with acetic anhydride and sulfuric acid, gave either noncrystalline materials or high melting materials different from those reported previously. This should not be interpreted as IVb being absent, however, since Lutz has found that known IVa under these conditions does not give IIIa, as expected, but instead gives a high melting material.[10]

The reaction of dibenzoylethylene with 95% ethanol for twenty-four hours, all other conditions being as described in the *n*-propanol experiment, gave a few crystals of high melting material and a residual oil. No IIIb was obtained.

Attempted reaction of ethanol and methanol with benzalacetophenone under precisely the same conditions described in the reaction of dibenzoylethylene with *n*-propanol failed. An 80% recovery of benzalacetophenone was obtained in each case.

Reaction of Dibenzoylmethoxyethane (IVa) in Methanol in the Presence of Triethylamine Hydrochloride and Hydrogen Chloride.—A solution of 0.9 g. of crystalline dibenzoylmethoxyethane (IVa),[10] 1.0 g. of triethylamine hydrochloride and 35 ml. of methanolic hydrogen chloride solution (indicated *p*H, *p*Hydrion paper, 2–3) was refluxed for twenty-six hours. The reaction mixture was worked up precisely as described in the reaction between dibenzoylethylene and *n*-propanol. Thus was obtained 0.15 g. of 3-methoxy-2,5-diphenylfuran (IIIa), 0.02 g. of dibenzoylethylene and an oily material (identifications by mixture melting points).

In a similar experiment using oily dibenzoylmethoxyethane, there was obtained 0.1 g. of the methoxyfuran (IIIa) and 0.2 g. of dibenzoylethylene (identifications by mixture melting points).

Reaction of dibenzoylmethoxyethane (0.9 g.) with ethanol in the presence of triethylamine hydrochloride and hydrogen chloride under precisely the same conditions described in the preceding experiment yielded 0.07 g. of 3-ethoxy-2,5-diphenylfuran (IIIb), 0.02 g. of dibenzoylethylene (I) and an oil. No 3-methoxy-2,5-diphenylfuran (IIIa) was isolated. Identifications were made by mixture melting points.

Reaction of 3-Methoxy-2,5-diphenylfuran (IIIa) with Ethanol.—To a solution of 1 g. of 3-methoxy-2,5-diphenylfuran (IIIa), 1 g. of triethylamine hydrochloride and 30 ml. of absolute ethanol was added enough ethanolic hydrogen chloride to give the solution an indicated *p*H of 2–3 (*p*Hydrion paper). This solution (*p*H kept constant at 2–3) was refluxed for twenty-four hours, after which the reaction mixture was worked up as described in the reaction between dibenzoylethylene and *n*-propanol. Thus was obtained 0.8 g. of the ethoxyfuran (IIIb), 0.1 g. of the methoxyfuran (IIIa) and a small amount of oil.

When this reaction was repeated, cutting the reflux time to ten hours, 0.6 g. of the ethoxyfuran, 0.1 g. of the methoxyfuran, 0.1 g. of the 186°-melting by-product,[4] and an oil were obtained. All of the above identifications were by mixture melting points.

Reaction of 3-ethoxy-2,5-diphenylfuran (IIIb) with methanol using 0.6 g. of the ethoxyfuran, 0.6 g. of triethylamine hydrochloride and 25 ml. of methanolic hydrogen chloride (indicated *p*H of 2–3) for twenty-four hours under the same conditions described in the preceding experiment yielded 0.3 g. of the methoxyfuran (IIIa) and 0.2 g. of material believed to be a mixture of the methoxy and ethoxyfurans (m.p. 85–110°). Identifications were by mixture melting points.

Attempted reaction of 3-chloro-2,5-diphenylfuran with ethanol under precisely the same conditions described in the methoxyfuran reactions gave a 92% recovery of starting material.

Summary

The reaction between dibenzoylethylene and alcohols in the presence of amine hydrochlorides and a trace of hydrogen chloride has been found to occur also with *n*-propanol and isobutyl alcohol, but not with more complex alcohols. The mechanism of the reaction has been given some study. 3-Methoxy-2,5-diphenylfuran under the conditions of this reaction in ethanol solution has been converted to the corresponding ethoxyfuran and the reverse has been carried out in methanol solution.

AUSTIN, TEXAS

RECEIVED MAY 5, 1948

[10] Lutz, THIS JOURNAL, **51**, 3008 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Kinetics of the Reactions of Thiosulfate Ion with Ethyl, Propyl and Isopropyl Bromides[1]

BY THOMAS I. CROWELL AND LOUIS P. HAMMETT

The reactivity of the saturated alkyl halides in bimolecular displacement reactions always decreases when alpha or beta hydrogen atoms are replaced by methyl groups. The rates of reactions of the type

$$B: + RX \longrightarrow BR + :X \qquad (1)$$

have been studied[2] in cases where :B, the nucleophilic displacing group, is bromide, iodide, hydroxyl, ethoxide, phenolate, benzyloxide and thiosulfate ion. In each of the second-order reactions, the rates for different R groups are in the relation Me > Et > *i*-Pr > *t*-Bu and Et > *n*-Pr > *i*-Bu > neopentyl. This effect of structure on reactivity has been explained in two ways: first, by the tendency of an accumulation of electrons around the reaction center to repel the entering group[3,2g]; second, by increased steric hindrance in the transition state in the higher members of both series.[4,5] An increase in the potential energy change accompanying formation of the transition state would be expected in either case. These explanations

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[1] Dissertation submitted by Thomas Irving Crowell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] (a) Conant and Hussey, THIS JOURNAL, **47**, 476 (1925); (b) Le Roux, Lu, Sugden and Thomson, *J. Chem. Soc.*, 586 (1945); (c) Seelig and Hull, THIS JOURNAL, **64**, 940 (1942); (d) McKay, *ibid.*, **65**, 702 (1943); (e) Bartlett and Rosen, *ibid.*, **64**, 543 (1942); (f) Bateman, Cooper, Hughes and Ingold, *J. Chem. Soc.*, 931 (1940); (g) Dostrovsky and Hughes, *ibid.*, 157 (1946); (h) Segaller, *ibid.*, **105**, 106 (1914); (i) Haywood, *ibid.*, **121**, 1904 (1922); (j) Slator and Twiss, *ibid.*, **95**, 93 (1909).

[3] Hughes, Ingold and Patel, *ibid.*, 529 (1933).

[4] Ogg and Polanyi, *Trans. Faraday Soc.*, **31**, 604 (1935); Evans, "The Reactions of Organic Halides in Solution," Manchester University Press, Manchester, 1946.

[5] Dostrovsky and Hughes, *J. Chem. Soc.*, 173 (1946).

and the accompanying calculations are concerned only with the potential energy difference between reactants and activated state and are invalid or incomplete unless the difference in entropies of activation of the reactions whose specific rates k_A and k_B are being compared[6]

$$\Delta S_A^{\ddagger} - \Delta S_B^{\ddagger} = R\frac{\mathrm{d}}{\mathrm{d}T}\left(T\ln\frac{k_A}{k_B}\right)$$

is negligible compared with the difference

$$\frac{\Delta H_A^{\ddagger} - \Delta H_B^{\ddagger}}{T} = RT\frac{\mathrm{d}}{\mathrm{d}T}\left(\ln\frac{k_A}{k_B}\right)$$

The aim of this research was to obtain reliable values of these energy and entropy differences, which could be used with confidence in the interpretation of relative reaction rates. It was necessary to select a displacement reaction well suited to kinetic measurement. The reaction of thiosulfate ion with alkyl halides, which can be followed by the very accurate iodine titration and is free from side reactions involving thiosulfate ion, appeared to be the best choice. This reaction is

$$S_2O_3^{=} + RBr \xrightarrow{k_2} RSSO_3^- + Br^- \qquad (2)$$

irreversible and relatively fast. The product, an alkyl Bunte salt, is stable except for slow hydrolysis to the mercaptan.[7] This paper describes

$$RSSO_3^- + H_2O \longrightarrow RSH + HSO_4^-$$

the measurement of the rates of reaction of ethyl, *n*-propyl and *i*-propyl bromides with thiosulfate ion in a water–alcohol solvent at three different temperatures. Many workers have made thorough kinetic studies using compounds in which R contains a carboxylate group,[8] but the only experiments with alkyl halides afford no comparison of different compounds under similar conditions.[9,2j]

The alkyl bromides undergo solvolysis which

$$RBr + \text{solvent} \xrightarrow{k_1} H^+ + Br^- + ROH\ (ROEt) \qquad (3)$$

not only complicates the kinetics, but necessitates the use of a buffer to avoid decomposition of thiosulfate ion in an acidic medium. Acetate ion was used for this purpose. The rate of the reaction

$$RBr + Ac^- \xrightarrow{k_3} RAc + Br^-\ (Ac^- = CH_3COO^-) \qquad (4)$$

was found to be so slow as to be negligible in the calculation of k_2.

Experimental

Apparatus.—Temperature was referred to the ice point by means of a thermometer calibrated by the Bureau of Standards, and was probably correct within 0.02°. The thermostat described by Price and Hammett[10] was used at 12.5°; it was modified by the substitution of a small centrifugal pump, without by-pass, for the high-capacity gear pump. Pipets were calibrated at each temperature. They delivered constant amounts of solvent only if dried before use rather than rinsed with the solution, possibly because of the mixed solvent employed.

Materials.—Commercial samples of alkyl bromides were fractionated in a 24-in. column packed with glass helices. The boiling point range of each main fraction was 0.3° or less. Samples of the purified compounds were hydrolyzed in sealed tubes with alcoholic sodium hydroxide, then titrated for bromide by the Volhard method. All samples contained 99.8–100.2% of the calculated amount of bromine, except that one sample of isopropyl bromide, analyzed after long standing, was 64.4% bromine (65.0 calcd.).

Baker and Adamson anhydrous sodium acetate was dried in a desiccator over sodium hydroxide, to remove free acetic acid. The dried salt was analyzed for sodium by evaporation with dilute sulfuric acid followed by ammonium carbonate fusion.[11] The weight of sodium sulfate obtained corresponded to 27.95% sodium in the original sample. The result for a fused sample was 28.08% (28.04 calcd.).

Sodium *p*-toluenesulfonate was prepared by the method of McCleary and Hammett.[12]

Baker and Adamson crystalline sodium thiosulfate was used; it gave no precipitate with barium nitrate.

Primary standards for titration were potassium acid phthalate, silver nitrate and resublimed iodine. The first two compounds were dried for five hours at 110°. Individual gravimetric analyses of the determinate silver solutions were all within 0.05% of the correct value, proving the salt to be pure.

The solvent for all the reactions was prepared by mixing equal volumes of water and U. S. I. absolute alcohol at 25°. The density of the solvent was checked with a pycnometer: d^{25}_4 0.9229, corresponding to 44.05% alcohol by weight.

The Thiosulfate Reaction.—The experiments to determine temperature coefficient of reaction rate were done as follows. To 6.205 g. of $Na_2S_2O_3 \cdot 5H_2O$ (0.025 mole) was added 50 cc. of 0.1 *M* sodium acetate solution (in the solvent) and 2.25 cc. of alcohol to compensate for the water of crystallization of sodium thiosulfate. In the experiments with ethyl bromide and *n*-propyl bromide, about 0.012 mole of the compound in 100 cc. solution, was added and the solution made up to 250 cc. in the thermostat. Shortly after mixing, the first 10-cc. sample was withdrawn and the clock started. If the reaction was stopped by adding the sample to an excess of iodine, the titer was too large, because iodine reacted with the Bunte salt or with the mercaptan produced by hydrolysis. The reaction could be stopped successfully by pipetting the sample directly into 100 cc. of ice water. When this procedure was followed and a large excess of iodine avoided in the subsequent titration, the results did not vary with slight excesses. The concentration of alkyl bromide at zero time was determined by taking a sample after allowing the reaction to go practically to completion at 25° or 37.5°. Weighed amounts of these two bromides reacted with 99.5–99.9% of the calculated quantity of sodium thiosulfate.

The large amount of solvolysis in the case of *i*-propyl bromide made it difficult to determine the starting concentration by such "infinity" measurements; this compound reacted so slowly, however, that it was possible to weigh it in a small sealed bulb, break the bulb under the sodium acetate–thiosulfate solution, adjust the volume and take a sample before 1% of the reaction had occurred. The concentration of thiosulfate at the time of mixing could be estimated accurately by extrapolation. The 10-cc. samples were pipetted into 100 cc. of cold water which had previously been neutralized with sodium hydroxide to the phenolphthalein end-point. The solution was titrated with 0.02 *N* sodium hydroxide, made slightly

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[6] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 119.

[7] Bunte, *Ber.*, **7**, 646 (1874).

[8] For example, see La Mer and Fessenden, THIS JOURNAL, **54**, 2351 (1932).

[9] Moelwyn-Hughes, *Trans. Faraday Soc.*, **37**, 279 (1941); *J. Chem. Soc.*, 1577 (1933).

[10] Price and Hammett, THIS JOURNAL, **63**, 2387 (1941).

[11] Kolthoff and Sandell, "Textbook of Quantitative Analysis." The Macmillan Co., New York, N. Y., 1936, p. 389.

[12] McCleary and Hammett, THIS JOURNAL, **63**, 2254 (1941).

acid with dilute acetic acid, and titrated with 0.03 N iodine solution, using starch indicator.

After the withdrawal of a sample, closed pieces of glass tubing were dropped into the reaction vessel in order to keep it full of liquid and prevent evaporation of the volatile alkyl bromide. The concentration of ethyl bromide in a known solution remained constant within 1% while five samples were taken in this way. It was not proved that this precaution was necessary, however.

Sodium acetate–thiosulfate solutions in the alcohol-water solvent were stable for long periods. Small amounts of alcohol, alkyl bromides and acetic acid did not affect the end-point of the iodine titration.

Three experiments of a preliminary nature were made to determine the effect of changing thiosulfate concentration on the rates of reaction of n- and isopropyl bromides in a solution of high ionic strength. Six reaction mixtures were made up in each experiment: to 25 cc. of 1.00 M sodium acetate (in solvent) was added $Na_2S_2O_3 \cdot 5H_2O$ together with 0.36 cc. of alcohol per gram of the latter salt. Ten cc. of a solution of the alkyl bromide was then added and the solution made up to 50 cc. at 25°. Only two samples were withdrawn and titrated with iodine—one soon after mixing and one after 1380 minutes (i-PrBr) or ninety minutes (n-PrBr).

Solvolysis.—It was necessary to measure the rates of reaction of the alkyl bromides with the solvent and with acetate ion. Solutions 0.1 M in sodium acetate and approximately 0.1 M in ethyl, n-propyl or isopropyl bromide were made up and 10-cc. samples were withdrawn at intervals to be titrated for acid and for bromide ion. The sample, diluted to 100 cc., was first titrated with 0.02 N sodium hydroxide, using phenolphthalein indicator; then 2 cc. of saturated ferric ammonium sulfate solution and 5 cc. of 1-1 nitric acid were added, and the solution was titrated with standard silver nitrate and potassium thiocyanate solutions. When isopropyl bromide was present, a few drops of the thiocyanate solution were added first as indicator, then the necessary amount of silver nitrate was run in; an excess of the latter reagent would react with the secondary halide.

Methods of Calculation

Only in the case of i-propyl bromide was the rate of reaction (3) large enough to necessitate a correction. In the following solutions of the rate equations, $a - x$ is the concentration of thiosulfate ion at time t and a is the initial concentration; $b - y$ is the concentration of alkyl bromide at time t and b its initial concentration. The rate equations for reactions (2) and (3) are

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)(b - y) \qquad (5)$$

$$\mathrm{d}y/\mathrm{d}t = k_2(a - x)(b - y) + k_1(b - y)$$

Regarding y as a function of x

$$\mathrm{d}y/\mathrm{d}x = 1 + k_1/k_2(a - x)$$

$$y = x + \frac{k_1}{k_2} \ln \frac{a}{a - x}$$

Since $y - x$ is the amount of alkyl bromide hydrolyzed, it is equal to [HAc] in the buffered solution. A relation therefore exists between thiosulfate concentration and the ratio of the specific rates of the competing reactions

$$k_1/k_2 = -\,[\mathrm{HAc}]/\ln z \qquad (6)$$

where $z = (a - x)/a$. The validity of this relation was established by the approximate constancy of the calculated quantity k_1/k_2, as shown in Table II. Substituting equation (6) into (5)

$$\mathrm{d}z/\mathrm{d}t = -k_2az\left(\frac{b - a}{a} + z + \frac{k_1}{k_2a} \ln z\right) \qquad (7)$$

This is essentially the equation of La Mer and Kamner,[13] who evaluated $\mathrm{d}z/\mathrm{d}t$ from the experimental data and calculated k_2 directly.

In the present work, equation (7) was integrated as follows

$$ak_2t = -\int_1^z \frac{\mathrm{d}z}{z(A + z + R\ln z)}$$

where $A = (b - a)/a$ and $R = k_1/k_2a$.

$$ak_2t = -\int_1^z \frac{\mathrm{d}z}{z(A + z)} + R\int_1^z \frac{\ln z\,\mathrm{d}z}{z(A + z)(A + z + R\ln z)}$$

$$k_2t = \frac{1}{b - a} \ln \frac{a(b - x)}{b(a - x)} + \frac{R}{a}\int_1^z \frac{\ln z\,\mathrm{d}z}{z(A + z)(A + z + R\ln z)} \qquad (8)$$

The integral was evaluated by the trapezoidal rule, using the value of k_1/k_2 obtained from equation (6). A plot of w, the right-hand side of equation (8), against t proved to be nearly linear up to 50% reaction, the first point being slightly high in all cases. The quantity k_2 for i-propyl bromide in Table III is the slope of a line through this set of points obtained from all experiments at a given temperature, calculated by the method of least squares. The line was constrained to pass through the origin.

Ethyl bromide and n-propyl bromide showed the usual second-order kinetics. The values of k_2 given in Table III are averages in single experiments of the quantity

$$\frac{1}{t(b - a)} \ln \frac{a(b - x)}{b(a - x)}$$

These values were then averaged, as shown in the table.

Instead of calculating the energies and entropies of activation from the rate constants obtained at different temperatures, a more direct method of averaging was used. Assuming that $\ln k_2 = A - E/RT$, substituting $w = k_2t$, and taking logarithms, $\log w = \log k_2 + \log t = 0.4343 \cdot (A - E/RT_1) + \log t$ where T_1 is the absolute temperature.

A plot of $\log w$ against $\log t$ would therefore be a straight line with slope of 1 provided the experimentally determined quantity w were truly proportional to t. At a second temperature T_2, the intercept is changed: $\log w = 0.4343(A - E/RT_2) + \log t$. The distance between the two lines, measured along either axis, is $0.4343(E/R)(1/T_1 - 1/T_2)$, a quantity from which E, the experimental activation energy, is easily calculated.

In practice, w is not quite proportional to t, but shows a drift, so that the logarithmic plots are not straight lines of slope 1. The experimental graph for T_1 can be compared with that for T_2 by means of tracing paper, and if the same type of deviation from linearity is found at different temperatures,

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[13] La Mer and Kamner, THIS JOURNAL, 53, 2837 (1931).

the individual points for T_1 can be made to fit the same smooth curve as those for T_2 *over the whole range of measurements.* The distance which the tracing paper must be moved (if the graphs are referred to the same scale) is an average value of $0.4343(E/R)(1/T_1 - 1/T_2)$ obtained without first calculating k_2 in a reaction where the latter quantity changes with time.

Since w varies over the same range while the times for reaction differ widely in experiments at different temperatures, the difference in intercepts is best measured along the axis of log t. Similarly

$$T_1 \log w = 0.4343(AT_1 - E/R) + T_1 \log t$$
$$T_2 \log w = 0.4343(AT_2 - E/R) + T_2 \log t$$

and the distance between the curves, measured along the T log t axis, is $0.4343A(T_1 - T_2)$.

Then for two compounds, A and B, $\Delta S^{\ddagger}_{\mathrm{A}} - \Delta S^{\ddagger}_{\mathrm{B}} = R(A_{\mathrm{A}} - A_{\mathrm{B}})$ and $\Delta H^{\ddagger}_{\mathrm{A}} - \Delta H^{\ddagger}_{\mathrm{B}} = E_{\mathrm{A}} - E_{\mathrm{B}}$.

The rate equations for solvolysis in the presence of acetate ion are

$$\frac{d[\mathrm{Br}^-]}{dt} = -\frac{d[\mathrm{RBr}]}{dt} = -\frac{d[\mathrm{Ac}^-]}{dt}$$
$$= k_1[\mathrm{RBr}] + k_3\,[\mathrm{RBr}][\mathrm{Ac}^-] \quad \frac{d[\mathrm{HAc}]}{dt} = k_1[\mathrm{RBr}]$$

Approximate equations for k_1 and k_3 are obtained by considering reactions (3) and (4) independent. This approximation becomes exact when k_1 is much larger than $k_3[\mathrm{Ac}^-]$, or when the reaction is in the earliest stage. These equations are $d[\mathrm{HAc}]/dt = k_1(b - [\mathrm{HAc}])$ and $d[\mathrm{Br}^-]/dt = k_4(b - [\mathrm{Br}^-])$ where $k_4 = k_1 + k_3[\mathrm{Ac}^-]_{\mathrm{initial}}$. Integration gives the forms from which k_1 and k_4 were calculated:

$$k_1 = \frac{1}{t}\ln\frac{b}{b - [\mathrm{HAc}]} \text{ and } k_4 = \frac{1}{t}\ln\frac{b}{b - [\mathrm{Br}^-]}$$

The values obtained were extrapolated to zero time to give those quoted in Table V.

Results

Tables I and II show experimental data for the reaction of 0.100 M sodium thiosulfate with n-propyl and i-propyl bromides in 0.0200 M sodium acetate solution at 37.50°. All the results for i-propyl bromide at this temperature are plotted in Fig. 1.

TABLE I

SAMPLE DATA FOR n-PROPYL BROMIDE

t, sec.	Iodine titer[a]	k_2, l./mole-sec.
0	37.63	......
1110	35.20	0.001658
2010	33.63	.001644
3192	31.90	.001649
5052	29.86	.001636
7380	28.04	.001618
11232	26.01	.001618
		Av. .001637
78840	22.24	......

[a] In cc. of 0.02572 N iodine solution per 10.02-cc. sample.

TABLE II

SAMPLE DATA FOR i-PROPYL BROMIDE

t, sec.	NaOH titer[a]	I_2 titer[b]	k_1/k_2, mole/l.	Solvolysis correction	w, l./mole
0	....	42.27[c]	....	...	....
600	0.03	42.15	....	...	....
10500	.33	40.30	0.0125	0.014	1.281
20940	.76	38.78	.0157	.053	2.449
36000	1.28	36.87	.0165	.166	4.229
92640	2.38	32.84	.0166	1.09	10.23
121740	2.74	31.81	.0169	1.76	12.71

[a] Cc. 0.0176 N NaOH per 10.02-cc. sample. [b] Cc. 0.02361 N iodine. [c] Extrapolated.

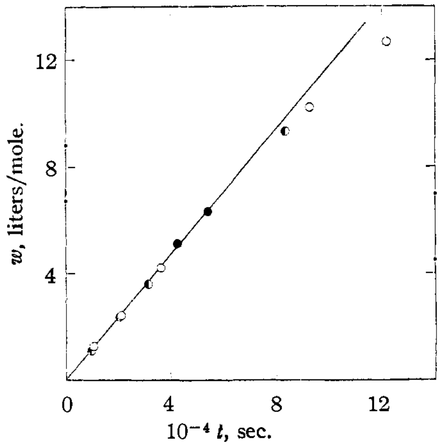

Fig. 1.—Thiosulfate-i-propyl bromide reaction at 37.5°: ○, first run (Table II); ◐, second run; ●, third run.

The specific rates k_2 for these reactions are shown in Table III; they refer to a reaction mixture containing, initially, 0.100 M sodium thiosulfate, 0.0200 M sodium acetate and 0.036–0.059 M alkyl bromide. The specific rate was found to decrease 1–2% when the initial concentration of alkyl bromide was increased from 0.045 to 0.055 M. One experiment in which the initial concentration was as low as 0.0309 was omitted from the

TABLE III

SPECIFIC RATES OF THIOSULFATE REACTION, $10^4 k_2$

	EtBr	n-PrBr	i-PrBr
12.50°	2.43	1.267	
	2.44	1.265	0.0677
	Av. 2.43	Av. 1.266	
25.00°	9.45	4.77	
	9.48	4.72	
	9.57	Av. 4.74	0.294
	9.63		
	Av. 9.53		
37.50°	33.5	16.30	
	33.2	16.37	1.180
	Av. 33.3	Av. 16.33	

TABLE IV

EFFECT OF SALT CONCENTRATION ON THE RATE OF REACTION OF THIOSULFATE WITH *i*-PROPYL BROMIDE

Temp., °C.	[RBr],[a] *M*	[NaAc], *M*	[$Na_2S_2O_3$], *M*	k_1/k_2	$10^4 k_2$	$10^6 k_1$[b]
25.00	0.1	0.1	0.2	0.1078	0.18	0.33
	.1	.1	.15	.0163	.22	.35
	.1	.1	.1	.0142	.25	.35
	.05	.02	.1	.0117	.294	.343
37.50	.1	.1	.1	.0182	1.0	1.8
	.1	.1	.025	.0150	1.1	1.7
	.05	.02	.1	.0164	1.180	1.91

[a] Initial concentrations given in all cases. [b] Calcd. from k_1/k_2 and k_2.

TABLE V

SOLVOLYSIS RATES IN 44.05% ALCOHOL CONTAINING 0.1 *M* NaAc

Temp., °C.	Compound	$10^6 k_4$, sec.$^{-1}$	$10^6 k_1$, sec.$^{-1}$	$10^5 k_3$, l./mole-sec.
25.00	*n*-PrBr	0.17	0.08	0.08
	i-PrBr	.40	.34	.05
	i-PrBr[a]	.34	.33	.015
37.50	EtBr	1.4	.7	.7
	n-PrBr	0.8	.45	.35
	i-PrBr	1.90	1.66	.24
	i-PrBr[b]	2.13	1.71	.28

[a] In 0.1 *M* sodium *p*-toluenesulfonate; k_3 for toluenesulfonate displacement. [b] In 0.15 *M* sodium acetate.

calculations; the others were started at molarities averaging 0.047.

Many experiments were done with different concentrations of reagents; uncertainty in b made them unsuitable for accurate determination of k_2, but the values of k_1/k_2 and approximate values of k_2 are interesting. Table IV summarizes these data, which are all for *i*-propyl bromide.

The rates of solvolysis and of acetate displacement are shown in Table V. It is apparent on comparison with Table III that in the case of the normal bromides, the rate of these two reactions combined (of which k_4 is a measure) is less than 1% of the rate of reaction with 0.05 *M* sodium thiosulfate, even in 0.1 *M* sodium acetate. The rate of reaction of *i*-propyl bromide with acetate ion is 16% of the solvolysis rate in 0.1 *M* sodium acetate; however, in 0.02 *M* sodium acetate, the concentration finally used, the rate would be only 3% of the solvolysis rate. Since the solvolysis correction was never more than 11% of the quantity to which it was added as a correction (except in a single case, the last sample of Table II), no correction for reaction (4) was necessary. The only correction made, therefore, was for the solvolysis of *i*-propyl bromide.

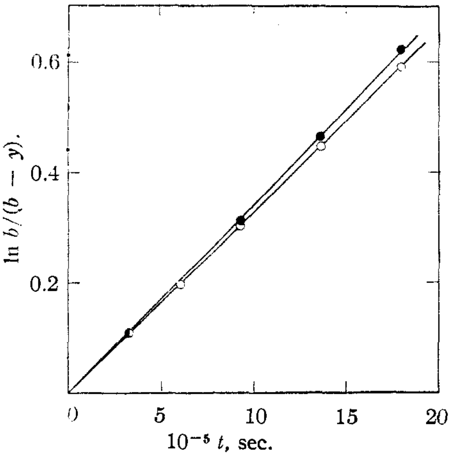

Fig. 2.—Solvolysis: O, y = [acid]: ●, y = [Br^-].

The rate of solvolysis of *i*-propyl bromide in the presence of 0.1 *M* sodium *p*-toluenesulfonate was measured in order to establish the fact that reaction with acetate ion did not change the rate of solvolysis. A slow reaction with *p*-toluenesulfonate ion was noticed, as in the case of ethyl bromide in dioxane–water.[12] Figure 2 shows the slight difference in rates of production of bromide ion and hydrogen ion at 25°.

The experimental activation energies E, and relative heats and entropies of activation for the thiosulfate reaction are given in Table VI; the reference compound is ethyl bromide. Figures 3 and 4 are typical graphs from which these results have been calculated. The curves for the three temperatures have been made to coincide by using three different horizontal scales. The logarithmic plots are straight lines of slope slightly less than one. The fact that the points obtained at different temperatures can be made to coincide, in spite of the variation in specific rate during the course of the reaction, is evidence that the results have not been seriously affected by the side-reactions or changes in medium which cause this variation.

TABLE VI

ENERGIES AND ENTROPIES OF ACTIVATION FOR THE REACTION OF THIOSULFATE ION WITH ALKYL BROMIDES

E, kcal./mole	EtBr	*n*-PrBr	*i*-PrBr
12.5–25°	18.5	17.9	19.9
25–37.5°	18.4	18.1	20.3
	Av. 18.5	18.0	20.1
$\Delta H^{\ddagger} - \Delta H_0^{\ddagger}$, kcal./mole			
12.5–25°		−0.6	1.4
25–37.5°	(0)	−0.3	1.9
		Av. −0.5	1.6
$\Delta S^{\ddagger} - \Delta S_0^{\ddagger}$, cal./mole-deg.			
12.5–25°		−3.6	−2.0
25–37.5°	(0)	−2.4	+0.2
		Av. −3.0	−0.9

The absolute entropy of activation for the reaction of ethyl bromide is −12.3 cal./mole-deg.[14]

Errors

The deviation measures of k_2 for ethyl and *n*-propyl bromides, calculated from the reproducibility of individual experiments, average 0.23%.

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(14) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

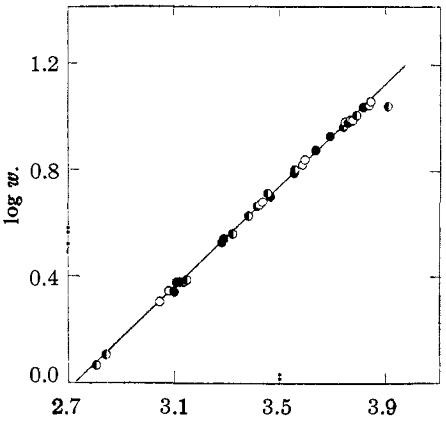

Fig. 3.—Graph for evaluation of energy of activation of *i*-PrBr: ●, 12.5° (add 64.0 to abscissa); O, 25°; ◐, 37.5° (subtract 60.0 from abscissa).

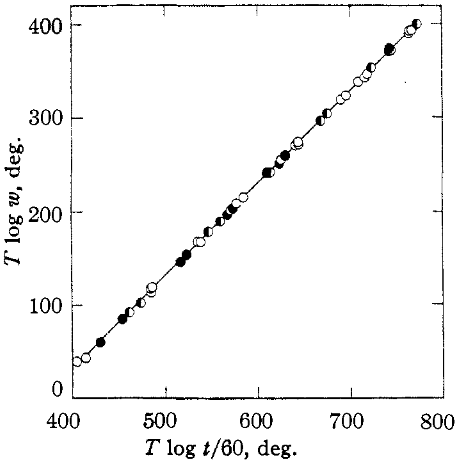

Fig. 4.—Graph for evaluation of entropy of activation of EtBr: ●, 12.5° (add 153.5 to abscissa); O, 25°; ◐, 37.5° (subtract 153.5 from abscissa).

Allowing for residual errors in concentration and temperature, the precision measure of k_2 is about 0.5%, giving rise to precision measures of 0.1 kcal. in E, 0.1(4) kcal. in $\Delta H^{\neq} - \Delta H_0^{\neq}$, and 0.4 cal./deg. in $\Delta S^{\neq} - \Delta S_0^{\neq}$.

The uncertainty in k_2 for *i*-propyl bromide is estimated to be 2%, due to the discrepancies between different methods of calculating this quantity. The consequent error in E would be 0.7 kcal.; the graphical method, however, probably reduces this error to about 0.2 kcal., corresponding to 0.7 cal./deg. in $\Delta S^{\neq} - \Delta S_0^{\neq}$.

Discussion

An alternative mechanism to the bimolecular displacement (1) is unimolecular ionization of the alkyl bromide followed by reaction with thiosulfate ion

$$\mathrm{RBr} + \text{solvent} \longrightarrow \mathrm{R}^+ + \mathrm{Br}^- \qquad (9)$$
$$\mathrm{R}^+ + \mathrm{S_2O_3}^= \longrightarrow \mathrm{RSSO_3}^-$$

Three arguments against the interference of such a mechanism are forthcoming from the data presented above.

First, the measured solvolysis rate in the absence of thiosulfate ion is an upper limit to the rate of reaction (9). The possibility of reaction of ethyl and *n*-propyl bromides by the above mechanism is therefore eliminated, and the proportion of unimolecular reaction of *i*-propyl bromide is limited to 7 to 14% of the total reaction with 0.1 *M* thiosulfate at 12.5 to 37.5°. It is evident from the values of k_1 in Table V, however, that the solvolysis rate is practically unchanged by the presence of thiosulfate, and that thiosulfate ion can be intervening only to a very slight extent in any unimolecular solvolysis. These considerations are subject to the condition that thiosulfate ion does not accelerate reaction (9) to a large extent and at the same time react with the carbonium ion.

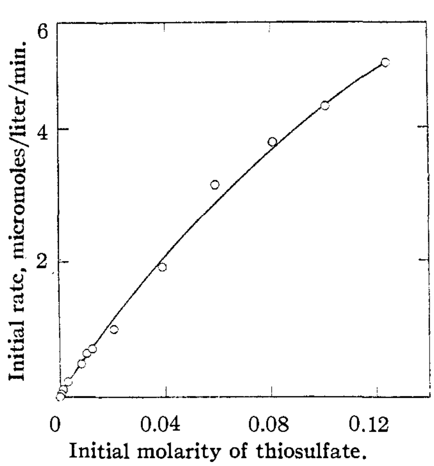

Fig. 5.—Effect of concentration on reaction rate.

In the second place, the rate of reaction of *i*-propyl bromide is approximately proportional to the concentration of thiosulfate ion. Figure 5 shows the results of the experiments in 0.5 *M* sodium acetate solution, described in the experimental section. The gradual decrease of specific rate with increasing concentration of thiosulfate appears to be an effect of changing medium, for it was observed to a larger extent with *n*-propyl bromide. The effect is qualitatively that which would be expected in a reaction such as (2), in which a relatively concentrated charge is spread out in the transition state and in the products, a process which should be facilitated by a decrease in ionic strength. The decrease in rate caused by increased initial concentration of alkyl bromide cannot be explained on this basis; it may be due to a retarding effect of the reaction products. These phenomena cannot be discussed further without studying the effect of each component of the system upon rate of reaction.

Finally, the reaction follows a second-order course.

The reactions of both primary and secondary bromides with thiosulfate ion are therefore believed to be true bimolecular substitution reactions. The important conclusions of this paper are derived from the relative heats and entropies of activation in Table VI. The rate of reaction of *n*-propyl bromide is only about half that of ethyl bromide in spite of the fact that its heat of activation is lower by about 0.5 kcal. A decrease in the entropy of activation well in excess of experimental error is responsible for the lower rate. On the other hand, the difference in rate between ethyl and *i*-propyl bromides is primarily due to a difference of 1.6 kcal. in the heats of activation of the two compounds. The difference in the entropies of activation is uncertain.

These results are in qualitative agreement with those of Seelig and Hull for the bromide ion–alkyl bromide reaction.[2c] The interesting calculations of Dostrovsky and Hughes[5] show that in the latter reaction, steric hindrance in the transition state would be equal for ethyl and *n*-propyl bromides, but would cause a rise of about 1 kcal. in the activation energy of *i*-propyl bromide. The results of the present paper show that these calculations may well be a valid explanation of the difference in rates between the primary and secondary compounds, but that no refinement of the calculation of activation energies will account for the difference in rates of reaction of ethyl and *n*-propyl bromides.

Steric hindrance and electric fields no doubt influence the entropy of activation; the only contention here is that the rate difference is not due to their influence on the energy barrier to the transition state, when a beta methyl group is added. The state of affairs is similar to that found in ester hydrolysis[15] and in the formation of semicarbazones,[10] where variations in rate are in many cases due to entropy, rather than energy differences.

Summary

The rates of reaction of thiosulfate ion with ethyl, *n*-propyl and *i*-propyl bromides have been measured at 12.50, 25.00 and 37.50° in an ethanol–water solvent (44.05% ethanol by weight) buffered with sodium acetate. Rates of solvolysis and reaction with acetate ion were also measured.

The replacement of an α-hydrogen atom of ethyl bromide by a methyl group increases the heat of activation of the first reaction by 1.6 kcal. This is the essential reason for a decrease in reaction rate. The replacement of a β-hydrogen atom also decreases the rate, but in this case the change is due primarily to a decrease of 3.0 cal./deg. in the entropy of activation.

[15] Smith and Steele, THIS JOURNAL, **63**, 3466 (1941).

NEW YORK, N. Y. RECEIVED MAY 27, 1948

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The System Uranyl Sulfate–Water. I. Temperature–Concentration Relationships Below 300°[1]

BY C. H. SECOY

At the outset of this research it was proposed to study the phase relationships in the system uranyl sulfate–water at high temperatures and pressures. However, an inspection of the literature revealed only very meager and inconsistent information concerning the system at low temperatures. Therefore, in order to make the study complete, the work described in this paper was undertaken.

The solubility of uranyl sulfate in water at or near room temperature is reported in the earlier literature by various workers with a great lack of agreement. Mellor[2] gives values reported by de Coninck as 0.461 molal at 13°, and 0.513 molal at 16°; by Buckholz as 3.95 molal at ordinary temperature and as 5.28 molal in boiling water; by Ebelman as 5.07 molal at 21° and 8.49 molal in boiling water; and other data from which one can calculate 4.30 molal at 25°. The only other pertinent data which could be found were those of Dittrick[3] for the freezing point depression for very dilute solutions. More recently, Helmholtz and Friedlander[4] have reported the solubility at 30, 35 and 40°. Values from the last two sources are included in Table I.

Experimental Procedure

Data for the ice curve were obtained by the usual techniques of thermal analysis. Since supercooling was great, warming curves were used for the most part. Most of the analyses were done volumetrically, reducing the uranyl ion to tetravalent and trivalent uranium with zinc amalgam, oxidizing the trivalent ion to tetravalent with air, and titrating the tetravalent uranium with standard potassium permanganate solution. Many of the analyses were checked gravimetrically by ignition to U_3O_8.

The solubility of the salt above room temperature was determined by the following steps: (1) a weighed amount of water and a weighed amount of salt of known composi-

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[1] This document is based on work performed under Contract No. W-35-058-eng-71 for the Atomic Energy Project at the Clinton National Laboratory (now known as the Oak Ridge National Laboratory). Presented before the Division of Physical and Inorganic Chemistry at the 113th national meeting of the American Chemical Society, Chicago, Illinois, April 19–23, 1948.

[2] Mellor, "A Comprehensive Treatise on Inorganic and Physical Chemistry," Vol. XII, Longmans Green and Co., New York, N. Y., 1932, pp. 103–105.

[3] Dittrick, *Z. physik. Chem.*, **29**, 449 (1899).

[4] Helmholtz and Friedlander, Manhattan Project Report, LAMS 30.