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

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

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 $dc/dt = \phi I_a - k_tC$ which may be solved for the period after illumination to yield

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

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

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

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

so that

$$\frac{\dot{V}}{\dot{V}_0} = -\gamma R_pe^{-\kappa t} + \frac{\alpha HR_p}{\sigma\rho} e^{-k_tt} - \frac{\alpha HR_p}{\sigma\rho} e^{-\kappa t} - \frac{\alpha HR_p\kappa}{\rho\sigma(\kappa - k_t)} (e^{-k_tt} - e^{-\kappa t}) \quad \text{(B4)}$$

and

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

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

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

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 $\bar{T}$ 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

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

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 $(\partial T/\partial r) = b_1r$; $(\partial T/\partial r)_{r_0} = b_1r_0$ where b_1 is a function of time but not of r. Under these conditions the assumption that $\bar{T} \propto (\partial T/\partial r)_{r_0}$ holds precisely.

Integrating equation C3 by parts again we obtain

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

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 $\partial^2T/\partial r^2$ = 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 stationary as $(\partial T/\partial r) - b_1r = b_2r^2$, it can be shown that the error of the $\bar{T}$ approximation is of the order of magnitude of $b_2r_0/5b_1$. When $b_2r_0/b_1 < 1$, 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 Peroxide[1]

BY A. J. ZIELEN, J. C. SULLIVAN, D. COHEN AND J. C. HINDMAN

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The rate of the forward reaction in the stoichiometric equation $2NpO_2^{+2} + H_2O_2 = 2NpO_2^+ + 2H^+ + O_2$ has been studied in a perchloric acid–sodium perchlorate medium. The rate law deduced, $(dNpO_2^+/dt)_{t=0} = k[H_2O_2][NpO_2^{+2}]/[H^+]\left(1 + k'\frac{[NpO_2^+]}{[NpO_2^{+2}]}\right)$ 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 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

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[1] Based on work performed under the auspices of the United States Atomic Energy Commission.

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

because we can predict, on the basis of our previous results, that any solvent effect on the rate will be minimal.

In addition recent experiments have indicated the desirability of obtaining information on the kinetics of the reaction between Np(VI) and hydrogen peroxide. Although the half-life for α-decay of Np^{237} is quite long (2.2×10^6 years), the radiolysis of solution by the α-particles[3] leads to the slow reduction of Np(VI). Hydrogen peroxide is considered to be a likely intermediate in this reaction.

Experimental

The preparation and standardization of the Np(V), Np(VI), perchloric acid and sodium perchlorate stock solutions have been described previously.[2] Approximately 0.1 *M* hydrogen peroxide stock solutions were made by diluting 90% H_2O_2 (without stabilizer), supplied by Buffalo Electro-Chemical Co., with triple distilled H_2O or D_2O. Peroxide solutions were analyzed the same day that kinetic experiments were run by titration against standard ceric perchlorate using nitro-ferroin indicator.

Stock solution aliquots of the neptunium ions, perchloric acid and sodium perchlorate (to maintain the ionic strength at 3) were added to 5 cm. quartz absorption cells at room temperature. The cells were then placed in the thermostated compartment of a Cary Model 14 MR Recording Spectrophotometer. The hydrogen peroxide was thermostated in a water-bath at the same temperature as the cell compartment.

After temperature equilibrium was attained, the reaction was started by adding an aliquot of peroxide to the absorption cell. The course of the reaction then was followed either by measuring the increase of Np(V) or decrease of Np(VI) as a function of time. The Np(V) analysis was made using the absorption band at 9800 Å. Analysis for the amount of Np(VI) utilized a broad band at 12235 Å. The molar extinction coefficient of Np(VI) at this wave length is *ca.* 45 at 25°. The extinction coefficient varies with spectrophotometer slit width, temperature and ionic strength. The use of this Np(VI) band for analysis is further complicated because of the presence of water absorption bands in this same region. This necessitates the use of large slit widths (1.0–1.4 mm.) and very carefully matched blanks in order to insure the desired precision.

Initial concentrations of neptunium and hydrogen peroxide were calculated on the basis of the stock solution concentrations and the aliquots used. A direct check on the calculated neptunium concentration also was made for a number of runs by radiometric assay. Satisfactory agreement was obtained consistently. Hydrogen ion concentration was determined directly by titrating samples of the solution after the experiment had been completed. Concentrations were corrected for changes in solution volume with temperature.

Results

Within the limits of our experimental error it was found that two moles of Np(V) were produced per mole of H_2O_2 added to a Np(VI) solution when the initial ratio $Np(VI)/H_2O_2 > 2$. It was therefore assumed that the amount of peroxide present at any time during the course of the reaction could be calculated from the initial concentration and the measured concentration of the Np(V) or Np(VI).

It was found that treatment of the rate data in terms of a simple bi-molecular reaction did not adequately describe the results. Since most reactions in solution are not of higher kinetic order than second, it was felt that either a back reaction was involved or that peroxide concentrations could not be calculated as described above. In order to avoid any uncertainty about the peroxide concentration, as well as to facilitate the interpretation of a possibly complex rate law, a graphical limiting slopes technique was employed for the calculation of the rate constants.

The procedure was to plot the observed optical density as a function of time on a large scale. A smooth curve was drawn through the points, and the tangent and normal to this curve at $t = 0$ were measured with a Gerber Derivimeter. To minimize bias, from 4–6 independent determinations of the limiting rate were made for each experiment.[4] The reaction rates are all given with respect to neptunium ions, the concentrations are expressed in moles/liter and the time is in seconds.

Initial Rate Law when $Np(V)_0 = 0$.—A series of 25 experiments was performed at 5° and an ionic strength of 3 to establish the differential rate equation in terms of the initial concentrations of [Np(VI)], $[H_2O_2]$ and $[H^+]$. In these experiments, the initial [Np(V)] concentration was zero. The results, which are presented graphically in Fig. 1, indicate that the observations may be adequately described by the rate law

$$(dNp(V)/dt)_{t=0} = -(dNp(VI)/dt)_{t=0} = R = k[Np(VI)]_0[H_2O_2]_0/[H^+] \quad (1)$$

From these data a mean value of $k = 1.97 \pm 0.07$ sec.$^{-1}$ is obtained.

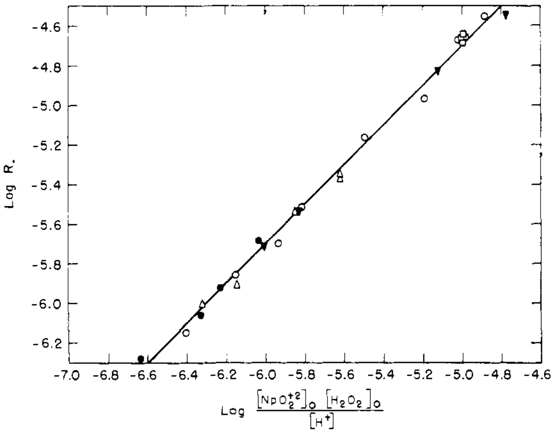

Fig. 1.—Test of initial rate law, $[Np(V)]_0 = 0$, $t = 5°$, $\mu = 3.0$: ○, H_2O_2 and H^+ constant, NpO_2^{++} varied; ●, NpO_2^{++} and H^+ constant, H_2O_2 varied; △, NpO_2^{++} and H_2O_2 constant, H^+ varied; □, NpO_2^{++}, H_2O_2, H^+ constant, difference in monitoring Np(V) and Np(VI) peaks; ▼, miscellaneous.

Effect of Np(V).—Preliminary experiments indicated that the presence of a finite amount of Np(V) markedly decreased the reaction rate. The explicit dependence of the differential rate law with respect to the Np(V) concentration was determined by a series of experiments at 5° and ionic strength of 3 with varying initial ratios of [Np(V)] to [Np(VI)]. The results are presented in

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(3) A. J. Zielen, J. C. Sullivan and D. Cohen, manuscript in preparation.

(4) The Gerber Derivimeter proved to be the most useful instrument we have found to date for the graphical determination of slopes. Given a smooth curve, the instrument allows a slope measurement with an accuracy of 1–2%. A considerably larger uncertainty arises from drawing the "best" smooth curve. We estimated our precision on the limiting slope measurements to be about 10%. Analytically the pooled standard deviation of the 68 kinetic runs covered in this work is 8.8%.

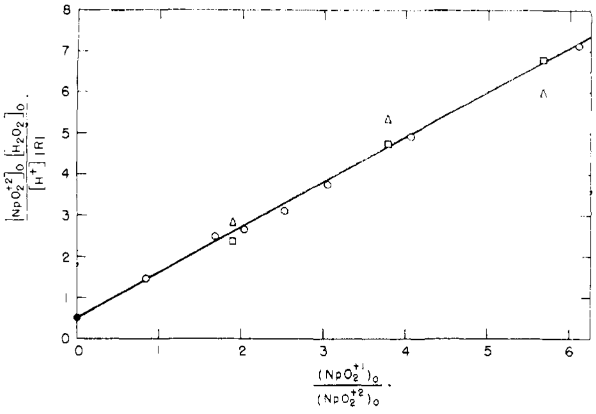

Fig. 2.—Test of complete rate law equation 9, 5°, $\mu = 3.0$: ●, average value of k for 25 runs with $NpO_2^{++} = 0$; ○, 3 M $HClO_4$; □, 2 M $HClO_4$; △, 1 M $HClO_4$.

Fig. 2. Also shown is the effect on the rate caused by change in $[H^+]$. The equation used in the preparation of this plot is

$$Y = \frac{1}{k} + \frac{k'}{k}\frac{[Np(V)]_0}{[Np(VI)]_0} \quad (2)$$

where $Y = [Np(VI)]_0[H_2O_2]_0/[H^+]_0(R)$. By a weighted least squares calculation,[5] using the value previously obtained for k, one obtains a value of $k' = 2.16 \pm 0.13$. Equation 1 then becomes

$$R = \frac{k[Np(VI)]_0[H_2O_2]_0}{[H^+]_0\left\{1 + \frac{k'[Np(V)]_0}{[Np(VI)]_0}\right\}} \quad (3)$$

The Effect of Temperature, Ionic Strength and Deuterium.—The effect of each of these parameters was determined by experiments designed to yield values of both k and k'. A minimum of at least three experiments were performed for each set of experimental conditions. Table I summarizes the results obtained; deviations are expressed at the 95% confidence level.

From these data the apparent Arrhenius activations energies were found to be $E_k = 12.4 \pm 1.1$ kcal./mole and $E_{k'} = -1.5 \pm 1.4$ kcal./mole.

The variation of k was small over the range of ionic strength investigated, but there was a marked decrease of k' with decrease in ionic strength.

From the data in Table I the effect of deuterium can be expressed in terms of the ratios $k_H/k_D = 4.5 \pm 0.6$ and $k'_H/k'_D = 0.96 \pm 0.16$. Uncertainties are given for the 95% confidence level.

Discussion

The values for the apparent rate constants and the form of the differential rate law are valid only for the initial rate of the reaction. Transforming equation 3 into a differential equation in terms of the reaction variable x, the increase in Np(V) concentration in time t, and integrating the resulting expression we have

$$(t)\left\{\frac{[H_2O_2]_0 - [NpO_2^{+2}]_0/2}{D[H^+]}\right\} = \frac{1}{k} + \frac{k'}{k}\left\{\frac{x([NpO_2^{+2}]_0 + [NpO_2^{+}]_0)}{[NpO_2^{+2}]_0([NpO_2^{+2}]_0 - x)D} - \frac{[H_2O_2]_0 + [NpO_2^{+}]_0/2}{[H_2O_2]_0 - [NpO_2^{+2}]_0/2}\right\} \quad (4)$$

where

$$D = \ln \frac{[NpO_2^{+2}]_0\left([H_2O_2]_0 - \frac{x}{2}\right)}{[H_2O_2]_0([NpO_2^{++}]_0 - x)}$$

We have not been able to verify the integrated form of the rate law experimentally. This is in part due to the peculiar algebraic form of the expression, *i.e.*, the expression becomes essentially indeterminate numerically for $[H_2O_2]_0 \cong [NpO_2^{+2}]_0$; for $[H_2O_2]_0 << [NpO_2^{+2}]_0$ the range of the dependent variable is small; the expression in the brackets on the right-hand side of equation 4 does not show significant differences between the first and second terms unless $[H_2O_2]_0 >> [NpO_2^{+2}]_0$. When the concentration ratio of $[H_2O_2]/[Np(VI)]$ is greater than 1, the integrated rate law shows a pronounced deviation from the linearity predicted by equation 4. The possible cause for the failure of the integrated rate law to hold under these conditions can be best discussed in terms of the proposed mechanism.

TABLE I[6]

SUMMARY OF THE VALUES OBTAINED FOR k AND k'

t, °C.	μ	k, sec.$^{-1}$	k'	Points
25	3	8.90 ± 1.57	1.90 ± 0.41	4
20	3	6.19 ± 1.09	1.79 ± .38	4
15	3	4.55 ± 0.82	2.01 ± .44	4
10	3	2.65 ± .46	1.60 ± .38	3
5	3	1.97 ± .07	2.16 ± .13	25, 13[a]
5	2	1.68 ± .30	1.33 ± .33	3
5	1	1.55 ± .27	0.98 ± .23	4
5	2.8[b]	0.437 ± .054	2.25 ± .34	8

[a] Number of points for k and k', respectively. [b] *Ca.* 95% D_2O.

The empirical rate law is consistent with the mechanism

$$H_2O_2 \underset{}{\overset{K}{\rightleftarrows}} H^+ + HO_2^- \quad (5)$$

$$HO_2^- + NpO_2^{+2} \xrightarrow{k_1} NpO_2^+ + HO_2 \quad (6)$$

$$HO_2 + NpO_2^{+2} \xrightarrow{k_2} NpO_2^+ + O_2 + H^+ \quad (7)$$

$$HO_2 + NpO_2^+ \xrightarrow{k_3} NpO_2^{+2} + HO_2^- \quad (8)$$

Applying the usual steady-state approximation for the concentration of HO_2 and solving for the rate of production of NpO_2^+ we obtain

$$\frac{d[NpO_2^+]}{dt} = \frac{2Kk_1[NpO_2^{+2}][H_2O_2]}{[H^+]\left\{1 + \frac{k_3}{k_2}\frac{[NpO_2^+]}{[NpO_2^{+2}]}\right\}} \quad (9)$$

In addition to the reactions 5–8 that have been postulated as a feasible mechanism, additional reactions may occur when the initial hydrogen peroxide concentration is high. These reactions are

$$HO_2 + H_2O_2 \longrightarrow OH + H_2O + O_2 \quad (10)$$

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \quad (11)$$

$$OH + NpO_2^+ \longrightarrow OH^- + NpO_2^{+2} \quad (12)$$

The failure of the integrated rate law to hold when the concentration ratio of $[H_2O_2]/[Np(VI)]$ is made greater than 1 would be expected if reactions 10–12 did become important. It also was observed

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[5] The basic assumption was that all limiting slopes, and hence R and Y values, had the same percentage uncertainty.

[6] Complete tables of original data are available from the authors.

spectrophotometrically that high peroxide concentration results in the formation of a small amount of Np(IV).

A variety of experiments were carried out to test other plausible reasons for failure of the integrated rate law: no evidence was found for the existence of peroxy–neptunium complexes. The extinction coefficients of both the Np(V) and Np(VI) were unaffected by hydrogen peroxide: the stability of H_2O_2 was not affected by the 3 M $HClO_4$ media; there was no indication of catalytic decomposition of H_2O_2 by Np(VI) and Np(V).

It is of interest to examine the proposed scheme with respect to parameters not occurring explicitly in the empirical rate expression. The mechanism proposed implies that $k = 2Kk_1$ and $k' = k_3/k_2$. Explicitly this tells us that the apparent activation energy for k is the sum of the activation energy for reaction 6 and the enthalpy of ionization of H_2O_2. The best value of the latter quantity appears to be that given by Evans and Uri.[7] They obtained a value of $\Delta H^0 = 8.2$ kcal. Using their data the energy of activation of reaction 6 is found to be *ca.* 4 kcal./mole.

The fact that k' is sensibly independent of temperature is not unreasonable on the basis of the postulated mechanism. Both reactions 7 and 8, involving the perhydroxyl radical as a common reactant, could be expected to have low energies of activation. The difference between the two energies would therefore be small and lead to an invariance of k' with temperature. A similar result has been obtained in the case of the hydrogen peroxide induced Ce(III)–Ce(IV) exchange reaction,[8] for which oxidation–reduction steps like those in reactions 7 and 8 have been assumed.

The results obtained when D_2O_2 was used as the reducing agent constitute a special but not critical test of the postulated mechanism. The invariance of k' in going from H_2O to D_2O solutions implies that reaction 7 is more complex than as written and should be presented in more detail as

$$NpO_2^{+2} + HO_2 = [NpO_2{\cdot}HO_2]^{+2} \xrightarrow{k_2} NpO_2^+ + HO_2^+ \qquad (7a)$$

$$HO_2^+ \longrightarrow H^+ + O_2 \qquad (7b)$$

where the dismutation of the activated complex is the rate-determining step. Then comparison with reaction 8 written in a similar manner as

$$NpO_2^+ + HO_2 = [NpO_2{\cdot}HO_2]^+ \xrightarrow{k_3} NpO_2^{+2} + HO_2^- \qquad (8a)$$

would suggest that the only variation to be expected would be that caused by the difference in the ratio between an O–H and an O–D vibration frequency in activated complexes which are quite similar.

The dependence of the rate on the inverse of the hydrogen ion concentration could arise from mechanisms other than the one suggested in equation 5. However, the effect of deuterium on k can be interpreted in a straightforward manner if the whole of the isotope effect is assigned to the pre-equilibrium. The activated complex which can be deduced from 6 is the same as that shown schematically in 8a. It is reasonable to expect only a small deuterium isotope effect for reactions of this type of molecule.

Unfortunately a search of the literature failed to reveal a measured value for the acid ionization of D_2O_2. However, it was possible to estimate a value for the ratio of $K_{H_2O_2}/K_{D_2O_2}$ by a graphical method. Using the weak acid dissociation constants tabulated by Gurney[9] a smooth curve was drawn through the points on a plot of pK_H *vs.* K_H/K_D. From this curve in conjunction with the value of the dissociation constant of H_2O_2,[7] an extrapolated value of $K_H/K_D = 4.2$ was obtained. Too much emphasis should not be placed on the agreement between this value and our experimentally determined value $k_H/k_D = 4.5$ because of the obvious assumptions that have been made. However, the fact that the calculated isotope effect is in reasonable agreement with experimental observations can be considered as supporting evidence for the mechanism we have outlined.

The qualitative similarity of the empirical rate law for the reduction of Co(III) by H_2O_2[10] with that deduced in this investigation can be construed as indicating corresponding mechanisms for the two reactions. However, detailed comparison of the two systems, in terms of the differences between the activation energies (14 kcal./mole) and the entropies of activation (49 e.u.), indicates variations greater than those to be expected on the basis of the charge differences between the two cations. These differences strongly suggest that Co(III) undergoes some reaction prior to the rate-determining step that is different from any that takes place with Np(VI). One possibility is that dimerization of Co(III) may occur.[10,11] If the dimer were involved, it would be possible for the oxidation of peroxide to take place as a two-electron step, giving oxygen directly. In this case, differences in the energies and entropies of activation of the magnitude calculated would not be unexpected.

In conclusion it should be mentioned that in the oxidation of H_2O_2 by metallic oxidation–reduction systems, stoichiometric data have been most often used to support the postulate of successive one-electron steps.[12] Direct evidence for reactions similar to 7 and 8 is not found. The present data, therefore, furnish the most definite kinetic evidence thus far available to support the idea that the oxidation of peroxide occurs in single electron steps in such systems.

LEMONT, ILLINOIS

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[8] P. B. Sigler and B. J. Masters, THIS JOURNAL, **79**, 6353 (1957).

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[11] D. W. Weiser, Thesis, University of Chicago, June, 1956.

[12] J. H. Baxendale, *J. Chem. Soc.* (London), Spec. Publication No. 1, "The Kinetics and Mechanism of Inorganic Reactions in Solution," 40 (1954).