cause a distortion of the wave. Not only was the kinetic current decreased considerably but also the wave was displaced to more negative potentials. As long as the current is entirely kinetically controlled, no "maxima" effects are involved and therefore it is unnecessary to add surface-active substances.

TABLE II

KINETIC CURRENTS OF 4 × 10^{-4} *M* PYRUVIC ACID IN 0.05 *M* PHOSPHATE BUFFER OF *p*H 6.80

Elect.	R.p.m.	*h*, cm.	*m*, g./sec.	*t*, sec.	i_k[a] × 10^6, amp.	$i_k/(mt)^{2/3}$ × 10^5, amp./g.$^{2/3}$
D.M.E.	..	82	0.002124	2.92	0.370	1.10
	..	52	.001307	4.73	0.350	1.04
R.D.M.E.	75	82	.01654	3.08	1.50	1.09
	150	82	.01654	2.51	1.32	1.10
	210	82	.01654	2.04	1.14	1.09
	210	42	.00847	3.92	1.14	1.10

[a] Measured at −1.4 volts *vs*. S.C.E.

The kinetic current of pyruvic acid was studied as another example. This acid is known to produce double waves at the d.m.e. in the *p*H range between 4 and 8 because of the fact that the undissociated form of the acid is reduced at a more positive potential than the pyruvate ion. The height of the first wave is partially or completely controlled by the rate of recombination of hydrogen and pyruvate ions.[21,23,24] As is to be expected, similar double waves are observed at the r.d.m.e. The recombination process is a second-order reaction, but if the hydrogen ion concentration is kept constant by using a proper buffer solution, the treatment becomes essentially the same as for a first-order reaction. At a sufficiently small hydrogen ion concentration, the concentration of the undissociated acid is so small that the current on the first wave is entirely controlled by the rate of recombination. The kinetic current observed under such conditions is given by equation 22 in which μk_f is replaced by $\mu k_f[H^+]$.

Experimental results obtained with a solution of 4 × 10^{-4} *M* pyruvic acid in a 0.05 *M* phosphate buffer at *p*H 6.80 are shown in Table II. Again, constant values of $i_k/(mt)^{2/3}$ were found both at the d.m.e. and at the r.d.m.e. at different heights of the mercury reservoir and at the r.d.m.e. at different speeds of rotation. The average value of μk_f calculated from these data was found equal to 1.7 × 10^6 cm.^{4} sec.$^{-1}$ mole.$^{-1}$. No surface-active substances were used in these experiments for the same reason as has been given in the description of the glucose experiment.

The nature of catalytic currents is essentially the same as that of kinetic currents, which was confirmed experimentally by measuring the catalytic current produced by hydrogen peroxide in the reduction of ferric ions. Since no further interesting feature was found, detailed results are not presented.

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[23] J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

[24] P. Delahay and T. J. Adams, THIS JOURNAL, **74**, 1437 (1952).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Application of the Potentiostatic Method to Electrode Processes with Fast Coupled Chemical Reaction—Kinetics of Dissociation of Monochloroacetic Acid

BY PAUL DELAHAY AND SYOTARO OKA[1] (WITH AN APPENDIX BY HIROAKI MATSUDA)[2]

RECEIVED JULY 10, 1959

It is shown that the kinetics of the chemical reaction preceding charge transfer in so-called "kinetic processes" can be studied by the potentiostatic method even for reactions which are too fast for polarographic study. Current–time curves are recorded with an electronic potentiostat and oscilloscope at a potential corresponding to the limiting current (i_l) range, and rate constants are calculated from a plot of $i_l t^{1/2}$ against $t^{1/2}$. Application is made to the kinetics of dissociation of monochloroacetic acid in 50–50 water–ethanol mixture (by volume) at an ionic strength of 1. Rate constants at 25°: (1.8 ± 0.5) × 10^6 sec.$^{-1}$ for dissociation, and (1.3 ± 0.3) × 10^{10} l. mole^{-1} sec.$^{-1}$ for recombination. Sources of error on these data are discussed. Experimental methods are outlined.

Electrode processes with a preceding coupled chemical reaction (so-called "kinetic processes") have been studied extensively in polarography since the classical work of Brdicka and co-workers and occasionally by the galvanostatic method (chronopotentiometry). The potentiostatic method,[3] since the development of electronic potentiostats with fast response, has not been applied to kinetic processes to our knowlege. Yet, this method and the galvanostatic method can be applied to chemical reactions which are too fast for kinetic study by polarography. The argument is as follows.

The limiting current for a kinetic process is controlled by the kinetics of the chemical reaction and diffusion of the reactants; and the influence of the latter process increases with the duration of electrolysis. Current–time curves in the potentiostatic method can be recorded in 10^{-3} sec. or even a shorter time, *i.e.*, in a time which compares very favorably with the drop time in polarographic electrolysis. Limiting currents which are practically diffusion-controlled in polarography still may exhibit a kinetic character in the potentiostatic method.

Quantitatively, according to Koutecky and Brdicka[4] the limiting current i_l for the first-order process $Z \rightleftarrows O + ne = R$, in which Z is not reduci-

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[1] On leave from Shimadzu Seisakusho Ltd., Instruments Division, Kyoto.

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[3] H. Gerischer and W. Vielstich, *Z. physik. Chem.* (*Frankfurt*), **3**, 16 (1955); **4**, 10 (1955).

[4] J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

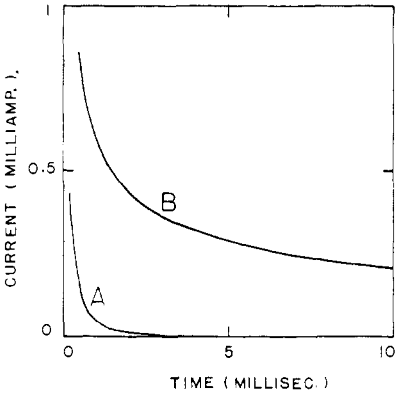

Fig. 1.—Current-time curves for the supporting electrolyte (curve A) and the reduction of 5 m*M* azobenzene (curve B) in 10 m*M* monochloroacetic acid, 1 *M* sodium monochloroacetate, in 50–50 water-ethanol mixture at 25°; ionic strength adjusted to 1 with sodium nitrate; electrode area, 0.032 cm.^{2}; change of potential from −0.150 v. to −0.450 v. *vs.* S.C.E.

ble, is

$$\frac{i_l}{i_d} = \pi^{1/2}\,\lambda\,\exp(\lambda^2)\,\operatorname{erfc}(\lambda) \qquad (1)$$

with

$$\lambda = (k_f K t)^{1/2} \qquad (2)$$

where K ($<<$ 1) is the equilibrium constant for Z $\rightleftarrows$ O, k_f the rate constant for the forward chemical reaction, t is time, and i_d is the diffusion current that would be observed if Z were reduced directly. Equation 1 holds for a plane electrode and for identical diffusion coefficients for Z and O. One has $i_l/i_d \rightarrow 1$ for $\lambda \rightarrow \infty$, and in practice the current is diffusion controlled for $\lambda > 5$. The same conclusion, with perhaps $\lambda > 10$, holds for the dropping mercury electrode.[5,6] It follows from eq. 2 that values of $k_f K$ larger by a factor of at least 10^3 in comparison with polarography can be determined by the potentiostatic method.

Application of the potentiostatic method is made here to the kinetics of dissociation of monochloroacetic acid. Mixtures of this acid and a large excess of its sodium salt were used as poor buffers in the reduction of a substance, azobenzene, whose half-wave potential is *p*H-dependent. A double wave was obtained with proper concentrations, the height of the first wave being controlled by the dissociation kinetics of monochloroacetic acid and by diffusion of this acid and hydrogen ions. This method already has been applied in polarography[7] and chronopotentiometry.[8] The difference in the diffusion coefficients of species Z and O, in this case the acid HA and H$^+$, must be taken into account according to Koutecky,[9] and the argument λ in eq. 1 is different from the value in eq. 2. This case is further examined by H. Matsuda in the Appendix.

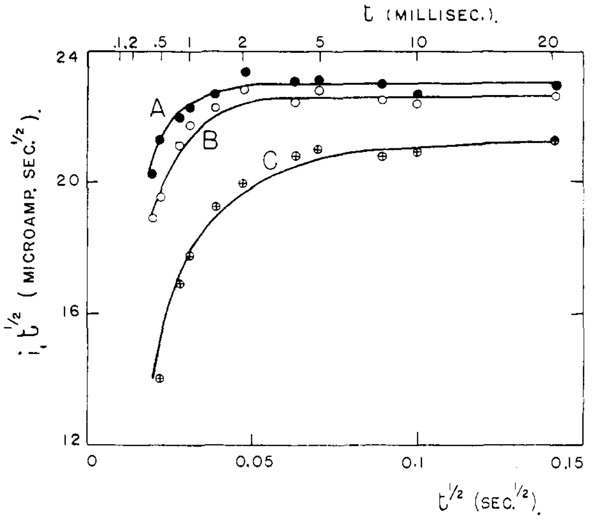

Fig. 2.—Variations of $i_l t^{1/2}$ with $t^{1/2}$ for the reduction of 5 m*M* azobenzene in 10 m*M* monochloroacetic acid, and 0.25 *M* (curve A), 0.5 *M* (B), and 1 *M* (C) sodium monochloroacetate. Other conditions are the same as in Fig. 1. The uncertainty on $i_l t^{1/2}$ in the reading of the oscillograms was 0.001 ma. sec.$^{1/2}$.

Experimental

Potentiostat.—A commercial electronic potentiostat[10] somewhat similar to the one developed by Schön and Staubach[11] was utilized. The potential-controlling switch of this instrument generated transients and was replaced by an outside switch with a polarization unit. Stability of potential was better than 2 mv. The rise time for the potential change was approximately 2 × 10^{-5} sec. Current-time curves were recorded with a Tektronix oscilloscope model 535 with a 53/54 D preamplifier.

Cell.—An H-cell with a saturated calomel electrode in one arm, as reference electrode, was utilized. A hanging mercury drop was the working electrode, and a platinum disk served as auxiliary electrode. The resistance of the cell between the calomel and working electrodes was below 20 ohms. Temperature was controlled at 25° within 0.1°.

Solutions.—Analytical reagent grades were used without further purification. Azobenzene (Matheson, yellow label) was used as supplied. A 6 *M* sodium salt of monochloroacetic acid was prepared by titration with a glass electrode, the *p*H at the equivalence point being 8.68. The *p*H of the mixtures of acid and salt, with the proper amount of sodium nitrate, was controlled in aqueous solution. Azobenzene was added as a 0.01 *M* solution in 100% ethanol, and the composition was adjusted to 50–50 volume % in ethanol. The ionic strength was 1. Deaerating of the solution followed polarographic practice (40 min. bubbling of nitrogen).

Description and Discussion of Results

Current–Time Curves.—A current-time curve is shown in Fig. 1 (curve B) for a change of potential from the bottom to the limiting current range of the first wave of the two waves which azobenzene gives in a buffer of a properly adjusted capacity. The residual (mostly capacity current) current for the supporting electrolyte (Fig. 1, curve A) was quite negligible in comparison with the faradaic current but, at any rate, a correction for the residual current was made. This correction, which was quite minor for $t > 5 \times 10^{-4}$ sec., was only approximate because the differential capacity of the double

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(5) J. Koutecky, *Collection Czechoslov. Chem. Commune*, **18**, 597 (1953).

(6) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 72–114.

(7) P. Rüetschi, *Z. physik. Chem. (Frankfurt)*, **5**, 323 (1955).

(8) P. Delahay and W. Vielstich, THIS JOURNAL, **77**, 4955 (1955).

(9) J. Koutecky, *Collection Czechoslov. Chem. Communs.*, **19**, 857 (1954).

(10) Available from Elektronische Werkstätten, Göttingen, Lichtenbergstrasse 15, West Germany.

(11) J. Schön and K. E. Staubach, *Regelungstechnik*, **7**, 157 (1954).

layer undoubtedly was not the same for the supporting electrolyte with or without azobenzene (adsorption of azobenzene).

Current–time curves were analyzed from a plot of $i_l t^{1/2}$ against $t^{1/2}$. Since the diffusion current i_d in eq. 1 is inversely proportional to $t^{1/2}$, a plot of $i_l t^{2/2}$ against $t^{1/2}$ should be represented by the function $p\lambda \exp(\lambda^2) \operatorname{erfc}(\lambda)$, where p is a proportionality constant. When $t^{1/2} \rightarrow \infty$, $i_l t^{1/2}$ approaches the value $i_d t^{1/2}$ corresponding to diffusion control. This is indeed the case (Fig. 2). Values of λ were determined (Table I), with the help of a plot of $\pi^{1/2}\lambda \exp(\lambda^2) \operatorname{erfc}(\lambda)$ against λ, from the ratio i_l/i_d read on Fig. 2.

TABLE I

DATA FOR THE CALCULATION OF k_d

C_{A^-}, mole l.$^{-1}$	t, msec.	i_l/i_d	λ	k_d, sec.$^{-1}$
0.25	0.4	0.906	2.20	2.10 × 10^6
.25	.5	.928	2.34	1.90
.5	.4	.845	1.42	1.72 × 10^6
.5	.5	.878	1.70	1.97
.5	.8	.923	2.26	2.18
.5	1	.935	2.48	2.13
1	0.5	.737	0.94	1.21 × 10^6
1	0.8	.82	1.27	1.39
1	1	.846	1.40	1.33
1	1.5	.896	1.90	1.64
1	2	.927	2.34	1.71
1	4	.962	3.40	1.97
1	20	1	..	..
			Av.	1.77 × 10^6

Calculation of Rate Constants.—In our case, dissociation of monochloroacetic acid in presence of a large excess of monochloroacetate ion is the pseudo-first order chemical reaction to be considered. The argument λ in eq. 1 then is[8,9] (see also Appendix)

$$\lambda = \frac{D}{D_{HA}}\left(\frac{D_{H^+}}{D_{HA}}\right)^{1/2}\left(\frac{k_d K_d}{C_{A^-}}\right)^{1/2} t^{1/2} \tag{3}$$

with

$$D = \frac{D_{H^+} + \dfrac{C_{A^-} D_{HA}}{K}}{1 + \dfrac{C_{A^-}}{K_d}} \tag{4}$$

where K_d is the dissociation constant of the acid HA, k_d the rate constant for dissociation of monochloroacetic acid, and C_{A^-} the bulk concentration of monochloroacetate ion present in large excess is comparison with the acid. From the literature[12] one has $K_d = 10^{-3.75}$ at 18° while our titration curves yielded $K_d = 10^{-3.78}$ in 50-50 volume water–ethanol mixture at an ionic strength of 1. For this value of K_d and the C_{A^-}'s used here, $D \approx D_{HA}$ according to eq. 4, and $\lambda t^{-1/2}$ is inversely proportional to $C^{1/2}_{A^-}$ (eq. 3). This is indeed the case: from Table I one deduces the average values of $\lambda t^{-1/2} = 107$, 68 and 48 sec.$^{-1/2}$ for the 0.25, 0.5 and 1 M chloroacetate solutions, respectively; *i.e.*, values of $\lambda t^{-1/2}$ are approximately in the ratio $4^{1/2}:2^{1/2}:1$.

The ratio D_{H^+}/D_{HA} of eq. 3 can be taken, with adequate accuracy for our purpose, as the ratio of the ionic conductances at infinite dilution of hydrogen and monochloroacetate ions, *i.e.*,[13] $D_{H^+}/D_{HA} = 8.8$. The corresponding values of k_d obtained from eq. 3 are listed in Table I, and the average value $k_d = (1.8 \pm 0.5) \times 10^6$ sec.$^{-1}$ can be cited at 25°. For recombination of H^+ and monochloroacetate ion one has $k_r = k_d/K_d = (1.3 \pm 0.3) \times 10^{10}$ l. mole^{-1} sec.$^{-1}$. The progressive increase in k_d with time in Table I may be caused (a) by distortion of the current–time curves by imperfect correction for the residual current and/or (b) by interference of convection.

The two remarks made in a previous paper[8] about two inherent sources of errors in such determinations also apply here: (a) second Wien effect in the reaction layer near the electrode, and (b) approximation resulting from the application of Fick's equation for diffusion to processes with a reaction layer of molecular dimensions.

Conclusion

It was shown that the potentiostatic method can be applied to so-called kinetic processes when the chemical reaction preceding charge transfer is too fast to be studied by polarography. Such a study was made here for conditions ($\lambda t^{-1/2} \approx 50$ to 100 sec.$^{-1/2}$) which would have corresponded in polarography to $\bar{i}_l/\bar{i}_d \approx 0.995$, *i.e.*, to diffusion control for all practical purposes.

Appendix

Limiting Current and Transition Time for First-order Kinetic Processes Involving Substances with Different Diffusion Coefficients

BY HIROAKI MATSUDA

The result of eqs. 3 and 4 obtained by Koutecky[9] will be derived by a new method and extension will be made to chronopotentiometry.

Limiting Current Density for the Plane Electrode.—The analysis follows the initial steps in the derivation of Koutecky and Brdicka[4] (see ref. 6 for review). The following system of equations is obtained after Laplace transformation

$$p u_Z - C_Z{}^0 = D_Z \frac{d^2 u_Z}{dx^2} - (k_f u_Z - k_b u_O) \tag{5}$$

$$p u_O - C_O{}^0 = D_O \frac{d^2 u_O}{dx^2} + (k_f u_Z - k_b u_O) \tag{6}$$

with the boundary conditions

$$(du_Z/dx)_{x=0} \tag{7}$$

$$(u_O)_{x=0} \tag{8}$$

$$(u_Z)_{x\rightarrow\infty} \rightarrow C_Z{}^0/p,\ (u_O)_{x\rightarrow\infty} \longrightarrow C_O{}^0/p \tag{9}$$

where the u's are the transforms of the C's, p is the parameter for transformation and the C^0's are the bulk concentrations.

The general solution of eq. 5 and 6, which are similar to the equations for coupled oscillators, is

$$u_Z = C_Z{}^0/p + A_1 \exp(-\beta_1 x) + A_2 \exp(-\beta_2 x) \tag{10}$$

$$u_O = C_O{}^0/p - A_1 f_1 \exp(-\beta_1 x) - A_1 f_2 \exp(-\beta_2 x) \tag{11}$$

with

$$\beta_1,\beta_2 = \frac{1}{2^{1/2}}\left\{\left(\frac{p+k_f}{D_Z} - \frac{p+k_b}{D_O}\right) \pm \left[\left(\frac{p+k_f}{D_Z} - \frac{p+k_b}{D_O}\right)^2 + 4\frac{k_f k_b}{D_Z D_O}\right]^{1/2}\right\}^{1/2} \tag{12}$$

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[12] L. Michaelis and M. Mizutani, *Z. physik. Chem.*, **118A**, 318 (1925).

[13] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 231.

$$f_j = -\frac{k_f}{\beta_j^2 D_O - (p + k_b)} = -\frac{\beta_j^2 D_Z - (p + k_f)}{k_b} \quad (j = 1,2) \qquad (13)$$

The integration constants A_1 and A_2, as determined from conditions 7 and 8, are

$$A_1 = \frac{C_O{}^0}{p}\frac{\beta_2}{f_1\beta_2 - f_2\beta_1} \qquad (14)$$

$$A_2 = \frac{C_O{}^0}{p}\frac{\beta_1}{f_2\beta_1 - f_1\beta_2} \qquad (15)$$

The Laplace transform of the current density, $I = nFD_O (du_O/dx)_{x=0}$, as deduced from eq. 10, 11, 14 and 15 is

$$LI = nFD_O C_O{}^0 \frac{\beta_1\beta_2}{p}\frac{f_1 - f_2}{f_1\beta_2 - f_2\beta_1} \qquad (16)$$

Inverse transformation is very complicated, and only an approximate solution will be obtained by retaining in the expansion of the β's into power series the first term. Thus

$$\beta_1 = \left[(k_f + k_b)\frac{D}{D_Z D_O}\right]^{1/2} \qquad B_2 = \left(\frac{p}{D}\right)^{1/2} \qquad (17)$$

with

$$D = (D_Z + KD_O)/(1 + K) \qquad (18)$$

Furthermore

$$f_1 = -D_Z/D_O \qquad f_2 = K \qquad (19)$$

By substitution of the β's and f's from eq. 17–19 into eq. 16 and by inverse transformation one obtains eq. 1 with the argument

$$\lambda = \frac{D}{D_Z}\left(\frac{D_O}{D_Z}\right)^{1/2} K(k_f + k_b)^{1/2} \qquad (20)$$

The same result was reported by Koutecky.[9] It should be noted that eq. 20 is valid provided that

$$K(D_O/D_Z) \ll 1 \text{ and } (k_f + k_b)^{1/2}t^{1/2}) \gg K(D_O/D_Z)^{3/2} \qquad (21)$$

Equations 3 and 4 are deduced readily from eq. 18 and 20 by consideration of the pseudo-first order character of the dissociation reaction.

Transition Time for a Plane Electrode.—The initial steps are the same as in the derivation of Delahay and Berzins[14] for the case in which $D_Z = D_O$. The integration constants now are

$$A_1 = \frac{1}{p}\frac{I}{nFD_O}\frac{1}{\beta_1(f_1 - f_2)} \qquad (22)$$

$$A_2 = -\frac{1}{p}\frac{I}{nFD_O}\frac{1}{\beta_2(f_1 - f_2)} \qquad (23)$$

where I is the current density. From eq. 11, 22 and 23 there follows

$$(u_O)_{x=0} = \frac{C_O{}^0}{p} - \frac{1}{p}\frac{I}{nFD_O}\frac{f_1\beta_2 - f_2\beta_1}{\beta_1\beta_2(f_1 - f_2)} \qquad (24)$$

or, after combination with eq. 17 to 19

$$(u_O)_{x=0} = \frac{C_O{}^0}{p} - \frac{1}{p}\frac{1}{nFD^{1/2}}\frac{K}{1 + K}\left\{\frac{1}{p^{1/2}} + \frac{D_Z}{D}\left(\frac{D_Z}{D_O}\right)^{1/2}\frac{1}{K(k_f + k_b)^{1/2}}\right\} \qquad (25)$$

After inverse Laplace transformation one obtains after introduction of the transition time τ_k ($C_O = 0$ at $x = 0$ for $t = \tau_k$

$$I\tau_k{}^{1/2} = \frac{\pi^{1/2}nFD^{1/2}C^0}{2} - \frac{\pi^{1/2}}{2K(k_f + k_b)^{1/2}}\frac{D_Z}{D}\left(\frac{D_Z}{D_O}\right)^{1/2} I \qquad (26)$$

Equation 26 is identical to the result of Delahay and Berzins[14] except for the factor $(D_Z/D)\,(D_Z/D_O)^{1/2}$. This correction factor is the same as for the limiting current (*cf.* eq. 20).

The correction factor in the dissociation of a weak acid in presence of a large excess anion of the acid is practically equal to $(D_{H^+}/D_{HA})^{1/2}$ or approximately $9^{1/2}$ (see above). The rate constants for dissociation of formic and acetic acid reported by Delahay and Vielstich[8] should be divided by the approximate factor nine since these authors did not make the above correction.

Acknowledgment.—This investigation was supported in part by the Office of Naval Research.

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[14] P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953).

BATON ROUGE, LOUISIANA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARKANSAS]

Activation Energy Measurements in the Reaction between Iodide and Persulfate Ions in the Presence of Different Salts

BY ANTONIO INDELLI AND EDWARD S. AMIS

RECEIVED JUNE 15, 1959

The rate of the reaction between persulfate and iodide has been measured at six temperatures in the presence of KCl, NaCl, $MgCl_2$, $LaCl_3$, $Co(NH_3)_6Cl_3$, and $UO_2(NO_3)_2$ (the latter only at 25°), at ionic strengths ranging from 0.0067 to 0.107. The temperature coefficient usually increases when the ionic strength is increased to 0.02–0.03, but, at least for KCl, NaCl and $MgCl_2$, at higher ionic strengths it decreases again. This fact cannot be interpreted by ordinary electrostatics. The difference in the temperature coefficient among various salts can explain the difference in the salt effects, the extent of which depends very specifically upon the nature of the cation. The $UO_2(NO_3)_2$ has a rather small accelerating effect on the reaction between persulfate and iodide, but it catalyzes markedly the reaction between persulfate and thiosulfate. The spectrum of the $UO_2{}^{++}$ ion is strongly modified by the presence of thiosulfate. A model is proposed for the mechanism of the non-electrostatic salt effect, which takes into account the polarization of the anion produced by a neighboring cation, and the lowering of the energy barrier in the electron transfer. The parallelism existing between the extent of the salt effect and the limiting equivalent conductivity of the cation is discussed in relation to this model.

In a preceding paper[1] the effects of different added salts on the reaction between persulfate and iodide ions were shown to be very specific and more dependent upon the nature and the concentration of cations than upon the ionic strength. In fact, at equal cation concentration the reaction rate does not increase when multivalent anions are substituted for univalent ones, but it remains constant at high dilution and decreases appreciably at moderate concentrations (0.04–0.1 g. ions of cation per liter). These results are in agreement with the Olson and Simonson findings[2] and are similar to those obtained previously for the alkaline hydrolysis of sodium trimetaphosphate.[3,4] In this last reaction the salt effects can be interpreted by pos-

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[3] R. M. Healy and M. L. Kilpatrick, THIS JOURNAL, **77**, 5258 (1955).

[4] A. Indelli, *Ann. Chim.* (*Rome*), **48**, 332 (1958).