Sprenger's work under their conditions of temperature and pressure; meanwhile the interpretation of Table II is ambiguous.

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Effect of Products on Energy Transfer Rates in Unimolecular Reactions

BY MILTON VOLPE AND HAROLD S. JOHNSTON

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If the products of a unimolecular reaction have an activating efficiency different from the reactant, the observed first-order rate constant k varies with time throughout the course of an experiment. In the low pressure region where the observed rate is the rate of activation, this effect can be analyzed quantitatively. The ratio $k(t)/k_0$ depends on (1) the method of analyzing data, that is, differential slope, single observation, or method of least squares; (2) the relative efficiency for reactants and products, $\bar{R}$; (3) the amount of added inert gas M relative to initial reactant A_0; and (4) the time of observation relative to the mean time of the reaction. Equations are derived for the effect of all of these parameters and methods, and illustrative graphs are given for special cases.

In the low pressure second-order region of a unimolecular reaction the rate is given by[1,2]

$$\text{Rate} = [\text{A}]\sum_{\text{m}}\sum_{\text{i}} a_{\text{mi}}[\text{M}_{\text{m}}] = [\text{A}]\sum_{\text{m}} a_{\text{m}}\,[\text{M}_{\text{m}}] \qquad (1)$$

where i denotes quantum states of the reactant which lead to reaction and m denotes identity of the gases present. For the reaction

$$\text{A} \longrightarrow r\text{B} + s\text{C} \qquad (2)$$

in the presence of one inert foreign gas M the rate constant expression is

$$k = a_1[\text{A}] + a_2[\text{B}] + a_3[\text{C}] + a_4[\text{M}] \qquad (3)$$

By virtue of stoichiometry this expression reduces to

$$k = a_1[\text{A}_0] + a_4[\text{M}] - (a_1 - ra_2 - sa_3)([\text{A}_0] - [\text{A}]) \qquad (4)$$

where subscript zero refers to initial conditions. By definition[1] the relative efficiency is $R_{\text{m}} = a_{\text{m}}/a_1$. The "relative efficiency of products" is defined as

$$\bar{R} = ra_2/a_1 + sa_3/a_1 \qquad (5)$$

The initial equivalent concentration[1] is

$$[\mathbf{M}_0] = [\text{A}_0] + \text{R}_4[\text{M}] \qquad (6)$$

Therefore the rate constant expression is

$$k = a_1[\mathbf{M}_0] - a_1(1 - \bar{R})([\text{A}_0] - [\text{A}]) \qquad (7)$$

The differential rate constant at the initial time is

$$k_0 = a_1[\text{A}_0] + a_4[\text{M}] = a_1[\mathbf{M}_0] \qquad (8)$$

The rate constant will have this value throughout the course of the reaction if and only if the products have the same efficiency as the reactants, or $\bar{R} = 1$. If $\bar{R}$ is not unity, the reaction will not be strictly first order throughout a run; the rate expression is

$$-(1/[\text{A}])\,\text{d}[\text{A}]/\text{d}t = k_0 - a_1(1 - \bar{R})([\text{A}_0] - [\text{A}]) \qquad (9)$$

which is of the form

$$-\text{d}[\text{A}]/\text{d}t = \alpha[\text{A}] + \beta[\text{A}]^2 \qquad (10)$$

where $\alpha = k_0 - \beta[\text{A}_0]$ and $\beta = a_1(1 - R)$. Equation 10 may be integrated to give

$$y = \log\frac{[\text{A}_0]}{[\text{A}]} = \alpha t + \log\left\{1 + \beta\frac{[\text{A}_0]}{\alpha}(1 - e^{-\alpha t})\right\} \qquad (11)$$

For $0.5 < \bar{R} < 2$, or for wider limits in the presence of a foreign gas, eq. 11 may be expanded to any desired degree of approximation.

$$\frac{y}{k_0t} = 1 - \frac{k_0t}{2}(1 - \bar{R})\frac{[\text{A}_0]}{[\mathbf{M}]} + \frac{(k_0t)^2}{6}(1 \quad \bar{R})\frac{[\text{A}_0]}{[\mathbf{M}]}\left\{1 - (1 - \bar{R})\frac{[\text{A}_0]}{[\mathbf{M}]}\right\} - \cdots \qquad (12)$$

If one has a series of observations y_{j} at a series of equally spaced times t_{j} and if these observations are forced by the method of least squares to fit the first-order relation

$$y = kt + l \qquad (13)$$

the value of the slope is given by solving for k from

$$\begin{aligned}\Sigma y_{\text{j}} &= k\Sigma t_{\text{j}} + nl\\ \Sigma y_{\text{j}}\, t_{\text{j}} &= k\Sigma t_{\text{j}}^2 + l\Sigma t_{\text{j}}\end{aligned} \qquad (14)$$

where n is the number of observations. By substitution of $t = x + \bar{t}$ where $\bar{t}$ is the middle time, one obtains

$$k = \Sigma x_{\text{j}}y_{\text{j}}/\Sigma x_{\text{j}}^2 \qquad (15)$$

By substitution of (12) into (15) and use of the fact that summation of odd powers of x is zero by symmetry, one finds, to an excellent approximation, that eq. 12 is recovered with t replaced by $t/2$ or $\bar{t}$.

For experimental data of extremely high precision one may use the differential method of finding rate constants, and the effect of products is given directly by eq. 9. For runs in which a single observation is made of [A] and t in addition to $[\text{A}_0]$, the error introduced by efficiency of products as measured by the ratio k/k_0 is given by eq. 12. For runs in which numerous equally spaced observations are made from 0 to t and for which a first-order constant is obtained by least squares, the ratio k/k_0 is also given by eq. 12 with t replaced by $\bar{t}$ or $t/2$. Further discussion is restricted to the case using least squares.

The ratio of the apparent slope k to the initial slope k_0 is a dimensionless number characterizing the error introduced by unequal efficiency of react-

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(1) Terminology used in this article is that of H. S. Johnston, THIS JOURNAL, **75**, 1567 (1953); *J. Chem. Phys.*, **20**, 1103 (1952).

(2) M. Volpe and H. S. Johnston, THIS JOURNAL, **78**, 3903 (1956).

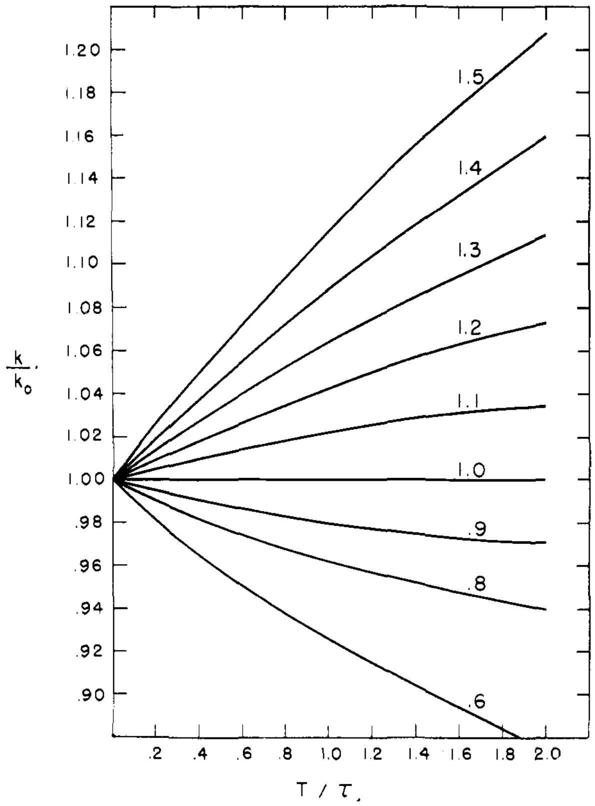

Fig. 1.—The first-order rate constant k observed by least-squares fit of the data observed from 0 to T divided by the zero time rate constant k_0 as a function of $\bar{R}$ from 0.6 to 1.5 and as a function of observation time T divided by mean life τ of the reaction.

ants and products. This error depends on three dimensionless parameters, $\bar{R}$, $[A_0]/[M]$ and t/τ, where τ is the mean life of the reaction, that is, the time for $[A_0]/[A]$ to equal e. The effect of $\bar{R}$ and t/τ is presented in Fig. 1. The effect of $[A_0]/[M]$ and t/τ for $\bar{R} = 1.41$, the value found for nitryl chloride,[2] is presented in Fig. 2. For the series of studies made with nitryl chloride the observation time was the same for each foreign gas, and thus low values of $[A_0]/[M]$ are coupled with high values of t/τ. Accordingly the error introduced by efficiency of products was a uniform 5%, or $k/k_0 = 1.05$, for all foreign gases studied. The detailed values of k/k_0 are listed in the preceding article.[2]

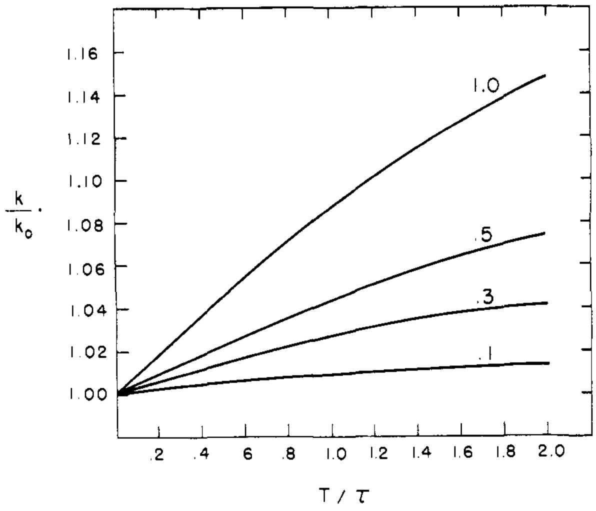

Fig. 2.—The ratio k/k_0 for various ratios of foreign gas pressure to reactant gas pressure, $[A_0]/[M]$, and as a function of T/τ for $\bar{R} = 1.4$, the value observed for nitryl chloride.

It should be emphasized that visual inspection of plots of log $[A_0]/[A]$ against t for curvature is a weak criterion for the effect of efficiency of products. For data with a slight amount of experimental error, such a plot will have a slope differing significantly from k_0 long before curvature is apparent.

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The Precise Manometric Determination of Rate Data[1]

BY DELOS F. DETAR

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Procedures are given for obtaining manometric rate data of high precision. By appropriate statistical treatment of these data it is possible to examine a reaction rigorously over its full course for compliance with a given rate expression.

Although manometric measurements have often been used for obtaining reaction rate data, most applications have been to reactions of assumed simple order. Either for want of precision of the data or more commonly for want of suitable techniques of interpretation the use of the manometric methods with complex reactions has been only moderately successful. In the course of a study of reactions of diazonium salts we have had occasion to reinvestigate methods of obtaining manometric data of high precision. In order fully to utilize this precision it has been necessary to apply statistical methods to the data. The use of such statistical methods should be helpful with rate data obtained by all techniques, for these methods make it possible to examine a reaction rigorously for compliance with a given rate expression.

[1] Supported in part by a grant from the National Science Foundation NSF G439 and in part by a grant from the Research Committee of the University of South Carolina.