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REVIEW ON RATE OF CHEMICAL REACTIONS IN TERMS OF FLASH PHOTOLYSIS AND LASER PUMP PROBE TECHNIQUES

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ABSTRACT

The rate of a reaction is defined in terms of the rates with which the products are formed and the reactants (the reacting substances) are consumed. For chemical systems, it is usual to deal with the concentrations of substances, which is defined as the amount of substance per unit volume. The rate can then be defined as the concentration of a substance that is consumed or produced in unit time. Sometimes it is more convenient to express rates as numbers of molecules formed or consumed in unit time. Transition-state theory also called activated-complex theory or theory of absolute reaction rates, treatment of chemical reactions, and other processes regard them as proceeding by a continuous change in the relative positions and potential energies of the constituent atoms and molecules. On the reaction path between the initial and final arrangements of atoms or molecules, there exists an intermediate configuration at which the potential energy has a maximum value. On the other hand flash photolysis has the advantage that because reactants are produced from well-mixed precursors, there is no mixing time to reduce the time resolution of the technique. The kinetic behavior of an ordinary chemical reaction is conventionally studied in the first instance by determining how the reaction rate is influenced by certain external factors such as the concentrations of the reacting substances, the temperature, and sometimes the pressure.

Keywords: chemical system, probe techniques etc .

I. INTRODUCTION

For a reaction in which two substances A and B react with each other, it is sometimes found that the reaction rate is proportional to the concentration of A, represented by [A], and to the concentration of B, or [B]. In that case, the reaction is said to be a second-order reaction; it is first-order in [A] and first-order in [B]. In such a case the reaction rate v can be expressed as $v = k[A][B]$, where k is a constant, known as the rate constant for the reaction. In flash photolysis, a reaction is initiated by a pulse of light (the 'flash') that dissociates a suitable precursor molecule in the reaction mixture to produce a reactive species, thereby initiating reaction. The concentration of the reactive species is then monitored as a function of time, usually spectroscopically using absorption spectroscopy or fluorescence techniques. For studying extremely fast reactions, such as some of the electron transfer processes involved in photosynthesis, laser pulses as short as a few tens of femtoseconds (1 fs = 10⁻¹⁵ s) may be used.

Also, because the reactants are generated and monitored in the centre of the reaction cell, there are no wall reactions to worry about as there are in-flow methods. Flash photolysis has the advantage that because reactants are produced from well-mixed precursors, there is no mixing time to reduce the time resolution of the technique.

II. MATERIALS AND METHODS

Pulse radiolysis is a variation of flash photolysis in which a short pulse of high-energy electrons (10⁻⁹ to 10⁻⁶ s in duration) is passed through the sample to initiate the reaction.

For very fast processes, the 'pump-probe' technique is often used, in which pulsed lasers are employed both to initiate the reaction (the 'pump') and to detect the products via a pulsed spectroscopic technique (the 'probe'). The time separation between the two pulses can be varied either electronically or with an optical delay line down to a resolution of around 10 femtoseconds

We see that the rate at which the concentrations relax to their new equilibrium values is determined by the sum of the two new rate constants. The new equilibrium constant is given by the ratio of the two rate constants, $K =$

k_f/k_r , so together a measurement of the rate of relaxation and the equilibrium constant allows the individual reaction rate constants for the forward and reverse reaction to be determined.

The details of the kinetic equations change for more complicated reactions, but the basic principle of the technique remains the same.

The method does have some major drawbacks, not least of which is the fact that the rapid heating is not selective for a particular molecules, and is likely to lead to at least partial dissociation of all of the species in the 'reactants' chamber. This leads to a complicated mixture of reactive species and often a large number of reactions occurring in addition to the reaction under study. Modelling the kinetics of such a system is often challenging, to say the least.

M	$E_{act}/\text{kJ mol}^{-1}$ $293 \leq T \leq 523$ K
He	-1.7
Ar	-5.4
O ₂	-6.3
CO ₂	-7.3
C ₆ H ₆	-7.1
C ₆ H ₅ CH ₃	-11.3
C ₂ H ₅ I	-10.0
C ₆ H ₅ (CH ₃) ₃	-17.2
I ₂	-18.4

Observed Values of increasing one atom – Flash Photolysis Values obtained from Chemical Kinetics experiment in different ions and group of ions

Experiment	[BrO ₃ ⁻] (M)	[Br ⁻] (M)	[H ⁺] (M)	Initial Rate (M/s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

Also, because each signal to noise levels are often low. Compare this with laser pump-probe methods, in which hundreds or even thousands of traces may be averaged to obtain a good signal to noise.

III. RESULTS AND DISCUSSIONS

Two different theoretical approaches to chemical kinetics have led to an understanding of the details of how elementary chemical reactions occur. Both of these are based on the idea of potential-energy surfaces, which are models showing how the potential energy of a reaction system varies with certain critical interatomic distances. The course of an elementary reaction is represented by the movement of the system over the potential-energy surface. One theoretical approach to the problem involves studying the region of the potential-energy surface that corresponds to the highest point on the energy barrier that separates the reactants from the products. This approach is relatively simple and leads to explicit general expressions for the reaction rate. The second approach involves considering the dynamics of the motion of the system over the potential-energy surface.

IV. CONCLUSION

Since the activated complexes are in equilibrium, their concentration can be expressed in terms of the concentrations of the reactants. The reaction rate is this concentration multiplied by the frequency with which they form products, which is known from kinetic theory. Despite the approximations involved in transition-state theory, it has been successful in providing insight into how chemical reactions occur and how their rates depend on various factors.

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