

(CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF SOUTHERN CALIFORNIA)

A Simple Dilatometric Method for the Determination of Rate Constants of Chain Reactions. I¹

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RECEIVED JUNE 6, 1958

A simple dilatometric method for the determination of rate constants in chain reactions is described. The method is based on the solution of the simultaneous differential equations for chemical reaction and heat flow which together govern the change in liquid volume during the non-stationary phase of a photo-sensitized reaction. Applying the solution to the decay period, following a photostationary period of reaction, one finds the equation $\Phi - 1 = BA_0e^{-\kappa t} + BA_1e^{-k_1 t}$ valid for time $t > 1/\kappa$ when termination is a 2nd-order process. κ is the experimentally determined cooling constant for the dilatometer, k_1 is proportional to the ratio of termination to propagation rate constants, k_t/k_p , Φ is the ratio of the rate of change of meniscus during the decay period to that during the "dark" period. The constants B , A_0 and A_1 are all independently determinable from the physical properties of the reaction system and the value of k_1 . Rate data give independent values for (BA_0) , (BA_1) and k_1 which latter then yields the ratio k_t/k_p . The ratio can be used with independent determinations of the ratio k_t/k_p^2 to yield the individual rate constants. Solutions are also given for the cases of negligible dark rate and of first-order termination. Results obtained with acrylate polymerizations are found to be in good agreement with other methods for measuring k_t/k_p . The range of usefulness of the method is examined and it is shown that it is applicable to the study of most of the known chain reactions in liquids, in addition to polymerizations.

Introduction

The kinetic study of complex systems of consecutive reactions seldom gives reaction rate constants for individual steps. Instead the usual data obtained are values for products or complex ratios of the rate constants of several steps. In the special case of chain reaction systems, application of the quasi-stationary state hypothesis permits the estimation of the quantity $(k_i/k_t)^{1/2} k_p$ where the rate constants refer, respectively, to the initiation, termination and propagation steps. In the case when the termination reaction is the reverse reaction to initiation, (e.g., as in gas phase brominations), the ratio $k_i/k_t = K_{eq}$, the equilibrium constant of these reactions. This may usually be evaluated separately. In this case k_p is separately evaluable. Methods for the independent determination of k_i , k_t and k_p must in general devolve on independent studies which are concerned with the kinetic observation of the non-stationary phase of the reaction, i.e., that part of the reaction in which the chain carriers are building up or decaying.

Two methods are in general use for the study of these non-stationary state regimes. The most widely used is the technique of "intermittent illumination" or the "rotating sector."³ This is a powerful technique of fairly general application. It is, however, circumscribed by the algebraic difficulty of translating data into rate constants,⁴ and by the absolute limitation that the propagation and termination steps must have different orders with respect to concentration of chain carriers.

The second technique is the use of photostationary states⁵ or of "flash photolysis"^{6,7} to observe the initiation and termination steps independently.

This is somewhat restricted in application and cannot be considered to have general utility.

In the present paper we shall discuss a third technique of observation of the non-stationary state which seems to be of quite wide application and for which the apparatus turns out to be quite simple. This is in contrast to those methods which require adiabatic conditions, or are applicable only to polymerization reactions.⁸⁻¹⁴ In addition its utility does not depend on any necessary relation of kinetic orders in a reaction scheme, so that it can complement the rotating sector as a kinetic tool.

The method involves the dilatometric study of the non-stationary state of a photo-sensitized chain reaction. The use of dilatometers for such studies has been limited by (a) the need for elaborate recording equipment when the non-stationary state time intervals were short, and (b) the absorption or liberation of heat by the reaction causing non-isothermal conditions which created serious errors in relating the observed volume changes to rate constants.¹²

Neglect of the thermal state of the system is reason to question the results obtained in studies of non-stationary systems either by direct observation or using the sector technique. In stationary state systems where emphasis is placed on data obtained in the initial period of the reaction, neglecting the approach to stationary conditions of the thermal state may cause considerable errors.

We have succeeded in the present instance in solving the coupled differential equations relating volume and temperature change to reaction rate in the non-stationary state region, thus making possible more accurate calculation of rate constants from dilatometric studies. The same investigation also makes possible the estimation of the error made in the assumption that the initial

(1) This work was supported by a grant from the Goodyear Tire and Rubber Co., Akron, Ohio.

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(3) See, for example, G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter VII.

(4) This severely restricts the accuracy not only of rate constants but also of derived data such as energies of activation and frequency factors.

(5) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 907 (1936).

(6) I. M. Christie, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc. (London)* **216A**, 152 (1953).

(7) G. Porter, *ibid.*, **200A**, 284 (1950).

(8) N. Grassie and H. W. Melville, *ibid.*, **207A**, 285 (1951).

(9) C. M. Burrell, T. G. Majury and H. W. Melville, *ibid.*, **205A**, 309 (1951).

(10) T. G. Majury and H. W. Melville, *ibid.*, **205A**, 313, 496 (1951).

(11) W. I. Bengough and H. W. Melville, *ibid.*, **225A**, 330 (1954); **230A**, 429 (1955).

(12) W. I. Bengough, *Trans. Faraday Soc.*, **53**, 1346 (1957), **54**, 54 (1958).

(13) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc. (London)*, **193A**, 309 (1948).

(14) G. Dixon-Lewis, *ibid.*, **198A**, 510 (1949).

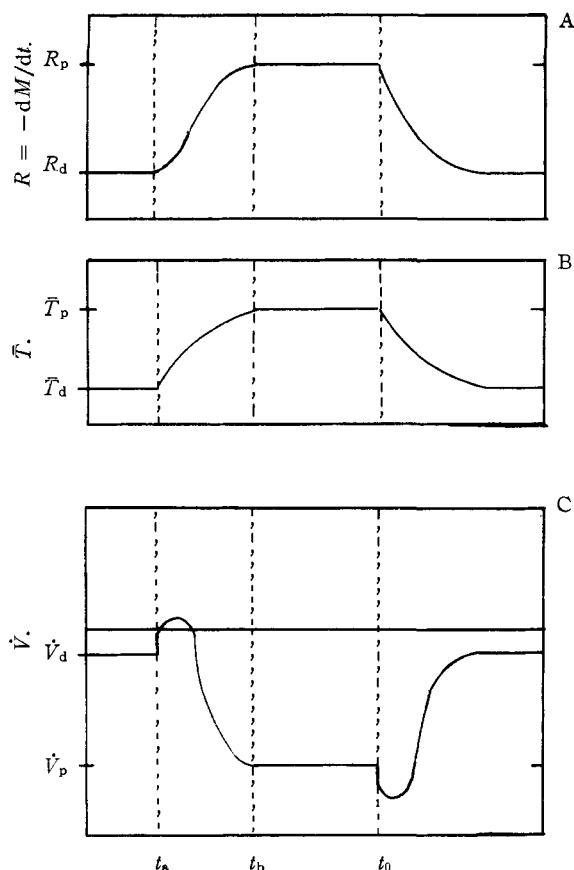


Fig. 1.—A, rate of reaction; B, average temperature; C, rate of volume change in the establishment and decay of a photostationary state of an exothermic chain reaction for which $\Delta V < 0$.

regime of a non-stationary state reaction is adiabatic. While we have applied the method to a number of studies of polymerization reactions, we shall report the experimental work in a subsequent paper. In the present publication are set forth only those results of general interest.

B. Description of the Dilatometer System.—Consider a reaction system, contained in a dilatometer and undergoing chain reaction of monomer at a "dark rate" R_d . This rate can be considered quasi-stationary and small in comparison to the maximum photo-rate to be established, though not necessarily negligibly small. The units of rate shall be fixed with respect to monomer concentration, hence $R = -dM/dt$, moles/l. sec. At some time, t_a , a light is switched on, and within a period of time ending at t_b , a new photostationary rate of reaction, R_p , is achieved. This is allowed to proceed to a time t_0 , when the light is switched off and the photostationary state decays to a new dark rate, R_d' . If the amount of reaction during the photostationary period has been sufficiently small, the conversion of both monomer and photoinitiator (if present) will be small and it is a reasonably good approximation to assume that $R_d' = R_d$.

The sequence of rates is shown in Fig. 1, curve A. Curve B shows the variation of the temperature T averaged with respect to volume, on the same time scale. The thermostat temperature is

taken as reference zero. The meniscus serves to measure the rate of reaction and the temperature change.

If the over-all reaction is accompanied by a diminution of volume, at constant temperature, the volume will decrease as monomer is consumed and at low conversion the rate of change of meniscus level will be proportional to $\dot{V} = dV/dt$. This is proportional to $R = dM/dt$. Thus \dot{V} will be negative and its behavior in the hypothetical experiment is shown in Fig. 1, curve C. There are two transient phenomena immediately following t_a and t_0 . The first of these which can cause \dot{V} to become zero and even positive happens just as the light is turned on and is due to the increased temperature of the system. As will be shown, there are two independent contributions to this transient, one from the increased heat evolution of the reaction and the other from the physical absorption of light energy and its conversion into heat. At time t_0 , when the light is turned off, the loss in heat input results in a cooling and an apparent discontinuous increase in the negative value of \dot{V} . We have observed experimentally both these transients.

C. Mathematical Model of the System.

The two equations to be solved simultaneously are those for the kinetic changes and for the heat flow. Let us assume for convenience that the termination reaction is second order in radical concentration C . Then the equation governing the radical concentration is

$$dC/dt = R_{id} + \phi I_a - k_t C^2 \quad (1)$$

where R_{id} is the specific rate of radical formation in the dark, ϕI_a is the specific rate at which the absorbed light I_a initiates radical centers and k_t is the specific rate constant for the termination reaction.¹⁵

In what follows we shall assume that R_{id} , ϕI_a and k_t are constant during the time of a single experiment carried out to low conversion.

Since the easiest non-stationary state period to examine is that following t_0 , *i.e.*, after the light has been switched off, we shall solve equation 1 when I_a is zero. The solution during this period is

$$X = \frac{C}{C_d} = \frac{(X_p + 1) + (X_p - 1)e^{-k_1 t}}{(X_p + 1) - (X_p - 1)e^{-k_1 t}} = 1 + \frac{2e^{-k_1 t}}{\left(\frac{X_p + 1}{X_p - 1}\right) - e^{-k_1 t}} \quad (2)$$

where C_d is the stationary concentration of radical centers during the dark period, C_p is the same during the light period, X_p is C_p/C_d , and k_1 is $2K_t C_d = 2(R_{id} k_t)^{1/2}$. The values

$$C_d = \left(\frac{R_{id}}{k_t}\right)^{1/2} \text{ and } C_p = [(R_{id} + \phi I_a)/k_t]^{1/2}$$

are obtained as stationary state solutions of equation 1.

(15) According to the general kinetic nomenclature this equation should contain the term $2k_t C^2$. In order to avoid confusion with the definition of the termination rate constant as is currently used in the field of polymer reactions, we have adopted the convention whereby the integer 2 is incorporated into the constant.

For long chains, the rate of monomer disappearance is given by

$$-dM/dt = k_p MC \quad (3)$$

The substitution of C from equation 2 leads to an equation which can be solved explicitly for M . However, at low conversion we can consider M constant over a single run, and set

$$R = -dM/dt \sim k_p [MC_d] X = R_d X \quad (4)$$

where the quantity inside the brackets is considered constant and the X is given by equation 2. X in equation 2 may then be replaced by the observable dimensionless parameter R/R_d , the rate of polymerization relative to the rate during the dark period. The special case when the dark rate is negligibly small will be considered separately in the Appendix.

The equation for the change of temperature T is given by

$$\frac{\partial T}{\partial t} = \frac{K}{\sigma \rho} \nabla^2 T + \vec{V} \cdot \nabla T + \frac{RH + E}{\sigma \rho} \quad (5)$$

where K is the coefficient of thermal conductivity of the system, ρ is the density, σ the specific heat, \vec{V} is the local vector convection velocity, H is the heat of polymerization per mole of monomer which is assumed to be constant, while E is the specific rate of conversion of absorbed light energy into heat. ($E = 0$ except during the irradiation when it is assumed to be constant.)

Since the dilatometer measures total volume which is proportional to the space-average temperature in the vessel, we are not concerned with the space variation of T , but only its space average, \bar{T} . Multiplying both sides of equation 5 by $d\tau$ the volume element, and integrating over the entire volume leads to a much simpler equation for the average temperature, \bar{T}

$$\frac{\partial \bar{T}}{\partial t} = -\frac{K \cdot S}{V \sigma \rho} \left(\frac{\partial T}{\partial r} \right)_{s_0} + \frac{\bar{R} \cdot H + E}{\sigma \rho} \quad (6)$$

where S is the surface area of the vessel, V the volume and $(\partial T/\partial r)_s$ is the temperature gradient at the surface of the dilatometer. The convection term has vanished since there is no component of flow through the surface. \bar{R} is the space average rate of reaction.

Now we may assume that the surface temperature gradient will be proportional to (\bar{T}/γ_0) where γ_0 is the average radius of the vessel. Equation 6 can be written as

$$\frac{d\bar{T}}{dt} = -\kappa \bar{T} + \frac{RH + E}{\sigma \rho} \quad (7)$$

where the Newtonian cooling constant $\kappa \propto \pi^2 K / \sigma \rho r_0^2$ 16 and \bar{R} and \bar{T} have been replaced by R and T , respectively, for convenience in notation. The approximations made will be discussed in the Appendix.

The general solution of equation 7 is obtained at once by quadrature, since $\exp(\kappa\tau)$ is an integrating factor for the equation. For time $t \geq t_0 = 0$ (*i.e.*, during the post-irradiation period) the result is

(16) S. W. Benson, *J. Chem. Phys.*, **22**, 46 (1954), has shown that for a sphere with no convection $\kappa = \pi^2 K / \sigma \rho r_0^2$ so that the constant of proportionality is approximately 3.3.

$$T = T_0 e^{-\kappa t} + \frac{H}{\sigma \rho} e^{-\kappa t} \int_0^t R e^{\kappa t} dt \quad (8)$$

where the photostationary solution T_0 at time t_0 is given by

$$T_0 = \frac{R_p \cdot H + E}{\sigma \rho \kappa} \equiv T_p \quad (9)$$

At times sufficiently long that stationary dark rate has been re-established, we find from equation 7 the stationary solution

$$T \xrightarrow[t \gg 0]{} T_d = \frac{R_d H}{\sigma \rho \kappa} \quad (10)$$

If now we substitute $R = R_d X$ with X given by equation 2, we can make a series expansion of the denominator of equation 2 and integrate equation 8 term by term to obtain

$$\begin{aligned} \frac{T}{T_d} &= \frac{T_p}{T_d} e^{-\kappa t} + \kappa e^{-\kappa t} \int_0^t X e^{\kappa t} dt \\ &= 1 + \left(\frac{T_p}{T_d} - 1 \right) e^{-\kappa t} + 2 \left(\frac{X_p - 1}{X_p + 1} \right) \left(\frac{e^{-\kappa t} - e^{-\kappa_1 t}}{1 - \kappa_1/\kappa} \right) + \\ &\quad 2 \left(\frac{X_p - 1}{X_p + 1} \right)^2 \left(\frac{e^{-2\kappa_1 t} - e^{-\kappa t}}{1 - 2\kappa_1/\kappa} \right) + \dots + \\ &\quad 2 \left(\frac{X_p - 1}{X_p + 1} \right)^n \left(\frac{e^{-n\kappa_1 t} - e^{-\kappa t}}{1 - n\kappa_1/\kappa} \right) + \dots \quad (11) \end{aligned}$$

If fortuitously the ratio κ_1/κ is an integer, the series in equation 11 terminates in a logarithmic term. As written, each term in the series is positive with a single maximum value given by

$$M \left[\frac{e^{-n\kappa_1 t} - e^{-\kappa t}}{1 - n\kappa_1/\kappa} \right] \text{ occurs at } t = \ln \left(\frac{\kappa}{n\kappa_1} \right) = \frac{x \ln \left(\frac{x}{n} \right)}{n\kappa \left(\frac{x}{n} - 1 \right)}$$

and has the value

$$\frac{1}{\left(\frac{x}{n} \right)^{1 - \frac{x}{n}}} \text{ where } x = \frac{\kappa}{\kappa_1} \quad (12)$$

It can be shown that this maximum value is always less than unity. In the special case that $\kappa = \kappa_1$, the solution becomes

$$\begin{aligned} \frac{T}{T_d} &= 1 + \left[\frac{T_p}{T_d} + 2 \left(\frac{X_p - 1}{X_p + 1} \right) \kappa t - 1 \right] e^{-\kappa t} + \\ &\quad 2 \left(\frac{X_p - 1}{X_p + 1} \right) e^{-\kappa t} \ln \left[\frac{(X_p + 1) - (X_p - 1)e^{-\kappa t}}{2} \right] \quad (13) \end{aligned}$$

The cooling constant κ can be varied within quite large limits by varying the dimensions and shape of the dilatometer. The radical decay constant κ_1 is also a disposable experimental parameter. It is adjustable over a smaller experimental range by choosing different dark rates, varying the concentration of photosensitizer, temperature or solvent. It is thus possible to bring the ratio $x = \kappa/\kappa_1$ into a convenient range, even to unity.

D. The Dilatometer Equation.—The relative rates of volume change of the dilatometer, $dV/V_0 dt = \dot{V}/V_0$, will be proportional to the rate of change of the meniscus level if the capillary is of uniform bore.

If ΔV_M represents the difference in partial molar volumes of monomer and polymer (per monomer unit), at the experimental conditions of temperature, pressure and composition, then the relationship between rate of monomer disap-

pearance and relative volume change is given by $\dot{V}/V_0 = \gamma\dot{M}$ where γ may be determined from the densities and concentrations of monomer and polymer. For most polymer systems \dot{V} and \dot{M} are negative and γ is positive.

There will be a further contribution to \dot{V} arising from the temperature changes during the non-stationary periods of the reaction. If α is the coefficient of expansion of the liquid, $1/V_0(dV/dT)$, then the equation for \dot{V}/V_0 becomes

$$\dot{V}/V_0 = \gamma\dot{M} + \alpha\dot{T} - \alpha_2\dot{T}_2 \quad (14)$$

where $\alpha_2\dot{T}_2$ represents the rate of volume change of the vessel and

$$\dot{V}/V_0 \sim \gamma\dot{M} + \alpha\dot{T}$$

since $\alpha_2\dot{T}_2$ is negligible in comparison with $\alpha\dot{T}$.

On substituting for \dot{M} from equation 4 and \dot{T} from equation 7 when $E = 0$ the equation for the post-irradiation period becomes

$$\dot{V}/V_0 = -\gamma R_d X - \alpha\kappa \left(T - \frac{RH}{\kappa\sigma\rho} \right) \quad (15)$$

$$\frac{\dot{V}}{V_0} = -\gamma R_d X - \alpha\kappa T_d \left(\frac{T}{T_d} - X \right) \quad (16)$$

During the stationary periods, either dark or light, \dot{T} is zero, so that

$$\frac{\dot{V}_p}{V_0} = -\gamma R_p \quad \text{and} \quad \frac{\dot{V}_d}{V_0} = -\gamma R_d \quad (17)$$

If we express the rates of volume change in terms of the dimensionless parameter $\Phi = V/\dot{V}_d$, then equation 16 becomes

$$\Phi = X + \frac{\alpha\kappa T_d}{\gamma R_d} \left(\frac{T}{T_d} - X \right) = X + B \left(\frac{T}{T_d} - X \right) \quad (18)$$

where B has been set $= \alpha\kappa T_d/\gamma R_d = \alpha H/\gamma\sigma\rho$.

On substitution of the value of X from equation 2 and T/T_d from equation 11, we obtain

$$\begin{aligned} \frac{\Phi - 1}{B} &= \left(\frac{T_p}{T_d} - 1 \right) e^{-\kappa t} - \\ 2 \left(\frac{X_p - 1}{X_p + 1} \right) &\left[e^{-k_1 t} \left(1 - \frac{1}{B} \right) - \frac{(e^{-k_1 t} - e^{-\kappa t})}{1 - k_1/\kappa} \right] - \dots - \\ 2 \left(\frac{X_p - 1}{X_p + 1} \right)^n &\left[e^{-nk_1 t} \left(1 - \frac{1}{B} \right) - \right. \\ &\left. \frac{(e^{-nk_1 t} - e^{-\kappa t})}{1 - nk_1/\kappa} \right] - \dots \quad (19) \end{aligned}$$

as the dilatometer equation.

By collecting the coefficients of similar exponents, the result may be written as

$$\frac{\Phi - 1}{B} = A_0 e^{-\kappa t} + A_1 e^{-k_1 t} + A_2 e^{-2k_1 t} + \dots + A_n e^{-nk_1 t} + \dots \quad (20)$$

where the coefficients are given by, $x = \kappa/k_1$

$$A_0 = -1 + \frac{T_p}{T_d} - 2 \sum_{n=1}^{\infty} \left[\left(\frac{X_p - 1}{X_p + 1} \right)^n / \left(1 - \frac{n}{x} \right) \right]$$

$$A_n = -2 \left(\frac{X_p - 1}{X_p + 1} \right)^n \left[-\frac{1}{B} + \frac{1}{1 - (x/n)} \right] \quad (20a)$$

Upon examination, equation 19 or 20 is seen to be composed of a series of exponents which fall off very rapidly with time. At long times, near the end of the post-irradiation period, only the first two

terms of the series are important, and the equation becomes

$$\frac{\Phi - 1}{B} \xrightarrow[t \gg 0]{} A_0 e^{-\kappa t} + A_1 e^{-k_1 t} \quad (21)$$

This is the most convenient region in which to fit data to the expression.

E. Application of the Dilatometer Equation.—Of the terms in equation 19 Φ and $X_p = R_p/R_d = \Phi_p$ are directly observable in any experiment as a function of time. The parameters k_1 , the decay rate of the radicals, B , κ , the Newtonian cooling constant of the system, the ratio T_p/T_d are so far undetermined. Of these four parameters, B and κ are measurable in separate experiments. We have found it convenient to measure the cooling constant directly, before and after a kinetic run, by immersing the dilatometer in a bath of temperature about 2° higher (or lower) than the thermostat bath. Upon reimmersion in the thermostat the rate of change in level of the meniscus may be measured. A plot of $\log V$ against time is found to be a straight line over many half-lives and over the range of temperature changes to be expected in such a system. This is equivalent to the solution of equation 7 with no reaction. Cooling constants found in this manner showed good agreement with the values predicted from the vessel dimensions and liquid properties.¹²

The constant B can be computed from a knowledge of the molar heat of polymerization H , and the measured density ρ , specific heat of the mixture of components σ and the difference in partial molar volumes γ .¹⁷ In most experimental cases it is usual to derive γ from the densities of monomer and polymer, which upon introduction of the monomer concentration gives a value which is an excellent approximation to γ .

The ratio T_p/T_d differs from Φ_p only because of the degradation of light energy into heat during the illumination. In principle it is possible to use filtered radiation thereby reducing E almost to zero whence $T_p/T_d = \Phi_p$.

It is thus in principle possible to obtain all the parameters of equation 19 but k_1 , which can now be determined by fitting equation 19, 20, 21 to the observed data.

In practice it has been found simplest to apply data late in the post-irradiation period to equation 21 in the form

$$(\Phi - 1)e^{\kappa t} = A_0 B + A_1 B e^{(\kappa - k_1)t} \quad (22)$$

Since the function on the left-hand side of this expression is experimentally measurable, this may be treated as an equation in the three unknowns, $A_0 B$, $A_1 B$ and k_1 . Widely separated points on smoothed plot of \dot{V} against time are used to solve for these three quantities. Once $A_0 B$ has been determined, equation 21 can be put in the form

$$\ln[\Phi - 1 - A_0 B e^{-\kappa t}] = \ln[A_1 B] - k_1 t \quad (23)$$

so that a plot of the function on the left-hand side against time will yield a straight line of slope $-k_1 = -2R_d k_t/[M]k_p$ and intercept $\ln A_1 B$. If required, this value of k_1 can be used to determine

(17) Note also that since B is an experimentally determinable constant (eq. 21), it is possible to use it together with α , γ , ρ and σ to determine H , the heat of reaction.

more accurately the value of A_0B and by successive evaluation of k_1 , a final accurate value may be achieved.

In Fig. 2 are shown some plots of data obtained by the photosensitized polymerization of butyl acrylate under varying conditions. In Fig. 3 are shown the same data plotted in the manner of equation 23. The acrylate systems, because of their relatively slow termination rates, are ideal for such studies.

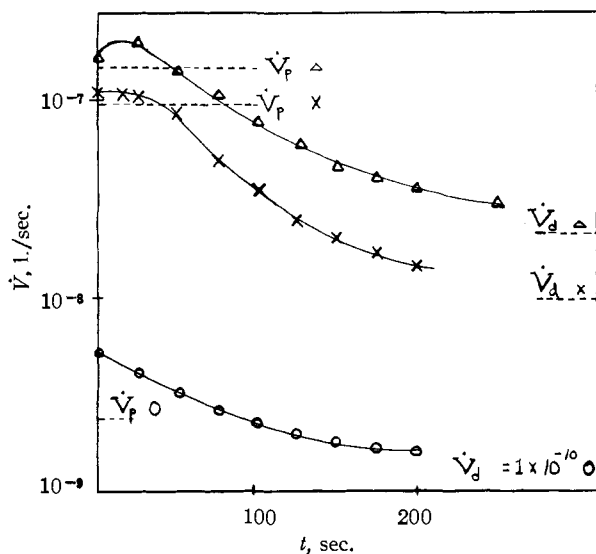


Fig. 2.— \dot{V} against time: Δ , butyl acrylate bulk, R_p 7.97×10^{-4} mole/l./sec.; \times , 2.91 M butyl acrylate in ethyl acetate, R_p 7.50×10^{-4} mole/l./sec., α, α' -azoisobutyronitrile photo-sensitizer; \circ , 0.70 M butyl acrylate in ethyl acetate, R_p 1.35×10^{-5} mole/l./sec., α, α' -azoisobutyronitrile photo-sensitizer.

A measure of the importance of the higher terms of equation 20 will be the deviation of the plot of equation 23 from a straight line at smaller times. In the acrylate systems it has not been found necessary to make allowance for these higher terms.

Once the value of k_1 has been determined from the observation of the transients, from the measured value of R_d the ratio of the propagation and termination rate constants is given by

$$k_p/k_t = 2R_d/[M]k_1 \quad (24)$$

This ratio of rate constants is also given by the sector method. The separate values of k_p and k_t are obtained only if one has an independent measurement of data such as the rate of initiation of chains or the degree of polymerization.

In chain systems not involving polymerization, such as the sensitized oxidation of aldehydes or the bromination of hydrocarbons, the equivalent datum is the mean chain length. From such stationary state experiments the ratio $k_p/k_t^{1/2}$ is obtained. If this ratio be denoted by k_2 , the separate rate constants can be expressed in terms of experimental parameters as

$$k_t = \frac{[M]^2 k_1^2 k_2^2}{4 R_d^2}; \quad k_p = \frac{[M] k_1 k_2^2}{2 R_d} \quad (25)$$

F. The Adiabatic Region.—There are two cases of general interest in which the techniques of the

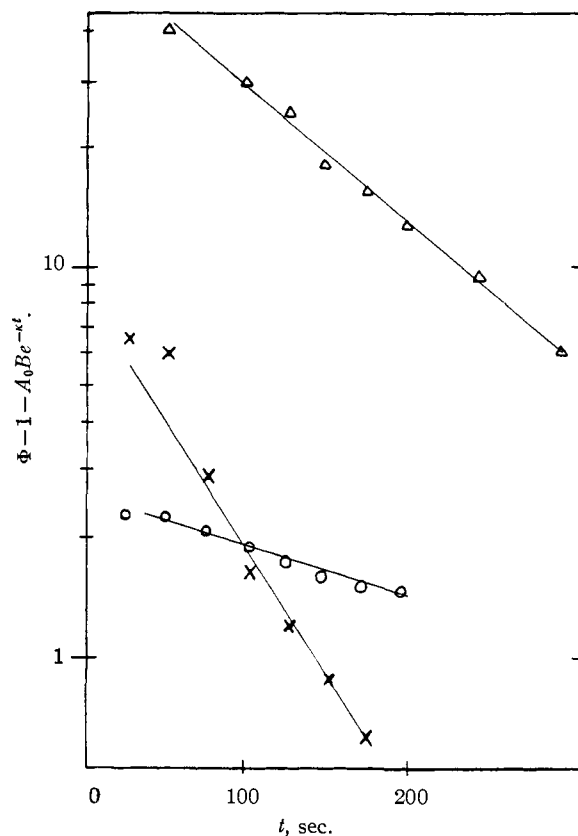


Fig. 3.— $\ln \Phi - 1 - A_0 B e^{-\kappa t}$

present method are applicable. One of these which we have discussed occurs when the rate of cooling is faster than (or of comparable magnitude to) the rate of radical decay. Under these conditions the change in heat flow serves to measure the decay of the chemical reaction. It is the latter which can be considered as the "rate-determining" step in the two stage consecutive reaction in which heat is an "unstable product."

For liquid systems the range of values of κ is governed by the vessel dimensions. Using the formula of Benson for a sphere¹⁰

$$\kappa = \frac{\pi^2 K}{\rho \sigma r_0^2} = \frac{\pi^2 D_r}{r_0^2} \quad (26)$$

where D_r is the coefficient of thermal diffusivity. For non-spherical shapes it is possible to make an approximate correction by increasing the value of κ by the ratio of the surface area of the vessel to that of a sphere of equivalent volume.

For systems in which the radical decay is much faster than the cooling, the reaction system approaches that of an adiabatic chemical reaction, and only data close to the time of cessation of illumination can be of use in the evaluation of rate constants, later data merely being a measure of the cooling rates. At these short times when $e^{-\kappa t} \sim 1$, examination of equation 15

$$-\dot{V}/V_0 = -\gamma R_d X - \alpha \kappa T + \frac{\alpha R H}{\sigma \rho}$$

yields that during ideally adiabatic conditions $\alpha \kappa T$ is zero and

$$\dot{V}/V_0 = R_d X \left(\frac{\alpha H}{\sigma \rho} - \gamma \right) = -\gamma R_d X (1 - B) \quad (27)$$

Thus depending upon whether $(1 - B)$ is negative or positive, expansion or contraction of the dilatometer contents will be observed. From a study of such conditions X and hence k_t/k_p can be directly calculated.¹¹ At a critical monomer concentration given by $\gamma = \alpha H/\sigma \rho$, no adiabatic volume change will be observed. This critical concentration is given by

$$[M] = \frac{\sigma \rho}{\alpha \beta H} \quad (28)$$

where $\beta = (\rho_p - \rho_M)/\rho_p$ and ρ_M and ρ_p are the densities of monomer and polymer, respectively.

Immediately after the light is turned off at time t_0 , and before much radical decay has occurred, the condition that $\kappa t \ll k_1 t \ll 1$ holds and we can make a general term by term expansion of equation 11. The general term takes the form

$$2 \left(\frac{X_p - 1}{X_p + 1} \right)^n \left[\kappa t - \frac{\kappa^2 t^2}{2} \left(1 + \frac{n k_1}{\kappa} \right) + \dots \right] \quad (29)$$

Substituting this in equation 11 and expanding the remaining exponential, we have correct to the first power of t

$$\frac{T}{T_d} = \frac{T_p}{T_d} - \kappa t \left[\frac{T_p}{T_d} - \frac{R_p}{R_d} \right] \quad (30)$$

On substituting for the term in brackets from equations 9 and 10

$$\begin{aligned} T &= T_p - t(E/\rho\sigma) \\ \dot{T} &= -E/\rho\sigma \end{aligned} \quad (31)$$

This result has the significance that when the light is turned off, there will be an immediate cooling of the system due to the loss of heat input E . In the preceding photostationary state the heat input was balanced by a heat flow to the thermostat. This latter is determined by the temperature gradients within the system and is undisturbed shortly after time t_0 . However E is discontinuously reduced to zero at time t_0 and so there is a discontinuity in \dot{T} at t_0 of amount given by equation 31, *viz.*, $E/\rho\sigma$. This discontinuity in \dot{T} is witnessed as a similar phenomenon in \dot{V} and is shown in Fig. 1c and in the experimental plots of Fig. 2. This somewhat paradoxical result predicts an instantaneous cooling rate independent of the cooling constant of the system. This is due to the photostationary heat flow achieved before t_0 .

When E is reduced to zero by the expedient of using filtered light, the first-order terms in t vanish and there is no discontinuity in \dot{T} or \dot{V} .

A Taylor's series expansion of the integral equation 11 then yields, correct to terms in t^2 ($\dot{E} = 0$)

$$\frac{T}{T_d} = \frac{T_p}{T_d} - (X_p^2 - 1) \frac{\kappa k_1}{4} t^2 + \dots \quad (32)$$

Under the same conditions, the Taylor's series for X becomes

$$\begin{aligned} X &= X_p - \frac{k_1}{2} (X_p^2 - 1)t + \\ &\quad \frac{k_1^2}{4} (X_p^2 - 1)(X_p t^2) + \dots \end{aligned} \quad (33)$$

Substituting these values into equation 18, we find

that for the dilatometer rate during the period which is quasi-adiabatic in nature

$$\begin{aligned} \Phi &= X_p - (1 - B) \frac{k_1}{2} (X_p^2 - 1)t + \\ &\quad \frac{k_1^2}{4} (X_p^2 - 1) \left[X_p(B + 1) + \frac{B\kappa}{k_1} \right] t^2 + \dots \end{aligned} \quad (34)$$

When $0 > B > -1$, so that contraction on polymer formation exceeds the expansion due to adiabatic heating, equation 34 predicts a decrease in rate of contraction during the initial period at a rate given approximately by the coefficient of t . For values of X_p of the order of 10 or more when $(X_p - 1) \sim X_p$ equation 34 can be put in the form

$$\dot{V}/\dot{V}_p = 1 - \frac{(1 - B)}{2} [1 - e^{-k_1 \Phi p t}] \quad (35)$$

These last two equations apply only to the decay following the photostationary state. A similar analysis can be made for the non-stationary state occurring after the light is turned on. Here, however, an analysis of heat transfer to the vessel and of the spatial temperature distribution must be made since there is negligible heat flow before illumination.

G. General Limits of Applicability.—The method can be applied to the study of three types of chemical reaction: (a) those characterized by both a specific volume change and an absorption or evolution of heat; (b) those involving only a specific volume change, the heat of the reaction being zero; (c) those involving only the evolution or absorption of heat (with the proviso that a method other than the use of dilatometers can be used to study the stationary state phases of the reaction).

Let us first consider reactions characterized by both a volume change and heat evolution, such as the polymerization reaction.

The principal limitation of the method must be set by the relative values of the cooling and radical decay rates. As has been shown in section F, when the radical decay constant is greater than the cooling constant, any observation of the volume of the system reduces to an examination of a slight deformation of the cooling curve. Under conditions which are not ideally adiabatic, equation 11 simplifies to

$$\begin{aligned} \frac{T}{T_d} &= e^{-\kappa t} \frac{T_p}{T_d} + (1 - e^{-\kappa t}) + \\ &\quad e^{-\kappa t} \frac{2\kappa}{k_1} \sum_{n=1}^{\infty} \frac{1}{n} \left(\frac{X_p - 1}{X_p + 1} \right)^n \end{aligned} \quad (36)$$

since $e^{-k_1 t} \ll e^{-\kappa t}$ and $n k_1/\kappa \ll 1$ for small values of n .

The time-temperature curves differ from the conventional cooling curves only by the small quantities

$$(1 - e^{-\kappa t}) + e^{-\kappa t} \frac{2\kappa}{k_1} \sum_{n=1}^{\infty} \frac{1}{n} \left(\frac{X_p - 1}{X_p + 1} \right)^n$$

At short times this difference is

$$\sim \frac{2\kappa}{k_1} \sum_{n=1}^{\infty} \frac{1}{n} \left(\frac{X_p - 1}{X_p + 1} \right)^n$$

When $k_1 \gg \kappa$ this quantity may cause a reduction in the slope of the cooling curve which may be

impossible to detect experimentally. In systems where the volume change due to cooling is at least of the same order of magnitude as the specific volume change, the term

$$\frac{2\kappa}{k_1} \sum_{n=1}^{\infty} \frac{1}{n} \left(\frac{X_p - 1}{X_p + 1} \right)^n$$

causes a variation of the cooling curve which may be experimentally measured only when $k_1 < 5\kappa$.

Since the coefficient of thermal diffusivity for most liquids, $D_T \sim 1 \times 10^{-3}$ cm.²/sec. within $\pm 50\%$ κ becomes $2.7 \times 10^{-2}/V^{2/3}$ sec.⁻¹. Since the range of useful volumes is from 1 to 100 cc., κ for spheres will lie in the range of about 0.027 to 0.001 sec.⁻¹. This corresponds to cooling half-lives of 25 to 700 seconds. In vessels of higher surface area such as long cylinders or thin disks, κ may be increased by a factor of approximately five. The considerations of the preceding section are therefore limited to systems in which the times of radical decay are of the order of one second or higher, k_1 is therefore restricted to values smaller than unity.

It appears that k_1 can be adjusted to any low value by suitable reduction of the dark rate, R_d . However, when the dark rate is negligible a different mathematical expression must be used—Appendix A. Since the dark rate is usually a thermal reaction, it is difficult to reduce it appreciably without also reducing the photo-rate. It is possible to increase the decay periods by lowering the radical concentration, *i.e.*, studying the reaction at low photo- and dark rates. Under these conditions the limit is set by the sensitivity of the method used to observe volume changes.

For dilatometers immersed in a thermostat bath regulated to $\pm 0.005^\circ$ temperature fluctuations may cause volume changes of approximately $5 \times 10^{-4}\%$. With sensitive dilatometers (*e.g.*, of 10-cc. capacity with a capillary stem of 0.75 mm. diameter) using a travelling microscope to observe the meniscus, it is possible to observe such changes as a meniscus movement of $\pm 1 \times 10^{-2}$ cm. In a conventional thermostat such fluctuations occur with a period of 10–50 seconds. The stationary state phases of the reaction may be studied over such times that effects due to thermostat fluctuations are not a serious source of error. During the non-stationary state, however, such fluctuations become important. It has been found that accurate results can be achieved only by the consideration of a number of experiments in which the volume change immediately after time t_0 is greater than five times the rate of volume change due to random temperature fluctuations. For a reaction such as the addition to a double bond, characterized by a usual volume change of 14% and a heat of reaction of the order of 16 kcal. per mole, a convenient minimum photo rate is thus fixed at 1×10^{-5} mole per liter per second. Combining this minimum rate of reaction with the maximum value of the radical decay constant k_1 yields that only those polymerization reactions for which $k_t/k_p < 1 \times 10^{+6}$ may be studied at all, and only those for which $k_t/k_p < 1 \times 10^{+6}$ may be studied without using photographic recording equipment.

For reactions involving greater volume change and/or greater heat absorption or evolution, cor-

respondingly slower reaction rates may be observed, and larger values of k_t/k_p studied. For reactions and apparatus as described in the preceding sections the temperature and specific volume changes cause effects of very similar magnitude on the volume changes observed during the non-stationary state. Consequently for reactions accompanied by no volume change the minimum convenient photo rate is approximately doubled. Assuming that the stationary state measurements of rate can be made by some method of comparable accuracy, the maximum values of k_t/k_p which can be conveniently studied are thus halved.

It should be noted that the theoretically limiting value of k_t for diffusion controlled reactions is of the order of 10^{10} liter/mole sec. When $k_t/k_p < 10^5$ this yields $k_p > 10^5$ liter/mole sec. as the minimum propagation rate for such fast terminating reactions. If we consider the values of rate constants for non-polymeric, chain reactions¹⁸ we find that at the temperatures where the rates are conveniently measurable, the radical decays may also be studied by the simple dilatometer technique.

APPENDIX A

The Dilatometer Equation in Absence of a Steady Dark Rate.—In absence of a steady dark rate, equation 1 is of the form

$$dC/dt = \phi I_a - k_1 C^2 \quad (A1)$$

which may be solved during the period after illumination to yield

$$R = \frac{R_p}{1 + k_2 t} \quad \text{where } k_2 = \frac{k_t R_p}{k_p M} \quad (A2)$$

The solution of equation 7 in this instance is

$$T = T_p e^{-\kappa t} + \frac{H R_p}{\sigma \rho} e^{-\kappa t} \int_0^t \frac{e^{\kappa t}}{1 + k_2 t} dt \quad (A3)$$

This integral may be represented as the difference of two exponential integrals

$$\frac{e^{-\kappa/k_2}}{k_2} \int_{-\infty}^{\kappa(t + 1/k_2)} \frac{e^V dV}{V} - \frac{e^{-\kappa/k_2}}{k_2} \int_{-\infty}^{\kappa/k_2} \frac{e^V dV}{V} \quad (A4)$$

so that

$$T = T_p e^{-\kappa t} + \frac{H R_p}{\sigma \rho k_2} e^{-\kappa(t + 1/k_2)} \left\{ E_1 \left(\kappa \left(t + \frac{1}{k_2} \right) \right) - E_1 \left(\frac{\kappa}{k_2} \right) \right\} \quad (A5)$$

$$= T_p e^{-\kappa t} + \frac{H R_p}{\sigma \rho k_2} G(t)$$

where

$$G(t) = e^{-\kappa(t + 1/k_2)} \left\{ E_1 \left(\kappa \left(t + \frac{1}{k_2} \right) \right) - E_1 \left(\frac{\kappa}{k_2} \right) \right\}$$

$G(t)$ is less than unity and tends to zero for the times and values of κ/k_2 encountered in the application of this method. From the stationary state solution

$$T_p = \frac{R_p H + E}{\kappa \rho \sigma}$$

and from equation 14

$$\frac{\dot{V}}{V_0} = - \frac{\gamma R_p}{1 + k_2 t} + \frac{R_p \alpha H}{(1 + k_2 t) \rho \sigma} - \frac{\alpha M R_p}{\sigma \rho k_2} G(t) - \frac{\alpha R_p M \kappa e^{-\kappa t}}{\sigma \rho} \quad (A6)$$

Therefore

$$\frac{V}{V_p} = \frac{1 - B}{1 + k_2 t} - B \left(e^{-\kappa t} + \frac{\kappa}{k_2} G(t) \right) \quad (A7)$$

(18) See, for example, compilation of data in A. F. Trotman-Dickenson, "Gas Kinetics," Academic Press, New York, N. Y., 1955.

This can be treated as an equation in the two unknowns k_2 and $G(t)$ and can be solved as before. It is simpler in this case to use the method of successive approximation for k_2 . This allows trial values of $G(t)/k_2$ to be determined, when

$$\frac{\dot{V}}{V_p} = \left[\frac{\dot{V}}{V_p} - Be^{-\kappa t} - \frac{B\kappa}{k_2} G(t) \right]^{-1} = \frac{1}{1-B} + \frac{k_2}{1-B} t \quad (\text{A8})$$

is obtained as the dilatometer equation.

Alternatively it is easy to expand $1/(1+k_2t) = \sum_0^n a_n e^{-nk_2t}$ and obtain a solution very similar to equations 19 and 20. For $k_2t < 2$ this can be approximated with good accuracy by the first three terms.

APPENDIX B

The Dilatometer Equation for First-order Termination.—In this appendix only the case when there is no steady dark reaction will be considered. Equation 1 is of the form $dc/dt = \phi I_a - k_t C$ which may be solved for the period after illumination to yield

$$R/R_p = e^{-k_t t} \quad (\text{B1})$$

The average temperature is expressed by the solution of equation 7 as

$$T = T_p e^{-\kappa t} + \frac{HR_p}{\sigma\rho} e^{-\kappa t} \int_0^t e^{(\kappa - k_t)t} dt \quad (\text{B2})$$

$$= T_p e^{-\kappa t} + \frac{HR_p}{\sigma\rho(\kappa - k_t)} (e^{-k_t t} - e^{-\kappa t}) \quad (\text{B3})$$

so that

$$\frac{\dot{V}}{V_0} = -\gamma R_p e^{-\kappa t} + \frac{\alpha HR_p}{\sigma\rho} e^{-k_t t} - \frac{\alpha HR_p}{\sigma\rho} e^{-\kappa t} - \frac{\alpha HR_p \kappa}{\rho\sigma(\kappa - k_t)} (e^{-k_t t} - e^{-\kappa t}) \quad (\text{B4})$$

and

$$\frac{\dot{V}}{V_p} = e^{-k_t t} \left(1 - B + \frac{\kappa B}{(\kappa - k_t)} \right) + e^{-\kappa t} \left(B - \frac{B\kappa}{(\kappa - k_t)} \right) \quad (\text{B5})$$

is obtained as the dilatometer equation. If $k_t \gg \kappa$

$$\frac{\dot{V}}{V_p} - Be^{-\kappa t} = (1-B)e^{-k_t t}; \ln \left[\frac{\dot{V}}{V_p} - Be^{-\kappa t} \right] = \ln(1-B) - k_t t$$

yields k_t directly.

APPENDIX C

The Quasi-stationary State Approximation for Heat Flow.—The assumption made in equation 6 that $(\partial T/\partial r)_s$ is proportional to T is equivalent to the assumption that the temperature distribution in the system adjusts itself to the changes in heat of reaction by passage through a series of quasi-stationary states. This is very much like the quasi-stationary state assumption of Bodenstein which is used in dealing with the concentrations of free radicals. The conditions for such stationary state approximations have been examined in some detail (S. W. Benson, *J. Chem. Phys.* 20, 1605(1952)). In the present instance, this requirement is satisfied by the condition that $k_1 < \kappa$, i.e., the rate of radical decay and thus of heat liberation be less than the rate of cooling. Under these conditions, the temperature distribution in the vessel will become quasi-stationary in a time of the order of magnitude of $1/\kappa$. In shorter times the system begins to approach adiabatic behavior.

Some quantitative idea of the approximation can be obtained by inspection of T . By definition

$$\bar{T} = \frac{1}{V_0} \int T d\tau \quad (\text{C1})$$

If for simplicity we consider a spherical vessel of radius r_0 , this can be written as

$$\bar{T} = \frac{3}{r_0^3} \int_0^{r_0} T r^2 dr \quad (\text{C2})$$

Integrating by parts this becomes: (note $T = 0$ at $r = r_0$)

$$\bar{T} = e - \frac{1}{r_0^3} \int_0^{r_0} r^3 \left(\frac{\partial T}{\partial r} \right) dr \quad (\text{C3})$$

If the system passes through a succession of quasi-stationary states, then it can be verified that in each of these $(\partial T/\partial r) = b_1 r$; $(\partial T/\partial r)_0 = b_1 r_0$ where b_1 is a function of time but not of r . Under these conditions the assumption that $\bar{T} \propto (\partial T/\partial r)_0$ holds precisely.

Integrating equation C3 by parts again we obtain

$$\bar{T} = -\frac{r_0}{4} \left(\frac{\partial T}{\partial r} \right)_0 + \frac{1}{4 r_0^3} \int_0^{r_0} r^4 \left(\frac{\partial^2 T}{\partial r^2} \right) dr \quad (\text{C4})$$

The presence of r^4 under the integral sign means that most of the contribution to this integral will come from regions of r near r_0 . This is particularly true since in the non-stationary states, when $\partial^2 T/\partial r^2 = \text{constant}$, its largest values will be reached near the surface of the vessel, its deviations from stationarity being expressible in terms of r and higher powers of r . In expressing the deviations from stationarity as $(\partial T/\partial r) = b_1 r = b_2 r^2$, it can be shown that the error of the \bar{T} approximation is of the order of magnitude of $b_2 r_0/5b_1$. When $b_2 r_0/b_1 < 1$, this is not too serious an error. Such a condition is satisfied even when $k_1 = \kappa$.

LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF ARGONNE NATIONAL LABORATORY]

A Kinetic Study of the Reduction of Neptunium(VI) by Hydrogen Peroxide¹

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RECEIVED MAY 10, 1958

The rate of the forward reaction in the stoichiometric equation $2\text{NpO}_2^{+2} + \text{H}_2\text{O}_2 = 2\text{NpO}_2^+ + 2\text{H}^+ + \text{O}_2$ has been studied in a perchloric acid-sodium perchlorate medium. The rate law deduced, $(d\text{NpO}_2^+/dt)_{t=0} = k[\text{H}_2\text{O}_2][\text{NpO}_2^{+2}]/[\text{H}^+]$ ($1 + k' \frac{[\text{NpO}_2^+]}{[\text{NpO}_2^{+2}]}$) has been verified for a wide range of the explicit variables. The effects of temperature, ionic strength and deuterium on the rate have been determined.

In previous studies we have attempted to add to our understanding of the mechanisms of oxidation-reduction reactions involving neptunium ions by comparing the rate laws and energetics observed in deuterium solutions with those observed in solutions where hydrogen is present. Interpretation

(1) Based on work performed under the auspices of the United States Atomic Energy Commission.

of the results is not entirely unambiguous since both reactants are solvated and in addition there is always the possibility of solvent participation in the activated complex.² Use of hydrogen peroxide as the reductant should provide further information

(2) The paper most germane to the present investigation is: J. C. Sullivan, D. Cohen and J. C. Hindman, *THIS JOURNAL*, 79, 3672 (1957).