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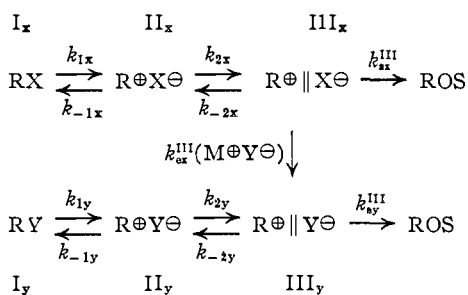
Salt Effects and Ion Pairs in Solvolysis and Related Reactions. XXI.¹ Acetolysis, Bromide Exchange and the Special Salt Effect²BY S. WINSTEIN, PAUL E. KLINEDINST, JR.,³ AND E. CLIPPINGER⁴

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The use of a salt like lithium bromide instead of lithium perchlorate permits one to gain further insight into the mechanism of the special salt effect. Diversion of reaction from solvolysis to formation of alkyl bromide by added bromide salts is very efficient in acetolysis of 1-anisyl-2-propyl *p*-toluenesulfonate and 3-anisyl-2-butyl *p*-bromobenzenesulfonate. At bromide salt concentrations in the normal salt effect range, formation of alkyl bromide shows good first-order behavior. The corresponding first-order rate constants for alkyl bromide formation, k_{RB} , show a linear dependence on bromide salt concentration, extrapolation to zero salt concentration leading to an intercept, k_{ext}^0 . For both the 1-anisyl-2-propyl and 3-anisyl-2-butyl systems, k_{ext}^0 values from bromide exchange are identical with k_{ext}^0 values from the special salt effect of lithium perchlorate. This agreement is evidence that bromide and perchlorate act as scavengers for the same solvolysis intermediates. Both trap the solvent-separated ion pair, but both permit internal return from the intimate ion pair.

As brought out in previous papers of this series, it is necessary to distinguish between various carbonium ion intermediates in acetolysis. Solvolysis scheme I is designed for systems whose reac-

SOLVOLYSIS SCHEME I

When $k_{1y} \gg k_{1x}$

$$\begin{aligned}
 \frac{1}{k_t} &= \frac{1}{k_{ext\ x}} \left[1 + \frac{1}{a_x + b_{ex}(MY)} \right] \\
 k_{ext\ x} &\equiv \left(\frac{k_1 k_2}{k_{-1} + k_2} \right)_x \\
 a_x &\equiv \left[\left(\frac{k_{ext}^{III}}{k_{-2}} \right) \left(\frac{k_{-1} + k_2}{k_{-1}} \right) \right]_x \\
 b_{ex} &\equiv \left[\left(\frac{k_{ext}^{III}}{k_{-2}} \right) \left(\frac{k_{-1} + k_2}{k_{-1}} \right) \right]_x
 \end{aligned}$$

When $k_{1y} \ll k_{1x}$ and (MY) relatively constant

$$\frac{1}{k_{RY}} = \frac{1}{k_{ROS}} = \frac{1}{k_{ext\ x}} \left[1 + \frac{1}{a_x + b_{ex}(MY)} \right]$$

If, also, (MY) is large

$$\frac{d(ROS)}{d(RY)} = a_y = \left[\left(\frac{k_{ext}^{III}}{k_{-2}} \right) \left(\frac{k_{-1} + k_2}{k_{-1}} \right) \right]_y$$

tions proceed by way of intimate and solvent-separated ion pairs II and III, respectively, but not dissociated carbonium ions, and whose solvolysis product ROS arises from the solvent-

separated ion pair III.^{2,5,6} It has been observed² that inclusion of salts such as lithium perchlorate in certain acetolyses gives rise to a steep special salt effect at low salt concentrations and a more shallow normal linear salt effect at higher concentrations. The steep special salt effect is evidently concerned with elimination of return from the solvent-separated ion pair^{2,6} (external ion pair return), and it is due to diversion of solvent-separated ion pair $R^{\oplus}||X^{\ominus}$ to a new species, $R^{\oplus}||Y^{\ominus}$ by exchange with the added special salt MY.^{2,6}

The use of a salt like lithium bromide permits one to gain further insight into the mechanism of the special salt effect and to extend the study of exchange reactions involving carbonium ion pair intermediates.^{2,6} This is because ion pair return is very effective with the new ion pairs $R^{\oplus}||Y^{\ominus}$ when Y is Br, covalent bromide RY being formed. Since the ionization rate constant k_{1y} of the latter is very much lower than that of the original arenesulfonate (k_{1x}), it accumulates during acetolysis in the presence of MY. In the present paper we report and discuss the results of a study of the acetolysis of 1-anisyl-2-propyl *p*-toluenesulfonate⁷ and *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate⁵ in the presence of lithium or tetrabutylammonium bromide.

Bromide Exchange.—When lithium bromide or tetrabutylammonium bromide is added in acetolysis of 0.01 *M* 1-anisyl-2-propyl toluenesulfonate at 50.0°, these salts are very effective even at low concentrations in diverting reaction from solvolysis to formation of alkyl bromide as judged by Volhard titration. Because acetolysis products are unstable in the presence of hydrobromic acid, the exchanges were studied in the presence of sufficient lithium or tetrabutylammonium acetate to keep the solutions basic. At the higher bromide salt concentrations in the normal salt effect range, namely, the 0.03–0.09 *M* range, covalent bromide was formed to the extent of 85–89%. Under these conditions, the ratio of alkyl bromide to solvolysis product which are formed is relatively constant in

(5) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).(6) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *ibid.*, **83**, 885 (1961).(7) (a) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); (b) A. H. Fainberg, G. C. Robinson and S. Winstein, *ibid.*, **78**, 2777 (1956); (c) S. Winstein and A. H. Fainberg, *ibid.*, **80**, 459 (1958).(1) Previous papers in this series: (a) XVIII, S. Winstein, M. Hojo and S. Smith, *Tetrahedron Letters*, No. **22**, 12 (1960); (b) XIX, S. Winstein, A. Ledwith and M. Hojo, *ibid.*, No. **10**, 341 (1961); (c) XX, A. Ledwith, M. Hojo and S. Winstein, *Proc. Chem. Soc.*, 241 (1961).(2) Reported in summary: (a) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *Chemistry & Industry*, 664 (1954); (b) S. Winstein, *Experientia Suppl. II*, 137 (1955); (c) VIth Reaction Mechanisms Conference, Swarthmore, Pa., Sept. 12, 1956; (d) S. Winstein, E. Allred and P. Klinedinst, Jr., Foreign Papers at VIIIth Mendeleev Congress of Pure and Applied Chemistry, Moscow, U.S.S.R., March, 1959, p. 48.

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(4) (a) National Science Foundation Predoctoral Fellow, 1952–1953; (b) U. S. Rubber Predoctoral Fellow, 1953–(1954).

a run. So also is k_{RBr} , a first-order rate constant for RBr formation evaluated with the aid of eq. 1. In this equation $(RBr)_\infty$ and (RBr) are concentrations of developed alkyl bromide at infinity and time t , respectively. A typical such determination of k_{RBr} is illustrated in Table I. In all cases, the

TABLE I
KINETICS OF REACTION OF 0.0100 *M* 1-*p*-ANISYL-2-PROPYL *p*-TOLUENESULFONATE WITH 0.0278 *M* LITHIUM BROMIDE AND 0.00301 *M* LITHIUM ACETATE IN ACETIC ACID AT 50.0°

Time, 10 ⁻³ sec.	Ml. AgNO ₃ per aliquot	10 ⁴ k_{RBr} , sec. ⁻¹
0	2.378	..
2.10	2.316	4.42
4.50	2.255	4.30
7.50	2.188	4.23
10.56	2.126	4.23
14.16	2.057	4.35
18.60	1.987	4.41
23.40	1.934	4.31
42.96	1.798	4.14
∞	1.680	..

Mean 4.30 ± 0.07

bromide infinity titer was the same at 10 and 20 reaction half-lives, indicating that organic bromide was not solvolysing to any measurable extent. The various determinations of k_{RBr} at the different

TABLE II
KINETICS OF BROMIDE EXCHANGE IN ACETOLYSIS OF 0.0100 *M* 1-*p*-ANISYL-2-PROPYL *p*-TOLUENESULFONATE AT 50.0°

Bromide salt	(MPr), 10 ² <i>M</i> Init.	(LiOAc), 10 ² <i>M</i> Av.	10 ⁴ k_{RBr} , sec. ⁻¹ Obsd.	10 ⁴ k_{RBr} , sec. ⁻¹ Corr.	
LiBr	2.78	2.37	3.01	4.30 ± 0.07	4.12
LiBr	4.64	4.21	2.01	5.38 ± .10	5.06
LiBr	6.94	6.49	2.01	6.74 ± .14	6.25
LiBr	9.02	8.58	2.00	7.94 ± .19	7.29
Bu ₄ NBr	2.68	2.28	3.01	3.64 ± .06	3.56
Bu ₄ NBr	4.46	4.04	5.04	4.18 ± .03	4.04
Bu ₄ NBr	6.69	6.26	2.01	4.90 ± .06	4.68
Bu ₄ NBr	8.76	8.31	2.00	5.53 ± .12	5.24

concentrations of lithium and tetrabutylammonium bromide are summarized in Table II.

$$2.303 \log \left[\frac{(RBr)_\infty}{(RBr)_\infty - (RBr)} \right] = k_{RBr} t \quad (1)$$

$$2.303 \log \left[\frac{(ROS)_\infty}{(ROS)_\infty - (ROS)} \right] = k_{ROS} t \quad (2)$$

The behavior of *threo*-3-anisyl-2-butyl bromobenzenesulfonate toward added lithium bromide during acetolysis was quite analogous to that of the 1-anisyl-2-propyl analog. At concentrations of lithium bromide in the normal salt effect range, solvolysis was diverted to formation of covalent bromide to the extent of 93–96%. The determination of k_{RBr} at *ca.* 0.065 *M* lithium bromide at 25° is illustrated in Table III, while the results of two such runs are summarized in Table IV.

Corrections for Direct Reaction.—In the case of the 1-anisyl-2-propyl arenosulfonate, less reactive toward ionization than the 3-anisyl-2-butyl ester, it was necessary to estimate a correction for direct bimolecular reactions in which bromide ion is involved as a nucleophile in the rate-determining step. To assess the importance of such reactions, 1-phenyl-2-propyl toluenesulfonate is a good model

TABLE III
KINETICS OF REACTION OF 0.0100 *M* *threo*-3-ANISYL-2-BUTYL *p*-BROMOBENZENESULFONATE WITH 0.0634 *M* LITHIUM BROMIDE AND 0.00120 *M* LITHIUM ACETATE IN ACETIC ACID

AT 25.00°		
Time, 10 ⁻³ sec.	Ml. KSCN per aliquot	10 ⁴ k_{RBr} , sec. ⁻¹
0	0.755	..
1.14	0.885	107
2.28	1.000	106
3.42	1.100	105
4.56	1.190	105
6.42	1.320	106
8.76	1.455	108
12.78	1.590	103
∞	1.900	..

Av. 106 ± 1

TABLE IV
SUMMARY OF KINETICS OF CONVERSION OF 0.0100 *M* *threo*-3-ANISYL-2-BUTYL *p*-BROMOBENZENESULFONATE TO BROMIDE IN ACETIC ACID AT 25.00° [(LiOAc) = 1.20 × 10⁻³ *M*]

(LiBr), 10 ² <i>M</i> Init.	Av.	10 ⁴ k_{RBr} , sec. ⁻¹
6.34	5.85	106 ± 1
3.16	2.71	76.0 ± 1.0

for the 1-anisyl-2-propyl ester, since the removal of the *p*-methoxyl group strongly retards ionization,⁷ but is without appreciable effect on the more direct substitution and elimination reactions involving bromide ion as a nucleophile.⁸ For this reason, the action of lithium and tetrabutylammonium bromides on 1-phenyl-2-propyl toluenesulfonate during acetolysis was investigated under the general conditions employed in the study of the 1-anisyl-2-propyl analog. As illustrated in Table V, k_{RBr} was relatively constant within a run with this substrate as well as the other two, and the results of the several runs with the 1-phenyl-2-propyl toluenesulfonate at 50° are summarized in Table VI.

TABLE V
KINETICS OF REACTION OF 0.0100 *M* 1-PHENYL-2-PROPYL *p*-TOLUENESULFONATE WITH 0.0278 *M* LITHIUM BROMIDE AND 0.0101 *M* LITHIUM ACETATE IN ACETIC ACID AT 50.0°

Time, 10 ⁻⁴ sec.	Ml. AgNO ₃ per aliquot	10 ⁴ k_{RBr} , sec. ⁻¹
0	2.410	..
7.248	2.300	3.01
10.968	2.249	3.09
16.056	2.200	2.92
20.430	2.157	2.94
28.362	2.094	2.93
41.532	2.015	2.96
63.132	1.935	2.99
∞	1.850	..

Mean 2.98 ± 0.05

In the runs with 1-phenyl-2-propyl toluenesulfonate in the presence of substantial concentrations of bromide salt, alkyl bromide was formed to the extent of 65–77% at 0.03–0.08 *M* lithium bromide and 57–65% at 0.04–0.08 *M* tetrabutylammonium bromide. While the data are of some interest in

(8) (a) S. Winstein, D. Darwish and N. J. Holness, *J. Am. Chem. Soc.*, **78**, 2915 (1956); (b) I. D. R. Stevens, unpublished work.

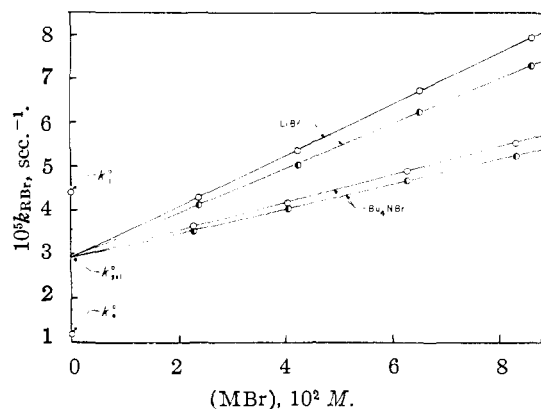


Fig. 1.—Effects of bromide salts in acetolysis of 1-*p*-anisyl-2-propyl toluenesulfonate at 50°: open circles, uncorrected k_{RB_r} values; semi-closed circles, corrected k_{RB_r} values.

connection with the subject of substitution and elimination by bromide ion as a nucleophile,⁸ the present interest in them is because they afford an estimate of the rate of direct reactions of 1-anisyl-2-propyl toluenesulfonate with bromide salts.

TABLE VI

KINETICS OF BROMIDE EXCHANGE IN ACETOLYSIS OF 0.0100 *M* 1-PHENYL-2-PROPYL *p*-TOLUENESULFONATE AT 50.0°

Bromide salt	(MBr), 10 ² <i>M</i> Init.	(MBr), 10 ² <i>M</i> Av.	(LiOAc) 10 ² <i>M</i>	Ex- change, %	10 ⁵ k_{RB_r} , sec. ⁻¹
LiBr	2.78	2.45	1.01	65	2.98 ± 0.05
LiBr	4.62	4.28	1.01	68	4.26 ± .06
LiBr	6.93	6.56	1.01	73	6.27 ± .10
LiBr	8.33	7.95	1.01	77	7.27 ± .21
Bu ₄ NBr	4.46	4.17	1.01	57	2.10 ± .06
Bu ₄ NBr	8.04	7.71	1.01	65	3.35 ± .08

The k_{RB_r} values listed in Tables I–VI which are derived from kinetic runs in which the (RY/ROS) ratio is constant within a run are also equal to first-order solvolyses rate constants k_{ROS} , defined by eq. 2, where (ROS)_∞ and (ROS) are concentrations of solvolysis product formed at infinity and time *t*, respectively. Also, k_{RB_r} (or k_{ROS}) is equal to the first-order rate constant for disappearance of the arenesulfonate, RX. The k_{RB_r} values for the 1-phenyl-2-propyl toluenesulfonate show a linear dependence on the average MBr concentration prevailing in the various runs so that they can be fit to eq. 3 with b_t equal to 148 for lithium bromide and 62 for tetrabutylammonium bromide. The k_t^0 value employed in eq. 3 is the acetolysis rate constant^{7a} in the absence of salt,^{9,10} 0.585×10^{-6} sec.⁻¹ at 50.0°. The b_t values to be expected if the only effect of the added bromide salts were normal salt effects on acetolysis can be estimated as 18 and 2.9 for lithium and tetrabutylammonium bromides, respectively. These are rough estimates based on observed regularities in the effects of various salts on various substrates.¹⁰ The contribution to the first-order k_{RB_r} values from direct

(9) The effect of the 0.0101 *M* lithium acetate in the runs may be judged¹⁰ to be negligible [see S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.*, **74**, 2171 (1952)].

(10) (a) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956); (b) S. Winstein, S. Smith and D. Darwish, *ibid.*, **81**, 5511 (1959); (c) S. Smith, unpublished work.

reaction with bromide ion may be taken equal to $[k_t^0(\text{MBr})\Delta b_t]$, where k_t^0 , (MBr) and Δb_t refer to eq. 3: (MBr) is the average bromide salt concen-

$$k_{RB_r} = k_t^0 [1 + b_t(\text{MBr})] \quad (3)$$

tration in the run, and Δb_t is the difference between observed and expected b_t values for a given bromide salt.

By evaluating the $[k_t^0(\text{MBr})\Delta b_t]$ contributions to the k_{RB_r} values of 1-phenyl-2-propyl toluenesulfonate at the average (MBr) values in the runs with the 1-anisyl-2-propyl ester, the corrections were estimated for the contribution of direct reactions with bromide to the k_{RB_r} values observed with the 1-anisyl-2-propyl arenesulfonate. As is clear from the measured and corrected k_{RB_r} values in Table II, the corrections represent only a small fraction of the observed k_{RB_r} values.

With the more reactive *threo*-3-anisyl-2-butyl system, any contribution to the observed k_{RB_r} values is quite negligible, judging by the behavior of *threo*-3-phenyl-2-butyl toluenesulfonate. A control experiment with the latter substrate showed that its rate of direct reaction with lithium bromide is quite low compared to the k_{RB_r} values obtained with the 3-anisyl-2-butyl system.

k_{ext}^0 Values.—Plots of the k_{RB_r} values vs. the average bromide salt concentration in each run are shown in Fig. 1 for the 1-anisyl-2-propyl system. It is quite clear that both the corrected and uncorrected k_{RB_r} values display the normal linear salt effect pattern in the 0.03–0.10 *M* salt concentration range. Also, extrapolation to zero salt concentration leads to an identical intercept, k_{ext}^0 , when either corrected or uncorrected k_{RB_r} values are employed. It is significant that the same k_{ext}^0 intercept value is obtained from both lithium and tetrabutylammonium bromide salts. This is shown graphically in Fig. 1 and numerically in Table VII.

TABLE VII

COMPARISON OF k_{ext}^0 VALUES FROM EFFECTS OF PERCHLORATE AND BROMIDE SALTS

System	Salt	10 ⁵ k_{ext}^0 , sec. ⁻¹
1-An-2-PrOTs ^a 50.0°	Bu ₄ NBr	2.92
	LiBr	2.91
	LiClO ₄	2.85
3-An-2-BuOBs ^b 25.0°	LiBr	5.01
	LiClO ₄	5.05

^a 1-Anisyl-2-propyl *p*-toluenesulfonate. ^b 3-Anisyl-2-butyl *p*-bromobenzenesulfonate.

It is quite clear from Fig. 1 that the k_{ext}^0 value for the 1-anisyl-2-propyl system is much above k_t^0 , the titrimetric acetolysis rate constant in the absence of salt, and yet it is considerably below k_1^0 , the ionization rate constant without added salt. The most interesting comparison is that between k_{ext}^0 obtained from k_{RB_r} values and k_{ext}^0 obtained previously^{7b} with lithium perchlorate as the special salt. As shown in Table VII, the two kinds of k_{ext}^0 values agree well within experimental error.

It is interesting to compare also for the 3-anisyl-2-butyl system the k_{ext}^0 values from lithium bromide and from lithium perchlorate as salts. The two k_{RB_r} values for this system at 25° lead to

a k_{ext}^0 intercept of $5.01 \times 10^{-5} \text{ sec.}^{-1}$. Again, as is summarized in Table VII, this k_{ext}^0 from lithium bromide as the salt is within experimental error identical with the k_{ext}^0 given by lithium perchlorate.⁵

Bromide and Perchlorate as Scavengers.—The agreement between k_{ext}^0 values from bromide exchange and from lithium perchlorate-accelerated solvolysis is evidence that bromide and perchlorate act as scavengers for the same solvolysis intermediates. In the special salt effect of salts such as lithium perchlorate, elimination of ion pair return is only partial; the best working hypothesis has been that perchlorate acts as a scavenger for the solvent-separated ion pair, thus eliminating external ion pair return.^{2,5-7} Evidently, bromide does this also.² On the other hand, both perchlorate and bromide permit internal return from the intimate ion pair. While both perchlorate and bromide trap the solvent-separated ion pair, the eventual products are different in the two cases. When perchlorate is the scavenger, solvolysis product is formed; when the scavenger is bromide, mainly alkyl bromide is produced.

The diversion of intermediate III by added salt MY is represented in solvolysis scheme I, the subscript x being used for RX and its related ion pairs, while y as subscript is employed for RY and its ion pairs. A subscript x or y outside a bracket pertains to all the rate constants within the brackets. When MY is lithium perchlorate, no RY accumulates, and the accelerated solvolysis rate constant k_t is given by the expression shown in the solvolysis scheme.⁶ This is written for the situation where MY exists very largely as ion pairs and these are the species which exchange with ion pairs III_x. At high MY concentration, all III_x is diverted to III_y, no return from III_x is permitted, and k_t is equal to $k_{\text{ext } x}$, the rate constant inclusive of internal return but without external ion pair return.

When MY is a bromide salt, diversion of III_x to III_y results in RY accumulation, since k_{1y} is small compared to k_{1x} . Where MY concentration is relatively constant, k_{RY} is given by an expression shown in the solvolysis scheme, which is, in fact, identical with the one for k_t in the case of a special salt such as lithium perchlorate. At high MBr concentrations, all III_x is diverted to III_y, and k_{RBr} becomes equal to $k_{\text{ext } x}$, just as does k_t for lithium perchlorate-accelerated solvolysis.

When diversion of $R^{\oplus} || X^{\ominus}$ to $R^{\oplus} || Br^{\ominus}$ is quite complete, the solvolysis product ROS arises by the k_{sy}^{III} path in the solvolysis scheme. Also, as

shown in the scheme, the ratio of solvolysis and bromide exchange products, [(ROS)/(RY)], is equal to the parameter a_y . The latter is related to the efficiencies of internal and external ion pair return associated with acetolysis of the alkyl bromide. Since [(ROS)/(RY)] is observed to be quite small in the present work, ion pair returns associated with alkyl bromide are obviously very efficient. There is other evidence of the relatively greater importance of ion pair return for bromides compared to the corresponding arenesulfonates. For example, the polarimetric:titrimetric ratio of rate constants in acetolysis is much greater for *exo*-norbornyl bromide than for the bromobenzene-sulfonate.^{2,11}

Experimental

Arenesulfonates.—The 1-anisyl-2-propyl toluene-sulfonate, m.p. 80.5–81.3°, acetolysis rate constant $(1.17 \pm 0.01) \times 10^{-5} \text{ sec.}^{-1}$ at 50.0°, and the *threo*-3-anisyl-2-butyl bromobenzene-sulfonate, m.p. 97.5–98.5°, were specimens employed previously.⁶ The 1-phenyl-2-propyl toluene-sulfonate was available from previous work.^{7a} Recrystallization gave rise to material, m.p. 91–92°.

Solvents and Salts.—Anhydrous acetic acid solvent was prepared in the usual way.⁶ Lithium and tetrabutylammonium acetates were those previously described.⁶ A stock solution of lithium bromide was prepared from Mallinckrodt N.F. grade material, water being destroyed with acetic anhydride. Lithium bromide solutions were standardized by Volhard titration.

Tetrabutylammonium bromide was prepared from Eastman Kodak Co. white label tetrabutylammonium iodide. The latter was treated with excess freshly prepared silver oxide in aqueous ethanol until the supernatant liquid tested free of iodide ion. The mixture was filtered and the filtrate was carefully neutralized with aqueous hydrobromic acid. Solvent was removed under reduced pressure and the crude product was twice recrystallized from ethyl acetate. The m.p. of the product, 102.7–103.5° (reported¹² 118°), was unchanged after several further recrystallizations. The equivalent weight of the material by Volhard titration was 324 (calcd. 322.4). There are apparently two crystalline forms of tetrabutylammonium bromide since a modification of m.p. 119° has been obtained by D. Darwish and I. D. R. Stevens¹³ in these laboratories. The latter also obtained the 103° modification with correct carbon, hydrogen and bromine analyses.

Kinetic Measurements.—Consumption of bromide ion was followed by pipetting a 5-ml. aliquot of reaction solution into a separatory funnel containing 25 ml. of pentane and 10 ml. of water. The mixture was given forty vigorous shakes, the aqueous layer was drained off, another 10 ml. of water was added and the procedure repeated. The combined aqueous extracts were acidified with nitric acid and excess standard aqueous silver nitrate was added from a calibrated buret. The excess silver nitrate was back-titrated with standard potassium thiocyanate solution.

(11) E. Clippinger, unpublished work.

(12) M. B. Reynolds and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 1709 (1948).

(13) D. Darwish and I. D. R. Stevens, unpublished work.