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

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, $I = nFD_O(\mathrm{d}u_O/\mathrm{d}x)_{x=0}$, as deduced from eq. 10, 11, 14 and 15 is

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

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

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

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

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

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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[1] A. Indelli and J. E. Prue, *J. Chem. Soc.*, 107 (1959).

[2] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

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

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

tulating the formation of ion pairs. The ion pairs react faster than the free ions because of the decreased electrostatic repulsion between the ions associated in pairs and the hydroxyl ions, as compared with the repulsion between the free ions and the hydroxyl ions.[5] However, the fact that the activation energy decreases when increasing the cation concentration[6] seems to suggest that the above factor is not the only one responsible for the increase in rate, but the difference in chemical nature of the ion pairs and the free ions must also be influential.[7,8] It seems impossible to interpret accurately the data for the persulfate–iodide reaction in terms of ionic association.[1] Nevertheless, we have considered it interesting to try to detect some non-electrostatic effect through accurate measurements of the temperature coefficient of the reaction in the presence of various salts. Data existing in the literature on the rate of this reaction at different temperatures refer to ionic strengths far outside the range where the simple electrostatic picture can be useful.[9,10] Moreover, since magnesium was the only bivalent cation studied in the quoted paper,[1] the effect of uranyl ion was also investigated.

Experimental

The reagents used were all C.P. grade chemicals, of various sources, and were not further purified. The $Na_2S_2O_3$ solution was prepared by weight and standardized against $KBrO_3$; the $K_2S_2O_8$ solutions were standardized against the $Na_2S_2O_3$ solution, following the procedure already described[7] and were used within a week from their preparation. The $MgCl_2$, $LaCl_3$, $Co(NH_3)_6Cl_3$ and KI solutions were standardized against an $AgNO_3$ solution, which in turn had been standardized against KCl. All the other solutions were prepared by weighing the solid salts. The water used had a conductivity of about 2×10^{-6} ohm^{-1} cm.$^{-1}$ and was obtained by passing ordinary distilled water through an ion exchange column. The procedure to determine the rate constants was very similar to that described in the previous paper,[1] only minor modification being introduced. The current between the electrodes was of 0.4 μa., and a potentiometric device partially compensated the potential difference, which was measured through a G.E. galvanometer, Cat. No. 9892910, with a 50,000 ohms resistance in series. In most kinetic experiments 200 ml. of solution was used, containing 0.00250 *M* KI, 0.00125 *M* $K_2S_2O_8$, 0.0005 *M* HCl, 5×10^{-6} *M* ethylenediaminotetraacetic acid disodium salt and an added electrolyte. Additions of a 0.1 *M* sodium thiosulfate solution were made from an "Agla" micrometer syringe, and the appearance of iodine was timed from the starting of the depolarization of the electrodes. Since the response of the electrodes to the addition of thiosulfate is not immediate, each addition was made when about 83 ± 2% of the corresponding iodine was already present, and a minimum of 2 minutes was left between additions. The 83% of the iodine was estimated from the time elapsed from the reappearance of iodine, as compared with the time interval required, determined from the previous measurement. The amount of $Na_2S_2O_3$ added each time varied therefore between 0.005 and 0.04 ml., and the total amount added never exceeded 0.4 ml. The amount of reaction studied varied between 0.9 and 8%, and good first order linear plots were obtained in almost every case, as it can be seen from Fig. 1. However, in the presence of $LaCl_3$ and $Co(NH_3)_6Cl_3$ a very small curvature, which can be detected through a least square treatment, seemed to be present. This curvature was neglected, and this can perhaps account for the fact that the experimental error, in these cases, is somewhat greater than in the case of other salts. In the case of $UO_2(NO_3)_2$, because of its catalytic effect on the reaction between persulfate and thiosulfate, the latter was added when 90 ± 2% of the corresponding iodine was already present, but the accuracy, particularly at temperatures higher than 25°, was not great enough to permit a reliable calculation of the activation energy. A few runs were carried out to test the effect of the reaction between persulfate and thiosulfate; the first part of the experiments was made as usual, then the successive increasing additions of $Na_2S_2O_3$ were made immediately after the appearance of iodine. The reaction between thiosulfate and persulfate was tested also by taking 10-ml. samples from a solution containing 0.00250 *M* $Na_2S_2O_3$, 0.00125 *M* $K_2S_2O_8$, and the added salt, diluting to 250 ml., and titrating with a 0.00045 *M* solution of I_2 in pure water. The polarized electrodes were used as indicator. The spectra were taken with a Beckman DK 1 recording spectrophotometer. The temperature in the thermostat was read on Beckmann thermometers, standardized against a N.B.S. thermometer. The temperature was constant to about 0.005°, but its absolute value was known only within 0.02°.

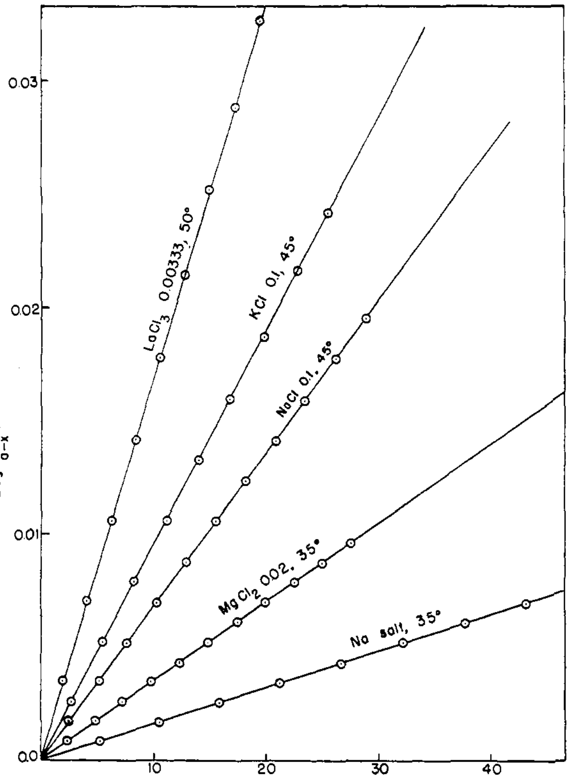

Fig. 1.

Results and Discussion

The Activation Energy.—Table I reports the values of the rate constants k_{exp} determined in the presence of various salts at different temperatures, together with the values, k_{int}, smoothed by fitting a log k_{exp} *versus* $1/T$ plot to the best straight line by the method of least squares. The percentage difference between k_{exp} and k_{int} has a maximum value of 1.5 and 2.2%, respectively, in the case of $LaCl_3$ and $Co(NH_3)_6Cl_3$, and exceeds 1% only three times in all other cases. Its average value is 0.4%. The values of $10^3 k$ of 2.841, 1.772 and 1.310 for NaCl 0.1 *M*, 0.02 *M* and in the absence of salt at 25°, are in agreement with the values 2.85, 1.78 and 1.30 found under similar conditions in the pre-

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(5) B. Topley, *Quart. Revs.*, **3**, 345 (1949).

(6) A. Indelli, *Ann. Chim.* (*Rome*), **46**, 367 (1956).

(7) A. Indelli, *ibid.*, **46**, 717 (1956).

(8) A. Indelli, *ibid.*, **48**, 345 (1958).

(9) V. Carassiti and C. Dejak, *Atti Accad. Sci. Ist. Bologna, Classe Sci. Fis., Rend.*, **11**, 2 (1955).

(10) W. J. Howells, *J. Chem. Soc.*, 203 (1946).

TABLE I

SECOND-ORDER RATE CONSTANTS, $10^3\,k$ (L. MOLE^{-1} SEC.$^{-1}$) FOR THE REACTION OF $S_2O_8^{=}$ WITH I^-

$[K_2S_2O_8] = 1.25 \times 10^{-3}$, $[KI] = 2.50 \times 10^{-3}$, $[HCl] = 5.0 \times 10^{-4}$, $[E.D.T.A.] = 5 \times 10^{-6}$ mole l.$^{-1}$

T Added salt, M	25°		30°		35°		40°		45°		50°	
	k_{exp}	k_{int}	k_{exp}	k_{int}	k_{exp}	k_{int}	k_{exp}	k_{int}	k_{exp}	k_{int}	k_{exp}	k_{int}
....	1.310	1.304	1.867	1.866	2.627	2.638	3.654	3.689	5.115	5.106	7.040	6.998
NaCl 0.02	1.772	1.764	2.526	2.532	3.574	3.592	5.048	5.040	6.993	6.997	9.638	9.619
NaCl 0.04	2.076	2.079	2.980	2.982	4.261	4.293	5.887	5.927	8.227	8.222	11.30	11.30
NaCl 0.1	2.841	2.833	4.054	4.042	5.693	5.699	7.853	7.948	10.99	10.97	15.09	15.00
KCl 0.02	2.078	2.064	2.957	2.958	4.165	4.190	5.839	5.869	8.093	8.137	11.29	11.19
KCl 0.04	2.721	2.700	3.838	3.850	5.455	5.426	7.547	7.565	10.52	10.44	14.06	14.27
KCl 0.1	4.049	4.047	5.741	5.746	8.082	8.065	11.18	11.20	15.37	15.39	21.00	20.96
$MgCl_2$ 0.01	2.300	2.285	3.301	3.307	4.708	4.728	6.629	6.684	9.377	9.349	13.01	12.95
$MgCl_2$ 0.02	2.766	2.762	3.996	3.987	5.672	5.687	7.973	8.021	11.74	11.72	15.52	15.47
$LaCl_3$ 0.00333	4.198	4.139	6.119	6.173	9.087	9.087	12.98	13.21	18.93	18.99	27.42	27.45
$Co(NH_3)_6Cl_3$ 0.000333	5.016	4.931	6.763	6.910	9.615	9.577	13.12	13.14	17.80	17.85	24.13	24.02
$UO_2(NO_3)_2$ 0.01	1.581	...	...	...	...	...	....	....	....	....	....	....

TABLE II

ACTIVATION ENERGIES OF THE REACTION OF $S_2O_8^{=}$ WITH I^- IN THE PRESENCE OF DIFFERENT SALTS

Salt added, M	E_{app}, cal.	$T_0\Delta S^*$
....	12,863 ± 60	−9135
NaCl 0.02	12,983 ± 34	−8836
NaCl 0.04	12,955 ± 48	−8763
NaCl 0.1	12,759 ± 65	−8780
KCl 0.02	12,926 ± 72	−8800
KCl 0.04	12,744 ± 90	−8823
KCl 0.1	12,590 ± 18	−8738
$MgCl_2$ 0.01	13,278 ± 60	−8388
$MgCl_2$ 0.02	13,187 ± 37	−8367
$LaCl_3$ 0.00333	14,357 ± 131	−6957
$Co(NH_3)_6Cl_3$ 0.000333	12,121 ± 130	−9089

vious paper.[1] Table II reports the activation energies under the different conditions, with their standard deviation r.m. The latter has been calculated using the formula[11]

$$\text{r.m.} = 4.574\sqrt{\frac{\Sigma(\log k_{exp}/k_{int})^2 \times n}{(n-2) \times [(\Sigma 1/T)^2 - n\Sigma 1/T^2]}} \qquad (1)$$

where n is the number of experimental points and T is the absolute temperature. The values of $T_0\Delta S^*$, where T_0 corresponds to 25°, are also reported in Table II. ΔS^* has been calculated using the formula[12]

$$k = \frac{KT}{h}e^{-\Delta S^*/R}e^{-\Delta H^*/RT} \qquad (2)$$

The positive salt effects are expected to be accompanied by an increase in the apparent activation energy E_{app}, which should be greater for a greater increase in rate. This holds both for the salt effect due to the influence of the ionic cloud,[13,14] and for the effect, arising from the formation of an ion pair, of the diminished repulsion between the two reacting ions.[7] This increase of the temperature coefficient is due to the fact that for the water, as a solvent, the product DT of the dielectric constant times the absolute temperature, decreases when the temperature increases. If the salt effect is to be accounted for by ordinary electrostatics, the correspondence between increase in rate and increase in E_{app} should be found even outside the range of validity of the Debye–Hückel limiting law; the same is true even if the ionic association hypothesis is only a mathematical approximation, which can be replaced by a more refined statistical treatment.[15] Deviations from this rule would be found if the dielectric constant, determining the extent of the electrostatic effect, varies with the temperature in a way drastically different from that of the dielectric constant of the pure solvent, or if the parameter "a" in the Debye–Hückel equation increases by a very substantial amount when increasing the temperature. Due to the long range of the electrostatic forces, and to the fact that the higher kinetic energy of the ions should allow a closer approach at higher temperatures, both the above possibilities appear rather unlikely, and they therefore have been neglected. In Fig. 2 the experimental activation energies (and their error, indicated by vertical lines) are plotted as a function of the equivalent concentration. It can be seen that in most cases E_{app} increases when a small amount of salt is added, but, at higher concentrations, a definite decrease is observed for magnesium chloride, sodium chloride, and, still more, for potassium chloride. A decrease in E_{app} by addition of potassium salts, can be observed also from other data in the literature.[9,10] This seems to indicate that besides the electrostatic effect, which should always be present, there is some other factor which decreases the true activation energy in such a way as to produce a decrease in E_{app}. Moreover, the activation entropy after a definite decrease in absolute value, with respect to the value in the absence of salt, remains almost constant when increasing the concentration of a particular salt. Ordinary electrostatics predicts values steadily less negative for ΔS^* accompanying the increase in rate due to the salt effect. The fact that the activation energy for potassium is smaller than for sodium and magnesium, seems to be significant in view of the greater increase in rate produced by potassium chloride. Magnesium chloride, particularly at high concentrations, has an accelerating effect smaller than potassium chloride,

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(11) O. F. Steinbach and C. V. King, "Experiments in Physical Chemistry," American Book Company, New York, N. Y., 1950, p. 15.

(12) S. Glasstone, K. T. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., New York, N. Y., 1941, p. 196.

(13) H. G. Davis and V. K. La Mer, *J. Chem. Phys.*, **10**, 585 (1942).

(14) E. A. Moelwyn-Hughes, "The Kinetics of Reaction in Solution," 2nd Ed., Clarendon Press, Oxford, 1956, pp. 102 ff.

(15) G. Scatchard, *Natl. Bur. Standards* (*U. S.*), Circ. No. **534**, 185 (1953).

when compared at equal ionic strength; this is surprising because, as a rule, bivalent cations have specific effects greater than univalent ones,[3,7,16,17] as it is to be expected from the probability of formation of ion pairs. The treatment of the salt effects given by Scatchard[15] on the basis of the Mayer theory[18] predicts also a greater effect of multivalent cations. It appears that the rather large difference in the activation energy can account for this anomalous result. The activation entropies for potassium and sodium are very similar, which seems to indicate that the difference between the two salts is due to non-electrostatic factors. On the other hand the entropies are less negative than those for magnesium and lanthanum salts, as is to be expected from the greater electrostatic effect due to the presence of multivalent cations. Particularly striking is the comparison between $LaCl_3$ and $Co(NH_3)_6Cl_3$: the latter has a salt effect of the same order of magnitude as the former, but at a concentration one-tenth as large. Correspondingly E_{app} is more than 2,000 cal. smaller. There seems to be little doubt that this difference in the activation energy is the chief factor in the difference in the salt effects, and it appears that this difference is due almost entirely to non electrostatic factors. The activation entropy for $Co(NH_3)_6Cl_3$ is only slightly less negative than that in the absence of salt, and this can be due to the extremely small concentration of the salt, which renders negligible the electrostatic effect.

The Uranyl Nitrate Salt Effect.—Uranyl nitrate appears to have a rather small influence on the rate of this reaction, even smaller than sodium chloride at the same equivalent concentration, despite the greater valence of its cation. Unfortunately it was impossible to obtain a reliable value of the activation energy, due to experimental difficulties. The reason for this is that the reaction of persulfate with thiosulfate, which is negligible in all other cases, has a great importance in the presence of uranyl nitrate, so that the measured value of the rate depends critically on the moment in which the additions of $Na_2S_2O_3$ are made.

The Reaction between Persulfate and Thiosulfate.—Table III reports the values of the apparent values of the rate constants of the reaction between persulfate and iodide, obtained in the absence and in the presence of different salts, adding various amounts of thiosulfate when the iodine just starts to appear. The results obtained in the same runs adding the thiosulfate when almost all the iodine is already present are also reported in Table III under the heading 0. These values are slightly different from the corresponding ones in Table I, because they are calculated by at least square treatment and not by a graphical treatment and because they refer to a single run and not to an average. It can be seen that while in all other cases there is only a small increase in rate when $Na_2S_2O_3$ is present in the solution all the time, in the case of $UO_2(NO_3)_2$ addition the increase is very large, amounting to almost 50%. For both KI and $Na_2S_2O_3$ reacting with $K_2S_2O_8$, we have the reactions

TABLE III

RATE CONSTANTS IN THE PRESENCE OF DIFFERENT AMOUNTS OF $Na_2S_2O_3$

Maximum amount of $Na_2S_2O_3$ present (10^{-6} mole l.$^{-1}$) Added salt	0	2.5	5.0	10.0	15.0
	$10^3 \times k$ (l. mole^{-1} sec.$^{-1}$)				
None	1.313	1.346	1.347	1.355	
$LaCl_3$	4.207		4.250	4.231	4.190
$Co(NH_3)_6Cl_3$ 0.000333 *M*	5.039		5.057	4.960	4.825
$UO_2(NO_3)_2$ 0.01 *M*	1.581	2.310	2.294	2.266	

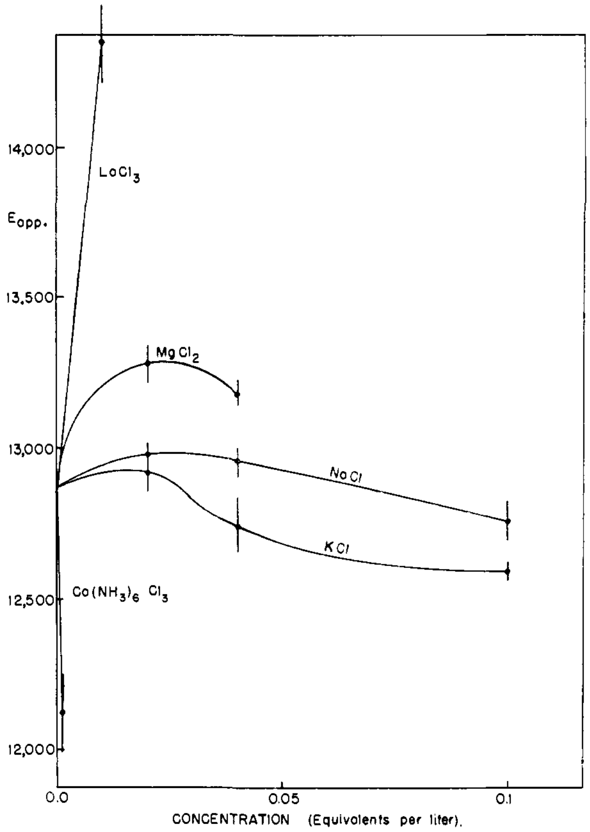

Fig. 2.

$$S_2O_8^{=} + 2I^- \xrightarrow{k_1} 2SO_4^{=} + I_2 \quad (A)$$

$$S_2O_8^{=} + 2S_2O_3^{=} \xrightarrow{k_2} 2SO_4^{=} + S_4O_6^{=} \quad (B)$$

$$I_2 + 2S_2O_3^{=} \longrightarrow 2I^- + S_4O_6^{=} \text{ very fast} \quad (C)$$

Supposing that the reaction B is first order with respect to $S_2O_8^{=}$ and first order with respect to $S_2O_3^{=}$ the rate of disappearance of $S_2O_3^{=}$ should obey the equation

$$-\frac{d(S_2O_3^{=})}{dt} = k_2(S_2O_8^{=})(I^-) + k_2(S_2O_8^{=})(S_2O_3^{=}) \quad (3)$$

Since the amount of $S_2O_3^{=}$ introduced in every addition is very small (equivalent to 0.1 to 0.9% of the $S_2O_8^{=}$ present) the concentration of $S_2O_8^{=}$ during the time required to consume the $S_2O_3^{=}$ can be considered constant, and so is the concentration of I^-. By integration, equation (4) is obtained for the time

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(16) V. K. La Mer and R. W. Fessenden, THIS JOURNAL, **54**, 2351 (1932).

(17) J. I. Hoppe and J. E. Prue, *J. Chem. Soc.*, 1775 (1957).

(18) J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950).

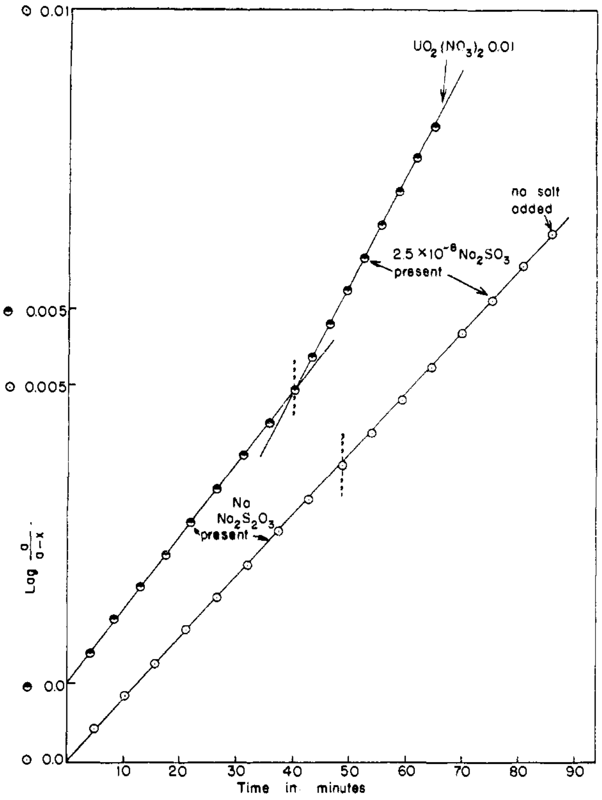

Fig. 3.

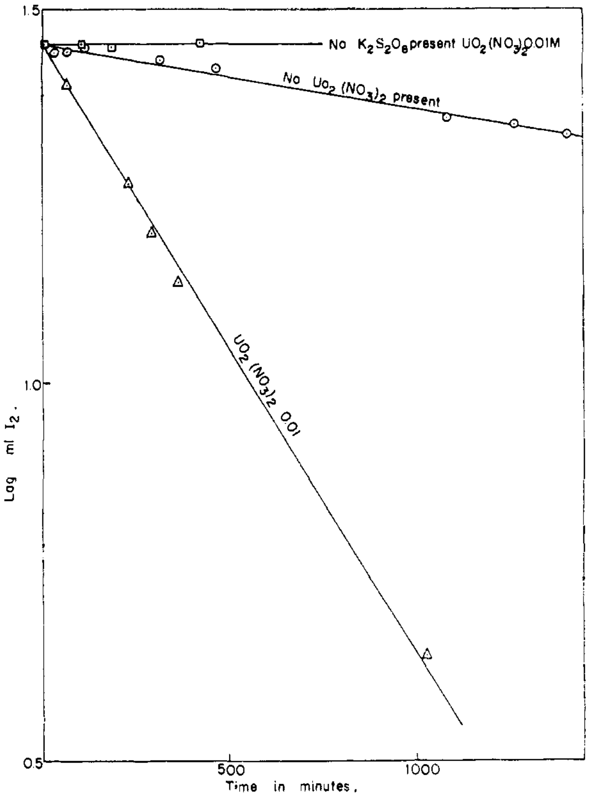

Fig. 4.

required for the reappearance of iodine

$$t' = \frac{1}{k_2(S_2O_8^{=})} \ln\left[1 + \frac{k_2(S_2O_3^{=})_0}{k_1(I^-)}\right] \quad (4)$$

where $(S_2O_3^{=})_0$ is the thiosulfate concentration added each time, that in this case is equal to the initial thiosulfate concentation. When the thiosulfate is added just before the reappearance of iodine, the time is given by

$$t = \frac{(S_2O_3^{=})_0}{k_1(S_2O_8^{=})(I^-)} \quad (5)$$

Dividing (4) by (5) one gets

$$\frac{t}{t'} = \frac{k_1(I^-)}{k_2(S_2O_3^{=})_0} \ln\left[1 + \frac{k_2(S_2O_3^{=})_0}{k_1(I^-)}\right] \quad (6)$$

The ratio between the times in the two conditions is therefore independent of the persulfate concentration, and this accounts for the fact that a linear first-order plot is obtained in both cases, as can be seen from Fig. 3. The inverse ratio of the corresponding first-order rate constants can therefore be substituted in the first member of (6), and developing in series one gets

$$\frac{k}{k'} = 1 - \frac{k_2(S_2O_3^{=})_0}{2k_1(I^-)} + \frac{1}{3}\left[\frac{k_2(S_2O_3^{=})_0}{k_1(I^-)}\right]^2 \quad (7)$$

It can be seen that the ratio between k and k' should be, for values close to the unity, a linear function of the amount of thiosulfate added each time. An examination of Table III shows that this is not true, but that k/k' is almost constant in the absence of foreign salts, and it increases in the other cases. This increase can perhaps be correlated with the slight curvature downward, which has been observed in the first-order plots for $LaCl_3$ and $Co(NH_3)_6Cl_3$ and has not been further investigated. The approximate constancy of k/k' seems to be due to the fact that the rate of the reaction between persulfate and thiosulfate is almost independent of the concentration of the latter. In this case in fact one gets simply

$$k' = k_1(I^-) + k_2 \quad (8)$$

and

$$k = k_1(I^-) \quad (9)$$

The fact that the reaction of persulfate with thiosulfate is almost zero order with respect to the latter was observed by King and Steinbach,[19] but it was rather unexpected to find it at a concentration in $S_2O_3^{=}$ less than 10^{-5} *M*.

The most important point, however, seems to be the enormous effect that the uranyl nitrate exerts on k_2. To check this point further the kinetic experiments by titration were performed, and Fig. 4 shows the first-order plots which have been obtained. The fact that the concentration of thiosulfate does not decrease appreciably with time when no persulfate is present rules out any possibility of an irreversible reaction between UO_2^{++} and $S_2O_3^{=}$.

Spectrum of the Complex between UO_2 and S_2O_3.—When $Na_2S_2O_3$ and $UO_2(NO_3)_2$ solutions are mixed, a strong yellow color is developed. The spectra of two solutions containing 0.005 *M* $UO_2(NO_3)_2$ and 0.005 *M* $UO_2(NO_3)_2$ and 0.005 *M* $Na_2S_2O_3$, respectively, are reported in Fig. 5. It can be seen that the absorption spectrum of the

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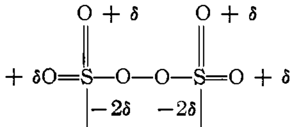
[19] C. V. King and O. F. Steinbach, THIS JOURNAL, 52, 4779 (1930).

UO_2^{++} ion in the ultraviolet, which is slightly modified by the presence of NO_3^- ions,[20] is displaced by about 120 mμ toward the red, and the characteristic peaks in the violet of the UO_2^{++} ion disappear and are perhaps replaced by a shoulder at about 440 mμ. The spectrum was taken immediately after preparing the solution, because after 1 hr. some turbidity appears, due perhaps to the precipitation of sulfur.

Mechanism of the Salt Effect.—A possible explanation of the decrease of the activation energy is the polarization which the cation exerts on the electrons of the anion when an ion pair is formed or when a cation is near enough to the activated complex. In fact, a fundamental step in the reaction must be an electron transfer from the iodide to the persulfate ion; it seems reasonable that an ion pair, which can be represented as



$$\begin{array}{ccccc} & O+\delta & & O+\delta & \\ & \| & & \| & \\ +\delta O= & S & -O-O- & S & =O+\delta \\ & |\,-2\delta & & -2\delta\,| & \\ & O^- & M^+ & O^- & \end{array}$$

should be a better electron acceptor than the free ion. Due to the particular structure of the $S_2O_8^-$ ion, cations of small radius can produce a greater concentration of negative charge toward the center of the molecule than cations of great radius. Unfortunately, there seems to be no unambiguous way to determine the ionic radius in aqueous solutions,[21] but a reasonable indication seems to be given by the ionic conductivity. The results reported in the preceding paper[1] can be useful as a test for this hypothesis, and in Table IV the rate constants obtained in the presence of different salts at the concentration of 0.04 equiv. $l.^{-1}$ at 25° are compared with the equivalent limiting conductivities of the cations.[22] A remarkable parallelism is observed between cations of the same valence, the only exception being the inversion between Li^+ and $N(CH_3)_4^+$. The present result for the uranyl nitrate is in agreement with this picture, because the limiting equivalent conductivity of the UO_2 ion is only 30.9.[23]

TABLE IV

COMPARISON BETWEEN THE SALT EFFECT IN THE REACTION BETWEEN PERSULFATE AND IODIDE[1] AND THE LIMITING EQUIVALENT CONDUCTIVITY OF THE CATION[22]

Salt	$10^3 k$	λ_0
KCl	2.70	73.50
NaCl	2.12	50.10
LiCl	1.91	38.6
$N(CH_3)_4Br$	1.89	44.9
$N(C_2H_5)_4Br$	1.48	32.6
$MgCl_2$	2.89	53.0
$Co(NH_3)_6Cl_3$	38.7	101.9
$LaCl_3$	~6.5[a]	69.7

[a] Extrapolated.

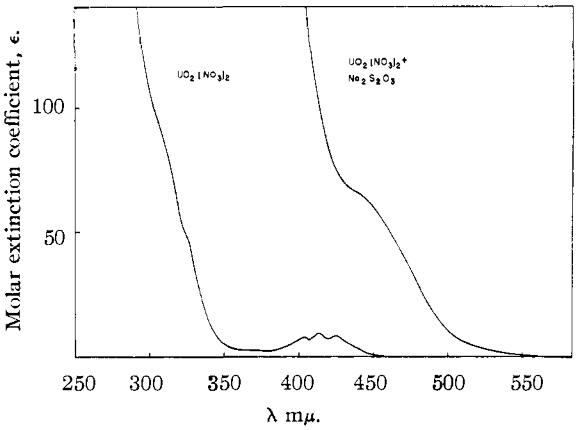


Fig. 5.—Absorption spectra of uranyl nitrate, and of the complex thiosulfate.

A similar explanation can also be advanced for other cases of specific salt effects for reactions between ions of the same sign, where the charges of the reactants and of the activated complex are small[17] or where E_{app} is found to decrease,[5,6] or at least not to increase,[24] in correspondence with the increase in rate. This is the case for the alkaline hydrolyses of condensed phosphates,[3–6,25] for the isotopic exchange between thiosulfate and trithionate,[24] for the catalytic rearrangement of tetrathionate,[26] for the hydrolyses of potassium ethyl malonate and oxalate[17] and probably for many others. In these reactions there is no electron transfer, but a nucleophilic attack by a negative ion, and this attack should be favored by a defect of electrons. In all these cases the cation, in the ion pair, is near enough to the bond to be broken during the reaction, to strongly polarize the electronic cloud. In other cases, however, the ion pair is formed in that part of the reacting system where there are no bonds to be broken. In the reaction between bromoacetate and thiosulfate, for instance, the bond to be broken is between the bromine and the carbon atom, while the ion pair is formed mostly with the thiosulfate ion.[27] It is therefore not surprising that the acceleration is due mainly, if not exclusively, to the electrostatic factor.[18,27–29] The distance of the Br–C bond from the charge on the carboxylic group may also be influential. In the case of the alkaline hydrolyses of potassium ethyl adipate and sebacate[17] the negative charge is very far from the point where the reaction takes place, and correspondingly the salt effects are normal. Another interesting example is given by the reaction between trimethylsilyl benzoate and hydroxyl ions.[30] Here too the distance between the reacting point and the center of the charge is rather large, and therefore no abnormal salt effects are to be expected. In fact, the small difference between the actions of potassium, sodium and lithium salts at

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high concentrations can be accounted for by the difference in the activity coefficients. In this, as in the preceding case, the lack of the electrostatic effect, due to the ion pairing, can be explained easily by the fact that the anions are monovalent.

It should be emphasized that the above picture does not require the existence of ion pairs as perfectly defined entities. In fact, for both the polarization and the electrostatic effect to be present, it is quite sufficient that an ion of opposite sign be within a certain distance of the reacting ion or of the activated complex. The extent of this "critical distance" is somewhat arbitrary, as it has been proven by Brown and Prue[31] and by Guggenheim[32] for the thermodynamic properties of the solutions of bi-bivalent electrolytes. Therefore, this picture is not in conflict with any more exact treatment, such as that of Scatchard,[15] but it also takes in consideration the polarization factor to explain the decrease in E_{app}. The distance of closest approach has therefore a double importance, determining the extent of the ion pairing and the polarization factor.

It seems, however, that some more specific factor must also be taken into consideration. In fact, the relative efficiency of various cations can be different for various reactions between anions, and even the order of efficiency can be reversed. In the hydrolyses of condensed phosphates[3,7] and of esters[17] calcium salts have a greater accelerating effect than barium salts; in the reactions between bromoacetate and thiosulfate[27] and between persulfate and iodide[9] the reverse is true. A striking example is given by the strong accelerating effect of uranyl nitrate on the reaction between persulfate and thiosulfate. In some cases this can be correlated with the different association constants of ion pairs,[27] but, even so, it seems that the ionic radius is not the only important factor in determining both the thermodynamic stability and the reactivity of ion pairs.

The shift of the absorption spectrum of the UO_2^{++} ion by addition of thiosulfate suggests a tentative explanation for the accelerating effect on the reaction between persulfate and thiosulfate. In fact, this absorption should correspond to an electron transfer between the anion and the cation,[33] and the fact that it is displaced toward greater wave lengths should correspond to a decrease in the energy required. The transfer of one electron from the uranyl–thiosulfate complex to a persulfate ion might be rendered easier, therefore, than the direct transfer of one electron from the thiosulfate to the persulfate ion. For the uranyl ion there is no possibility of acting as a donor–acceptor of electrons in this reaction, such as the copper or iron ions, which also act as catalysts.[19] In fact, the ion UO_2^{++} neither is reduced by the thiosulfate, as it is proven by Fig. 4, nor is oxidized by the persulfate, as it is proven by the fact that the reaction between persulfate and iodide is only slightly influenced. However, lowering the energy requirement for the transfer of an electron from the thiosulfate ion can provide an easier path for the over-all reaction. A mechanism of this kind could also be responsible for the great accelerating effect of the hexamminecobalt ion in the case of the persulfate–iodide reaction, since it is known that the electron transfer absorption spectrum of the $Co(NH_3)_6I^{++}$ ion pair is also displaced toward greater wave length, in comparison with the free I^+ ion.[33]

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