1954, 17, 114-234. (The earlier part of this discussion, pp. 1-113, relates to fast reactions in gases).

[4] The papers read at this conference were published in *Z. Elektrochem.* 1960, 64, 1-204.

required for mixing and observation by conventional methods. A reaction with a half-time of a second or less would certainly be fast according to this criterion, though the borderline would depend on the experimental details. But a second-order reaction may have a very high rate constant under ordinary conditions and yet take place comparatively slowly if the concentrations are low enough; the highest second-order rate constant accessible by a given method depends as much on the sensitivity of the technique to low concentrations of reagent as on the least time-interval that it can resolve. Moreover, reactions that are fast at room temperature may become amenable to conventional measuring techniques if the temperature is lowered. In a loose sense, therefore, the term 'fast reaction' may be used to include reactions which would be too fast for normal methods if conducted at 'ordinary' temperatures and concentrations. These remarks are not intended as precise definitions; they serve only to indicate in a preliminary way the range of rates for which the methods described in this book are needed.

This range may now be considered more quantitatively. When conventional methods are used, rate measurements cannot be made accurately on reactions with half-times much less than 10 sec. Several of the new techniques can measure half-times down to 10^{-7} sec, and some of them to 10^{-9} sec. The range of first-order rate constants amenable to these techniques is from about 1 sec^{-1} to 10^9 sec^{-1} , so that the accessible range has been extended by about ten powers of ten.^[5] The corresponding range of second-order rate constants depends on the concentration at which the minimum half-time can be measured. Values up to 10^{10} or $10^{11} \text{ l mole}^{-1} \text{ sec}^{-1}$ have been determined by several techniques, and the range extends down to meet the 'conventional' range, for which the maximum may be taken somewhat arbitrarily as around $1 \text{ l mole}^{-1} \text{ sec}^{-1}$, which is the value for a half-time of 10 sec measured with concentrations of 0.1 M, or a half-time of 100 sec with concentrations of 0.01 M.

[5] For details see Table 1.1 below (p. 8). The half-time $t_{1/2}$ of a first-order reaction is related to the rate constant k by $kt_{1/2} = \ln 2 \approx 0.7$; for a second-order reaction, with each reactant at concentration a , $t_{1/2}$ is related to the rate constant k' by $k't_{1/2} = 1/a$.

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The range of rate constants accessible only by means of special techniques is greater than the whole of the 'conventional' range. The longest half-time that is commonly convenient to measure is of the order of one day, or 10^5 sec; by measuring initial rates it is possible to extend this by a factor of perhaps 10^2 . The range of first-order rate constants accessible by ordinary methods is thus about 10^{-7} to 10^{-1} sec^{-1} , for second-order rate constants^[6] it is about 10^{-7} to 1.0 $\text{l mole}^{-1}\text{sec}^{-1}$. These ranges are shorter, in powers of ten, than the new ranges whose measurement requires fast-reaction techniques (Fig. 1.1). As there is no evidence that reaction rates are

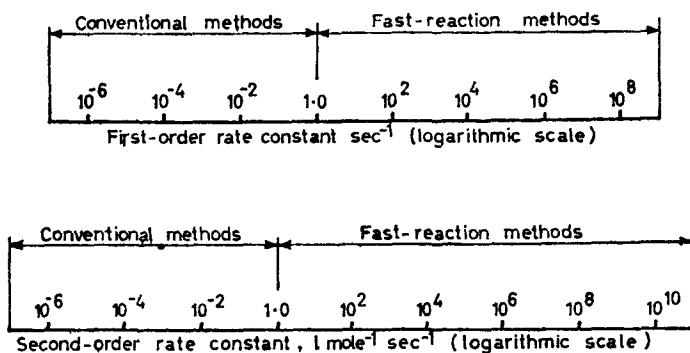


FIG. 1.1. Ranges of rate constants accessible by conventional and by fast-reaction techniques.

grouped in any way, we may expect very many reactions to have rates in the 'fast' range.

Classification of methods for fast reactions in solution

The methods to be surveyed in the following chapters may be grouped according to the general principles which they exemplify. These principles will be fully explained in their appropriate places, and will be only briefly indicated here. The classification that

[6] The great majority of the second-order rate constants recorded in *Tables of Chemical Kinetics: Homogeneous Reactions* (N.B.S. Circular 510; 1951) lie in the range 10^{-7} to 1.0 $\text{l mole}^{-1}\text{sec}^{-1}$. The lowest directly-determined value is 5×10^{-10} $\text{l mole}^{-1}\text{sec}^{-1}$.

follows, and the characteristics of each method, are summarized in Table 1.1 below.

(i) The rate is brought by various means into the 'normal' range, where the half-time is long compared with the times required to mix the solutions and take an observation, so that the reaction can be followed by conventional methods. Applications of low concentrations and of low temperatures are examples of such devices (chapter 2).

(ii) The reagent solutions are mixed rapidly, but matters are arranged so that the observations can be taken at leisure, or at least without special fast techniques. The thermal-maximum and quenching methods, which achieve a slight improvement in conventional methods, are among the applications of this principle (chapter 2); the continuous-flow method is another (chapter 3).

(iii) The solutions are mixed rapidly, and the reaction is then followed by fast techniques. The stopped-flow method (chapter 3) uses this principle.

The shortest half-time that can be measured by any of the preceding methods is determined by the least time of mixing, which is about a millisecond. Several principles are available by which mixing can be avoided altogether, as follows.

(iv) If a reversible reaction is initially in equilibrium, and the conditions are then suddenly altered, the reaction proceeds in one direction or the other until the new position of equilibrium is reached. For example, a sudden change of temperature has this effect on the dissociation of a weak acid. The course of the reaction is followed by a fast oscillographic method (chapter 4): A periodic change of temperature can also be effected, by means of ultrasonic waves; when the half-time of the reaction is comparable with the period of the disturbance, there is a sharp increase in the power absorbed (chapter 5). These methods make use of small displacements from equilibrium, and are called relaxation methods.

(v) Some reactions can be initiated photochemically; the absorption of radiation usually introduces a considerable change into a system, such as the production of free radicals. In some instances a single powerful flash can be used, and the reaction is

followed by a fast oscillographic technique (chapter 6). With the lower intensities usually used in photochemical work, other methods must be adopted, such as the rotating-sector technique, which has been applied especially to polymerization reactions (chapter 7).

(vi) When a substance is fluorescent in solution, the excited molecules have a certain mean lifetime before they emit light; this can be determined, and is of the order of 10^{-8} sec. If a substance is added which reacts rapidly with these excited molecules, so that an appreciable number of them are destroyed before emission can take place, the fluorescence intensity is reduced. From the relation between intensity and concentration, the rate constant of the reaction can be found.

(vii) Polarographic and other electrochemical processes can be arranged in which, for example, a current which would normally be controlled by the rate of diffusion of some species is affected also by the rate at which that species is produced by a reaction in solution (Chapter 9). The principle is analogous to that of the fluorescence methods (vi), in that the reaction is combined with another rate process occurring in the solution.

(viii) Fast reactions can alter the properties of systems of spinning magnetic particles, whether electrons or nuclei. Methods for determining reaction rates can be based upon electron-spin resonance (also called paramagnetic resonance) and upon nuclear magnetic resonance (chapters 10 and 11).

Reaction half-times and rate constants accessible by the various methods

The reaction half-times and rate constants accessible by the various methods are indicated, as regards order of magnitude, in Table 1.1. The smallest half-times, about 10^{-9} sec, have been detected by the ultrasonic, fluorescence, and e.s.r. methods; next come the temperature-jump and electric-impulse methods (10^{-7} – 10^{-6} sec), and the flash method (10^{-5} sec). Some typical time-intervals for molecular and atomic processes are given for comparison in the Appendix, Table 13.1 (p. 293).

The upper limit for first-order rate constants that can be observed

by a given method is approximately the reciprocal of the least half-time that can be measured. For a second-order reaction, however, as we have noticed, the upper limit depends also on the concentration at which the reaction can be observed, and so on the sensitivity of the technique. The maximum second-order constant that has been observed by means of each method is given in Table 1.1. It will be noticed that this is of the order of 10^9 l mole⁻¹sec⁻¹ or over for many of the methods, even though for some of them the least half-time is no lower than 10^{-4} sec. The lower limits are also shown in Table 1.1.

The energetics of very fast reactions

Many reactions with activation energies around 10 kcal mole⁻¹ are fast in the sense that special means are required to measure their rates, but there is nothing exceptional about their energetics. The temperature-variation of their rate constants is represented by the Arrhenius equation $k = A \exp(-E_A/RT)$, and this equation is interpreted in the normal way. The activation energy E_A represents a critical energy without which a collision will not result in reaction. The fraction of effective collisions is $\exp(-E_A/RT)$ and is quite small. The lower the activation energy, the higher is this fraction, and therefore the higher the rate constant at a given temperature. To illustrate the relation, Table 1.2 shows the second-order rate

TABLE 1.2

Second-order rate constants at 25° calculated from $k = 10^{11} \exp(-E_A/RT)$ for various values of E_A , to nearest order of magnitude

E_A (kcal mole ⁻¹)	14	12.5	10	7	4	(0)
k (l mole ⁻¹ sec ⁻¹)	10	10 ²	10 ⁴	10 ⁶	10 ⁸	(10 ¹¹)

constants at 25° calculated from the Arrhenius equation for various values of E_A , with $A = 10^{11}$ l mole⁻¹sec⁻¹ (a representative value for many reactions between an ion and a molecule).

For the fastest reactions, however, this interpretation of the Arrhenius equation breaks down. Quite a few reactions are known

TABLE 1.1

Characteristics of fast-reaction methods

'Min. $t_{1/2}$ ' = minimum reaction half-time in sec.'Max. k ' = maximum observed second-order rate constant in $l \text{ mole}^{-1} \text{ sec}^{-1}$.

Principle	Method	Method requires			Reaction type	Min. $t_{1/2}$ (sec.)	Max. k ($l \text{ m}^{-1} \text{ s}^{-1}$)
		Fast mixing	Fast obsn.	Equilibrium			
(i) Bring rate into 'normal' range	1 Low concentration				General	—	10^{10}
	2 Low temperature				General	—	—
	3 k_f from Kk_b			*	General	—	10^{11}
(ii) Fast mixing, not fast observation	4 Competition			*	General	—	10^8
	5 Thermal maximum	*			General	0.2	10^3
	6 Quenching	*			General	0.05	10^3
	7 Capacity flow	*			General	1	10
	8 Continuous flow	*			General	10^{-3}	10^8
(iii) Fast mixing, fast observation	9 Stopped flow	*	*		General	10^{-3}	10^8
	10 Accelerated flow	*	*		General	10^{-3}	10^7
	11 Baffle	*	*		General	10^{-3}	10^2
(iv) Shift of equilibrium; relaxation	12 Temperature-jump		*	*	General	10^{-6}	10^{11}
	13 Pressure-jump		*	*	General	10^{-4}	10^3
(v) Initiation by irradiation	14 Electric impulse		*	*	Ionic	10^{-7}	10^{11}
	15 Ultrasonics		*	*	General	10^{-9}	10^{11}
(vi) Combine with another rate process	16 Flash		*	*	Light-sensitive system	10^{-5}	10^{10}
	17 Rotating sector, etc.		*	*	Photochem. initiation	10^{-3}	10^{10}
(vii) Magnetic spin resonance	18 Fluorescence			*	Fluorescent reagent	10^{-9}	10^{11}
	19 Electrochemical			*	Ionizable reagent	10^{-4}	$> 10^{11}$
	20 E.s.r.			*	Free radicals	10^{-10}	10^{10}
	21 N.m.r. (proton)			*	Various	10^{-4}	10^{11}