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

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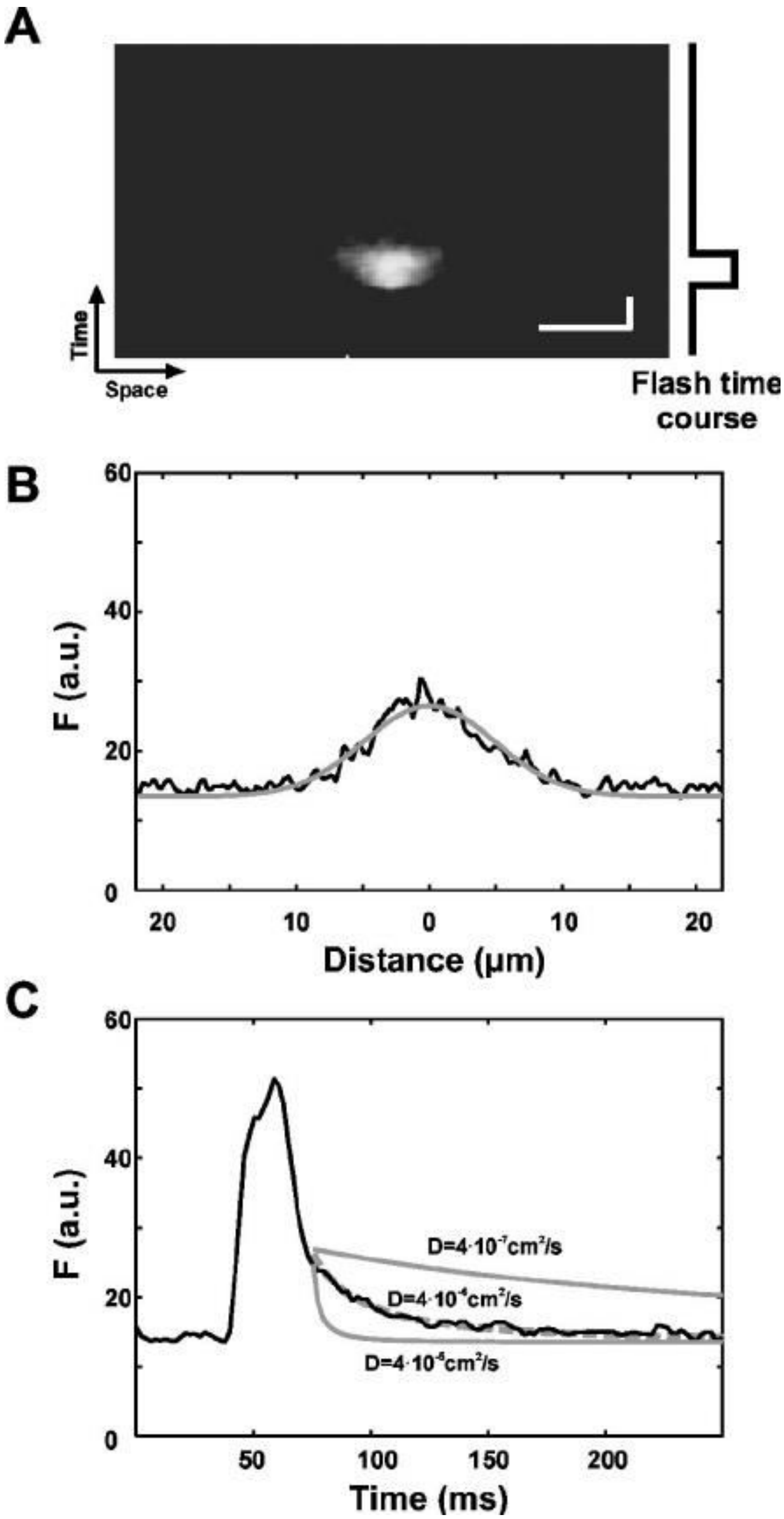
Abstract

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. 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.

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, 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 . The shortest timescale over which reactions may be studied using this technique is determined by the duration of the 'flash'. Originally, the flash was provided by a discharge lamp, with durations in the region of tens of microseconds to several milliseconds. However, in most modern experiments the flash is provided by a laser pulse, typically with a duration of a few nanoseconds (1 ns = 10-9 s). 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.

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. 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.



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

For very fast processes, the ‘pump-probe’ technique is often used, in which pulsed lasers are employed both to initiate 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 = k2f/k2r, 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. 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 good signal to noise.

Observed Values of increasing one atom – Flash Photolysis

M	E_{act}/kJ mol^{-1} 293 ≤ T ≤ 523 K
He	−1.7
Ar	−5.4
O_2	−6.3
CO_2	−7.3
C_6H_6	−7.1
$C_6H_5CH_3$	−11.3
C_2H_5I	−10.0
$C_6H_5(CH_3)_3$	−17.2
I_2	−18.4

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}

Discussion of Result by theories of reaction rates

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-energysurfaces, 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.

Transition-state theory

The idea of a potential-energy surface sprang from the ideas of Dutch physical chemist Jacobus Henricus van ’t Hoff and Swedish physicist Svante August Arrhenius that were put forward to explain the effect of temperature on reaction rates. An important advance was made in 1931 by American chemist Henry Eyring and British chemist Michael Polanyi, who constructed, on the basis of quantum mechanics, a potential-energy surface for the simple reaction $H^{\alpha} + H^{\beta}{-}H^{\gamma} \rightarrow H^{\alpha}{-}H^{\beta}{-}H^{\gamma} \rightarrow H^{\alpha}{-}H^{\beta} + H^{\gamma}$.For convenience the labels α, β, and γ are added as superscripts. When this reaction occurs, an atom H^{α}attacks a hydrogen molecule $H^{\beta}{-}H^{\gamma}$ and abstracts one of the hydrogen atoms from it. As the bond begins to form, the $H^{\beta}{-}H^{\gamma}$ bond becomes more and more extended and finally breaks. Somewhere along the reaction path, there is a particular intermediate state corresponding to the maximum value of the potential energy.

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 an insight into how chemical reactions occur and how their rates depend on various factors.

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