

was omitted. Results of gas chromatographic analysis are given in Table I, run 35.

A mixture of 88.3% 2-methyl-1-phenylpropene and 11.7% 2-methyl-3-phenylpropene (total 0.013 mole) was refluxed for 35 hours with 2 moles of acetic acid containing 0.02 mole of sodium acetate. After the usual work-up, the product was analyzed by gas chromatography (Table I, run 33).

Gas Chromatographic studies were carried out on two instruments: Aerograph model A-90-C and Aerograph model A-110-C (Wilkins Instrument and Research, Inc.). Chromosorb (Johns-Manville, Inc.) was the stationary phase on all columns. Most of the work was done on two columns: $10' \times \frac{3}{8}"$ Carbowax 20M (Union Carbide Co.—a polyethylene glycol having a molecular weight of about 20,000) and $10' \times \frac{1}{4}"$ Ucon Polar (Wilkins Instrument and Research, Inc.—a polypropylene glycol of unstated molecular weight). Approximate operating conditions for the Carbowax 20M column were 200 ml. He/min. at a column temperature of 120° and for the Ucon column 60 ml. He/min. at 160°.

Good separations of the olefins from each other and from the alcohols were obtained, except for the failure to separate V and VIIb. Attempts to separate *sec*-butylbenzene and isobutylbenzene with a wide variety of column materials failed.

Analysis for the small amounts of VIIa required special

techniques. Except with large samples, VIIa appeared as a slope change on the tailing end of IV. Therefore a large (1.5–2.0 ml.) sample was introduced and the olefins and alcohols collected separately. Re-introduction of the olefins at a higher injector temperature usually gave essentially complete resolution of IV and VIIa. In one run enough VIIa was collected for an infrared spectrum. The sample was shown, by comparison with authentic samples, to be mainly VIIa, with some IV as the only detectable contaminant.

Under the usual conditions of the gas chromatographic analyses, neophyl chloride partially decomposes in the injector block to hydrogen chloride and rearranged olefins. Consequently, the products from neophyl chloride solvolyses were run through the gas chromatograph at lower injector temperatures to remove unreacted neophyl chloride (usually about 30% of the total product). The olefin fraction was then resubmitted with the injector at its usual temperature (about 50° above the column).

When reaction products containing formate esters were introduced without prior conversion of the esters to alcohols, partial decomposition to olefin and alcohol occurred (Table I, runs 11, 18, 19). That this occurred in the gas chromatograph was shown by submission of pure ester, which still gave olefin and alcohol peaks. The alcohols were stable under the conditions adopted for the analyses.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIF.]

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. XVII.¹ Induced Common Ion Rate Depression and the Mechanism of the Special Salt Effect²⁻⁴

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For the mechanism of the special effect of non-common ion salts in acetolysis of certain arenesulfonates, there were previous strong indications against some type of "physical" explanation. The occurrence of induced common ion rate depression by added common ion salts supports a mechanism for the special salt effect involving diversion of a carbonium ion pair to a new ion pair species, thus suppressing ion pair return. The kinetic form of the special salt effect and induced depression is appropriate for this mechanism. Also, it shows that the ion pair exchanges responsible for the special salt effect and induced depression phenomena involve ion pairs of the added salts. The parameters derived from the kinetics of the special salt effect and induced depression in acetolysis of 1-anisyl-2-propyl and 3-anisyl-2-butyl arenesulfonates provide considerable insight into the magnitude of various rate ratios and equilibrium constants connected with the solvolysis scheme. Ingold's interpretation of the nucleophilic substitution and exchange reactions of trityl chloride in benzene is discussed and criticized.

As illustrated in solvolysis scheme I, it is helpful to distinguish between three varieties of carbonium ion intermediate in acetolysis of various systems,^{5,6} the intimate and solvent-separated ion pairs II and III, respectively, and the dissociated carbonium ion IV. Scheme I is designed for systems such as those with which we are concerned in the present

manuscript, where solvolysis product ROS is visualized^{1a,b,6,7} to arise from solvent-separated ion pair III and also the dissociated carbonium ion IV when the latter is formed. Return^{5,6} of carbonium ion intermediates toward covalent RX may occur from the dissociated carbonium ion stage (external ion return) or from ion pairs (ion pair return).⁶ Ion pair return may be further dissected^{6,7} into return from the intimate ion pair (internal return) and return from the solvent-separated ion pair (external ion pair return).

Certain systems in acetolysis respond to the addition of salts like lithium perchlorate with a combination of steep special^{1a-c,6,7,8} salt effects at low concentrations of added salt and the more shallow linear normal^{1d,6,9} salt effects at higher concentrations of salt. It is clear that the special salt effect is concerned with prevention of ion pair return.^{1a-c,6-9} However, in acetolysis of several systems examined in detail, namely, the 3-anisyl-2-butyl,⁷ 2-anisyl-1-propyl,^{1a} 2-anisyl-1-ethyl^{1b} and 4-methoxy-1-pentyl^{1c} arenesulfonates, the elimination of ion pair return

(1) Previous papers in this series: (a) X, S. Winstein and A. H. Fainberg, *THIS JOURNAL*, **80**, 459 (1958); (b) XI, E. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); (c) XII, S. Winstein, E. Alked and P. Klinedinst, Jr., page 48, Foreign Papers at VIIIth Mendeleev Congress of Pure and Applied Chemistry, Moscow, U.S.S.R., March, 1959; (d) XIII, S. Winstein, S. Smith and D. Darwish, *THIS JOURNAL*, **81**, 5511 (1959); (e) XIV, S. Winstein, S. Smith and D. Darwish, *Tetrahedron Letters*, **16**, 24 (1959); (f) XV, S. Winstein and J. S. Gall, *ibid.*, **2**, 31 (1960); (g) XVI, S. Winstein, J. S. Gall, M. Hojo and S. Smith, *THIS JOURNAL*, **82**, 1010 (1960).

(2) Presented in part at: (a) VIth Reaction Mechanism Conference, Swarthmore, Pa., Sept. 12, 1956; (b) VIIth Mendeleev Congress of Pure and Applied Chemistry, Moscow, U.S.S.R., March, 1959.

(3) Research supported by the National Science Foundation.

(4) Research sponsored by the Office of Ordnance Research, U. S. Army.

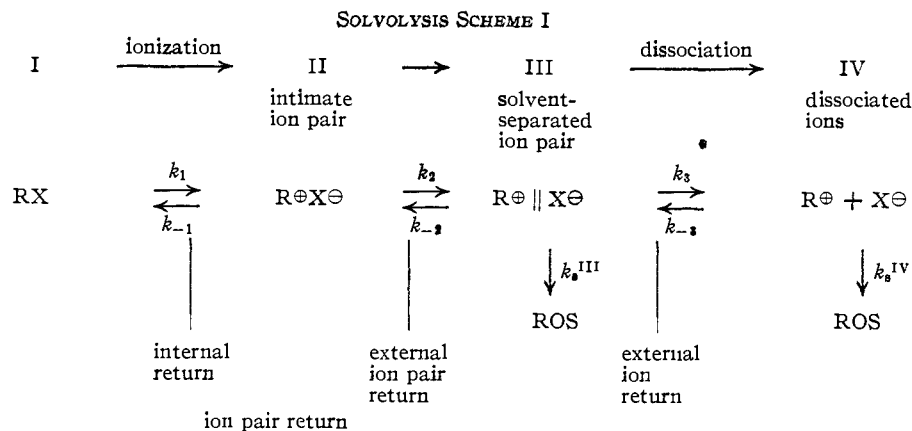
(5) (a) W. G. Young, S. Winstein and H. L. Goering, *THIS JOURNAL*, **73**, 1953 (1951); (b) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (c) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165, 2171 (1952).

(6) (a) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *ibid.*, **76**, 2597 (1954); (b) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *Chemistry & Industry*, 664 (1954); (c) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *THIS JOURNAL*, **78**, 328 (1956).

(7) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(8) (a) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956); (b) S. Winstein and E. Clippinger, *ibid.*, **78**, 2784 (1956).

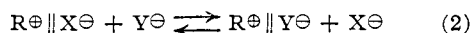
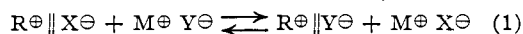
(9) (a) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2780 (1956).



by the special salt effect is only partial; a discrete fraction of ion pair return is not eliminated. The best explanation^{6,7} of the available facts is that external ion pair return is prevented by salts such as lithium perchlorate in the special salt effect, internal return still being permitted. What we shall be concerned with in the present manuscript is the mechanism and kinetic form of the special salt effect. Most of the observations will deal with the 1-anisyl-2-propyl toluenesulfonate system^{1b,10} but two others, namely, *threo*-3-anisyl-2-butyl⁷ and norbornyl^{6b} bromobenzenesulfonate, will be touched on briefly.

Mechanism of Special Salt Effect; Induced Common Ion Rate Depression.—For the mechanism of the special salt effect, one may consider either some type of "physical" explanation, or one involving specific chemical reactions between the added salt and ion pair intermediates in solvolysis. There are strong objections⁷ to the former type of explanation, the most compelling being the unique specificity of the special salt effect which makes a common ion salt ineffective.⁷ Therefore, the latter type of explanation must apply.

As regards the nature of the reaction between the special salt and the ion pair intermediate, the most attractive *a priori* possibility is an exchange reaction which diverts the solvent-separated ion pair, $R^\oplus \parallel X^\ominus$, to a new species and prevents ion pair return.^{6b,7,11} This exchange is formulated in eq. 1 and 2 as involving either an ion pair or only one of the ions of the added salt, respectively.



The expected reversibility of such exchange reactions suggests a new common ion salt effect which should appear if exchange is indeed the mechanism of the special salt effect.

In exchanges 1 or 2, the ion pair, $M^\oplus X^\ominus$, or common ion, X^\ominus , is produced. Addition of the common ion salt, MX , should depress the special salt-enhanced rate, thus giving rise to what may be termed "induced common ion rate depression." The occurrence of such induced depression would be support for the exchange mechanism of the special salt effect.

(10) A. H. Fainberg, G. C. Robinson and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2777 (1956).

(11) S. Winstein, *Experientia Supplementum II*, 137 (1955).

Previous work on the acetolysis of 1-anisyl-2-propyl toluenesulfonate^{6c,10,12} demonstrated the absence of common ion rate depression due to accumulating toluenesulfonic acid, HOTs. In the present work, the addition of the common ion salt, LiOTs, resulted in a very shallow linear salt effect illustrated in Fig. 1. With this salt the acetolysis kinetics were cleanly first order, the data being summarized in Table I. This table also shows that the experimental points fit the linear⁹ eq. 3 very well, the derived b_t value being 4.0. It is clear that addition of LiOTs by itself

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

results in no visible rate depression but gives instead the shallow accelerative normal salt effect. Following a previous discussion,^{6c} the present work confirms further that dissociation of the solvent-separated ion pair III may be neglected in acetolysis of 1-anisyl-2-propyl toluenesulfonate.

TABLE I
NORMAL SALT EFFECT OF LITHIUM *p*-TOLUENESULFONATE IN ACETOLYSIS OF 0.0100 *M* 1-*p*-ANISYL-2-PROPYL *p*-TOLUENESULFONATE AT 50.0°

(LiOTs), 10 ² <i>M</i>	10 ⁵ <i>k_t</i> , sec. ⁻¹		Fit, % of <i>k_t</i>
	Obsd.	Calcd. ^b	
0	1.17 ± 0.01 ^a	1.17	0.0
1.99	1.265 ± .005	1.263	.2
3.99	1.36 ± .01	1.36	.0
5.98	1.45 ± .01	1.45	.0

^a Previously¹² reported at 49.72°: 10⁵*k_t* = 1.20 ± 0.01; previously^{6c,10} reported at 50.0°: 10⁵*k_t* = 1.198 ± 0.007. The value, 1.918, in ref. 10 is a typographical error. ^b Calculated from 10⁵*k_t* = 1.17 [1 + 4.01 (LiOTs)].

The test for induced common ion rate depression in acetolysis of 1-anisyl-2-propyl toluenesulfonate was performed by adding LiOTs to acetolysis solutions containing 0.005 *M* LiClO₄. This concentration of special salt is sufficient to raise *k_t* to 2.47 × 10⁻⁵ sec.⁻¹, a value well above *k_t*⁰, which is 1.17 × 10⁻⁵ sec.⁻¹. Addition of the common ion salt at this lithium perchlorate concentration does indeed cause rate depression. Table II contains the results of this probe for induced common ion rate depression. Keeping the lithium perchlorate concentration constant at 0.005 *M* and adding more and more LiOTs over the range 0.001–0.04 *M* results in progressive depression of the lithium perchlorate-

(12) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *THIS JOURNAL*, **74**, 1140 (1952).

enhanced acetolysis rate constant, good first-order rate constants being obtained in each run (Table II).

TABLE II
INDUCED COMMON ION RATE DEPRESSION BY LITHIUM *p*-TOLUENESULFONATE IN ACETOLYSIS OF 0.0100 *M* 1-*p*-ANISYL-2-PROPYL *p*-TOLUENESULFONATE AT 50.0°

(LiClO ₄), 10 ³ <i>M</i>	(LiOTs), 10 ³ <i>M</i>	10 ³ <i>k</i> ₁ , sec. ⁻¹		Fit, % of <i>k</i> ₁
		Obsd.	Calcd. ^a	
4.96	0	2.47 ± 0.01	2.44	1.2
5.04	0.0997	2.41 ± .01	2.42	0.4
5.04	.300	2.35 ± .01	2.37	.9
5.04	.399	2.33 ± .01	2.35	.9
5.04	.997	2.25 ± .02	2.24	.4
5.04	1.99	2.13 ± .02	2.14	.5
5.04	3.99	2.07 ± .01	2.06	.5

^a Calculated from: $k_1/(k_{\text{ext}} - k_1) = 0.670 + [475(\text{LiClO}_4)]/[1 + 78.48(\text{LiOTs})]$ with $10^3 k_{\text{ext}} = 2.85 [1 + 27.4(\text{LiClO}_4) + 4.0(\text{LiOTs})]$.

Just as LiOTs fails to give common ion rate depression but does lead to induced depression in acetolysis of 1-anisyl-2-propyl toluenesulfonate, lithium bromobenzenesulfonate, LiOBs, behaves analogously in acetolysis of *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate.^{6c,7} Several pertinent measurements summarized in Table III show clearly that induced common ion rate depression can be made important in acetolysis of the 3-anisyl-2-butyl system. In fact, the phenomenon of induced common ion rate depression has been observed in these laboratories in acetolysis of every system which displays the special salt effect.

TABLE III
SOME ACETOLYSIS RATES AT 25.0° OF 3-ANISYL-2-BUTYL AND *exo*-NORBORNYL *p*-BROMOBENZENESULFONATES

ROBs	Added salt	Concn., 10 ² <i>M</i>	(LiOBs), 10 ² <i>M</i>	10 ³ <i>k</i> ₁ , sec. ⁻¹	10 ³ <i>k</i> ₁ , calcd. ^a
<i>dl</i> - <i>threo</i> -3- Anisyl-2- butyl ^{b,7}	LiClO ₄	0.10		1.96 ± 0.03	1.90
	LiClO ₄	.50		2.68 ± .08	3.03
	LiClO ₄	.50	2.50	4.69 ± .16	4.62
	LiClO ₄	1.00		3.47 ± .18	3.65
	LiClO ₄	1.00	1.00	5.70 ± .07	5.48
	LiClO ₄	1.00	2.50	5.14 ± .17	5.05
	LiClO ₄	1.00	2.50	4.80 ± .20	4.67
	LiOAc	1.00		2.83-2.12 ^c	
	LiOAc	3.00		3.58-2.82 ^d	
<i>exo</i> -Nor- bornyl ^{e,13}			2.50 ^f	9.0	
	LiClO ₄	5.00		9.8	
	LiClO ₄	5.00	2.50 ^f	26.7 ^g	
	LiClO ₄	5.00	2.50 ^f	29.8 ± 0.7	

^a Calculated from: $k_1/(k_{\text{ext}} - k_1) = 0.60 + [829(\text{LiClO}_4)]/[1 + 163(\text{LiOBs})]$ with $10^3 k_{\text{ext}} = 5.05 [1 + 21.6(\text{LiClO}_4) + 5(\text{LiOBs})]$. ^b Ca. 0.01 *M*. ^c 14-87% reaction range. ^d 20-78% reaction range. ^e 0.01-0.03 *M*. ^f LiOTs instead of LiOBs. ^g Interpolated value based on data at 0.03 and 0.06 *M* lithium perchlorate.

It is of some interest to examine the combined effect of both the common ion salt and the non-common ion salt, lithium perchlorate, in acetolysis of a system which does not show the special salt effect in acetolysis. *exo*-Norbonyl bromobenzenesulfonate is such a system, lithium perchlorate displaying essentially the normal pattern of salt effects on the titrimetric rate constant.^{9b,13} As

(13) E. Clippinger, S. Smith and P. Klinedinst, Jr., unpublished work.

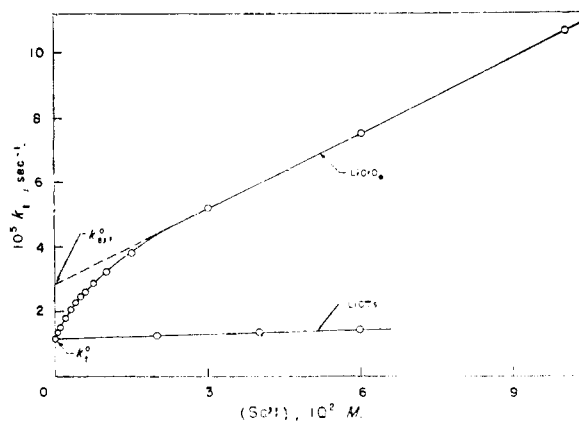


Fig. 1.—Effects of lithium perchlorate and toluenesulfonate in acetolysis of 1-*p*-anisyl-2-propyl toluenesulfonate at 50°.

summarized in Table III, LiOTs was added by Clippinger¹³ in acetolysis of norbornyl bromobenzenesulfonate in the presence of sufficient lithium perchlorate (0.05 *M*) to bring about a considerable rate enhancement. The addition of LiOTs instead of LiOBs permits one to detect not only a depression of initial rate constant but also any downward drift in rate constant due to conversion of alkyl bromobenzenesulfonate to alkyl toluenesulfonate during the acetolysis.^{6c} Actually, neither effect of the added LiOTs was observed, only normal slight increases in rate constant being caused by the extra added salt.

The results obtained with the norbornyl system confirm the explanation of the mechanism of induced common ion rate depression. Since induced depression counteracts the special salt effect, and the latter is concerned with elimination of ion pair return from the solvent-separated ion pair III, neither the special salt effect nor induced depression can be expected to occur with a system which does not show external ion pair return in acetolysis. Norbornyl bromobenzenesulfonate is thought to be just such a system.⁷

While the occurrence of induced common ion rate depression represents qualitative support for a mechanism of the special salt effect involving diversion of the solvent-separated ion pair III to a new species by exchange, only the kinetics of the special salt effect will disclose whether the exchange mechanism involves an ion pair or a dissociated ion of the salt, and whether it accounts quantitatively for the special salt effect. However, before treating the kinetics of the special salt effect, it is necessary to inquire into the state of aggregation of the various salts in glacial acetic acid solvent.

Salts in Acetic Acid Solvent.—The chemical literature contained some information on the nature of electrolytes in glacial acetic acid solvent when we began the solvolytic studies in this solvent. More information appeared while the solvolytic studies were in progress, and this information has been supplemented with conductivity studies on various salts carried out in these laboratories.¹³ As can be expected¹⁴ for a solvent with a dielectric

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publishing Corp., New York N. Y., 1958, Chapter 7.

In eq. 10, the term $b_s(M^{\oplus}Y^{\ominus})$ corresponds to the special salt effect and $c(M^{\oplus}X^{\ominus})$ is associated with induced depression. In the absence of added common ion salt, eq. 10 reduces to 11, and this

$$Z = \frac{k_t}{k_{\text{ext}} - k_t} = a + b_s(M^{\oplus}Y^{\ominus}) \quad (11)$$

is the predicted kinetic form of the special salt effect if it is due to ion pair exchange as in eq. 1.

An analogous steady state derivation of the kinetic form of the special salt effect where it is due to exchange of carbonium ion pair with a single salt ion, as in eq. 2, leads to an equation identical with 11, except that the ion concentration (Y^{\ominus}) is substituted for the ion pair concentration ($M^{\oplus}Y^{\ominus}$).

In the previous experimental work on the special salt effect of lithium perchlorate in acetolysis of 1-anisyl-2-propyl toluenesulfonate¹⁰ no detailed examination of the effect of lithium perchlorate at low salt concentrations was carried out. Such an examination has now been made. Steady first-order rate constants were observed over the whole range of lithium perchlorate concentrations employed, and these are summarized in Table IV. As is clear from this table, there was good agreement between the results of the present work and those of the earlier investigation at the few isolated points where there was duplication. The results are shown graphically in Fig. 1, where the familiar two-stage effect of lithium perchlorate is evident. The points on the k_{ext}^0 , k_t line are from the earlier work.

TABLE IV

SPECIAL SALT EFFECT OF LITHIUM PERCHLORATE IN ACETOLYSIS OF 0.0100 M 1-*p*-ANISYL-2-PROPYL *p*-TOLUENESULFONATE AT 50.0°

(LiClO ₄), 10 ³ M	10 ⁵ k _t , sec. ⁻¹		Fit, % of k _t
	Obsd.	Calcd. ^d	
0	1.17 ± 0.01 ^a	1.14	2.6
0.0503	1.36 ± .01	1.38	1.5
.100	1.53 ± .01 ^b	1.56	2.0
.201	1.80 ± .02	1.86	3.3
.298	2.06 ± .02	2.08	1.0
.399	2.28 ± .01	2.27	0.4
.496	2.47 ± .01	2.44	1.2
.596	2.61 ± .02	2.58	1.1
.744	2.86 ± .01	2.77	3.1
1.01	3.21 ± .02 ^c	3.08	4.0
1.51	3.79 ± .01	3.57	5.8

^a Previously reported¹⁰: 10⁵k_t = 1.198 ± 0.007. ^b Previously¹⁰ reported: 10⁵k_t = 1.52 ± 0.02. ^c Previously¹⁰ reported: 10⁵k_t = 3.19 ± 0.04. ^d Calculated from $k_t/(k_{\text{ext}} - k_t) = 0.670 + 475(\text{LiClO}_4)$ with 10⁵ $k_{\text{ext}} = 2.85 [1 + 27.4(\text{LiClO}_4)]$.

In order to test the applicability of eq. 11 to the special salt effect of lithium perchlorate in acetolysis of 1-anisyl-2-propyl toluenesulfonate, a plot of Z or $[k_t/(k_{\text{ext}} - k_t)]$ vs. salt concentration, (LiClO₄), was prepared. The k_{ext} values, corresponding to points on the k_{ext}^0 , k_t straight line of Fig. 1, are given by eq. 12, where k_{ext}^0 and b_t are 2.85×10^{-5} sec.⁻¹ and 27.4, respectively.¹⁰ Figure 2 shows

$$k_{\text{ext}} = k_{\text{ext}}^0 [1 + b_t(\text{salt})] \quad (12)$$

the plot of Z vs. (LiClO₄) values of 5×10^{-4} to $5 \times 10^{-3} M$. In this concentration range (LiClO₄) is a good approximation to the salt ion pair concentra-

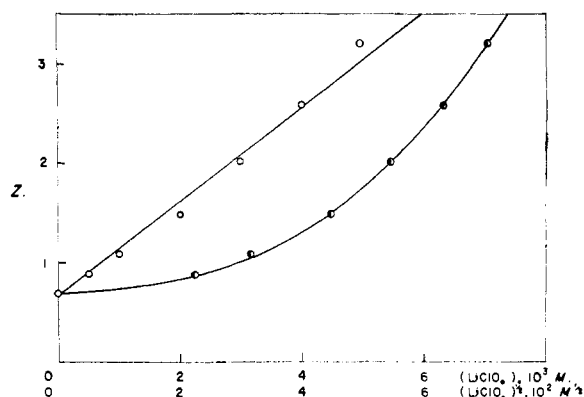


Fig. 2.—Analysis of special salt effect of lithium perchlorate in acetolysis of 1-anisyl-2-propyl toluenesulfonate at 50°: open circles, first power salt; semi-closed circles, half power salt.

tion ($M^{\oplus}Y^{\ominus}$) as explained in a previous section of the paper. Another reason for omitting points at higher (LiClO₄) values from Fig. 2 is that $[k_t/(k_{\text{ext}} - k_t)]$ becomes very inaccurate as k_t approaches k_{ext} .

It is evident from Fig. 2 that $[k_t/(k_{\text{ext}} - k_t)]$ is nicely linear in the first power of the lithium perchlorate concentration. Using a - and b_s -values of 0.670 and 475, respectively, as determined from the slope and intercept of the straight line plot, eq. 11 reproduces the data with a mean deviation of 2.4% of k_t even up to (LiClO₄) equal to 0.015 M. This is shown explicitly in Table IV.

Included in Fig. 2 is a plot of $[k_t/(k_{\text{ext}} - k_t)]$ vs. (LiClO₄)^{1/2}. In the range of salt concentrations involved, (ClO₄⁻) is fairly closely proportional to (LiClO₄)^{1/2}, so this plot should lead to a straight line if the special salt effect involves a single salt ion. As indicated by the extensive curvature of this plot, exchange with a salt ion pair accounts much more satisfactorily for the special salt effect than does the alternative exchange with a single ion.

Kinetic Form of Induced Common Ion Rate Depression.—The kinetic form of induced common ion rate depression may be examined with the aid of eq. 13. This is a modification of eq. 10 based on exchanges between two ion pairs as in eq. 1. On this basis, a plot of Z vs. common ion salt concentration (MX) at a fixed special salt concentration

$$Z = \frac{1}{\left(\frac{k_t}{k_{\text{ext}} - k_t}\right) - a} = \frac{1}{b_s(M^{\oplus}Y^{\ominus})} + \left[\frac{c}{b_s(M^{\oplus}Y^{\ominus})}\right](M^{\oplus}X^{\ominus}) \quad (13)$$

(MY) should be linear. On the other hand, if exchanges of carbonium ion pairs involve single salt ions, the plot of Z vs. (MX)^{1/2} should be linear.

In applying eq. 13 to the data in Table II, the parameter a was available as the intercept of the straight line plot of Fig. 2. For k_{ext} the method of eq. 12 was used, assuming normal salt effects of the perchlorate and toluenesulfonate salts to be additive.^{9a} A plot of Z vs. (LiOTs) at 0.005 M lithium perchlorate turns out to be nicely linear, the fit of the data by eq. 13 being very satisfactory. The slope of the plot leads to a value of 78.5 for the

parameter c , while the intercept corresponds to a b_s -value of 470, in excellent agreement with the value of 475 previously obtained from the treatment of the special salt effect data. Using the graphically determined parameters, eq. 13 reproduces the data on induced common ion rate depression with a mean deviation of less than 1%, as indicated in Table II.

A plot of the complex quantity Z of eq. 13 vs. $(\text{LiOTs})^{1/2}$ shows definite curvature, the fit of the data to the first power of the concentration of common ion salt being definitely superior. Thus both induced depression and the special salt effect are better accounted for by exchange of carbonium ion pairs with salt ion pairs than with single salt ions. That the same version of the exchanges occurs in both phenomena is, of course, to be expected from the principle of microscopic reversibility.

Parameters for the *threo*-3-Anisyl-2-butyl System.—The fragmentary data for acetolysis of *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate in Table III permit one to estimate the a , b_s and c parameters for this compound. Since dissociated carbonium ions are not involved in acetolysis of this system,^{6,7} the equations developed for scheme II were employed in the analysis. In the treatment of the data, the published values⁷ of 5.05×10^{-5} sec.⁻¹ for k_{ext}^0 and 21.6 for b_t for lithium perchlorate and an estimated value of 5 for b_t for lithium bromobenzenesulfonate were employed.

A plot of $[k_t/(k_{\text{ext}} - k_t)]$ vs. (LiClO_4) for the runs containing only added perchlorate salt leads to values of 0.60 and 829 for a and b_s , respectively. With these parameters, values of c were calculated with the aid of eq. 10 from the data of each run with added lithium bromobenzenesulfonate. An average c -value of 163 was determined by this procedure. Using the above parameters, eq. 10 reproduces the experimental data reasonably well, as shown in Table III.

Special Salt Effect of Lithium Acetate and Induced Depression.—The kinetic behavior of a system displaying special salt effects in acetolysis is especially complex when the added special salt is lithium acetate. As already indicated previously,^{6b,8b} lithium acetate is relatively ineffective as a special salt compared to lithium perchlorate. Also, it is consumed during a run. For these reasons alone, k_t may be expected to drift down badly in a run. However, the fact that lithium arenesulfonate accumulates and causes induced rate depression in a run provides an additional cause for downward drift.

Two runs with *threo*-3-anisyl-2-butyl bromobenzenesulfonate which illustrate the above situation are summarized in Table III, and one of them is shown in more detail in Table V. The concentrations of lithium acetate employed were necessarily much above the 10^{-4} – 5×10^{-8} M range discussed earlier, but the data were arbitrarily treated as though salt concentrations were low.

From the data for acetolysis of 0.01 M *threo*-3-anisyl-2-butyl bromobenzenesulfonate in the presence of 0.0300 M lithium acetate summarized in Table V, b_s for lithium acetate, LiOAc, and c for lithium bromobenzenesulfonate, LiOBs, were eval-

TABLE V
ACETOLYSIS OF 0.00996 M *threo*-3-ANISYL-2-BUTYL *p*-BROMOBENZENESULFONATE WITH 0.0300 M LITHIUM ACETATE AT 25.0°

Time, 10 ⁻¹ sec.	(LiOAc), 10 ³ M	(LiOBs), ^a 10 ³ M	Integ. 10 ³ k_t , sec. ⁻¹	Instant. Obsd. ^b	10 ³ k_t Calcd. ^c	Fit. % of k_t
0	2.92	0.07		3.41	3.47	1.8
3.78	2.80		3.58			
5.00	2.78 ^a	.22		3.22	3.17	1.6
7.20	2.70		3.47			
10.00	2.65 ^a	.35		2.99	2.98	0.3
15.00	2.55 ^a	.45		2.85	2.85	0.0
18.15	2.51		3.07			
20.00	2.47 ^a	.53		2.76	2.77	0.4
27.85	2.39		2.91			
30.00	2.35 ^a	.65		2.44	2.66	9.0
46.00	2.22		2.82			

^a Smoothed values from a plot of concentration vs. time.
^b Obtained graphically from a plot of $\log [a/(a-x)]$ vs. time.
^c Calculated with eq. 10; normal salt effects of lithium acetate and bromobenzenesulfonate were neglected, k_{ext}^0 being used for k_{ext} .

uated from a plot of $Z(\text{LiOAc})$ vs. (LiOBs) , following eq. 13. The necessary instantaneous k_t -values were obtained graphically. The intercept of the line $1/b_s$ corresponded to a b_s of 67, while the slope c/b_s was 5.18, corresponding to a c of 345. As shown in Table V, these b_s - and c -values reproduce the instantaneous k_t -values quite well. They reproduce similarly the k_t -values in the other run at 0.01 M lithium acetate listed in Table III.

Tetrabutylammonium Salts.—In order to contrast tetrabutylammonium salts with their lithium counterparts, some attention was given to the effects of tetrabutylammonium perchlorate and toluenesulfonate in acetolysis of 1-anisyl-2-propyl toluenesulfonate, although more extended studies with these salts have been carried out for other systems.^{1c} Table VI lists the observed k_t -values for acetolysis of 0.01 M 1-anisyl-2-propyl toluenesulfonate in the presence of the tetrabutylammonium salts.

The first four entries in Table VI refer to acetolysis with added tetra-*n*-butylammonium *p*-toluenesulfonate (Bu_4NOTs). As is evident from Fig. 3, only the shallow linear normal salt effect is visible. Thus, there is no evidence of common ion rate depression even with Bu_4NOTs , a common ion salt which is more dissociated in acetic acid solvent than lithium toluenesulfonate¹³ and more efficient in common ion rate depression. As is evident from Table VI, the data are described very well by the normal salt effect eq. 3 with a b_t -value of 4.3.

The few runs made with added tetrabutylammonium perchlorate, Bu_4NClO_4 , summarized in Table VI and Fig. 3, show that this salt causes the steep special salt effect but somewhat less efficiently than lithium perchlorate. The addition of various concentrations of Bu_4NOTs in acetolysis of 1-anisyl-2-propyl toluenesulfonate in the presence of 0.01 M Bu_4NClO_4 obviously give rise to induced common ion rate depression (Table VI).

The data on induced common ion rate depression were analyzed graphically in terms of eq. 13 as was done in the case of the lithium salts. As before, the plot of the complex quantity Z vs. (Bu_4NOTs) was

TABLE VI

SOME ACETOLYSIS RATES OF 1-*p*-ANISYL-2-PROPYL *p*-TOLUENESULFONATE WITH ADDED TETRABUTYLAMMONIUM SALTS

Added salt	Concn., 10 ³ M	10 ⁵ k _t , sec. ⁻¹		Fit, % of k _t
		Obsd.	Calcd.	
Bu ₄ NOTs	0.800	1.19 ± 0.01	1.20 ^b	0.8
Bu ₄ NOTs	1.98	1.26 ± .01	1.26 ^b	.0
Bu ₄ NOTs	3.96	1.36 ± .01	1.36 ^b	.0
Bu ₄ NOTs	5.94	1.46 ± .02	1.46 ^b	.0
Bu ₄ NCIO ₄	0.300	1.73 ± .02		
Bu ₄ NCIO ₄	1.01	2.44 ± .01	2.44 ^a	.0
Bu ₄ NCIO ₄	2.49	3.25 ± .01		
Bu ₄ NCIO ₄	1.01	2.21 ± .01	2.21 ^a	.0
Bu ₄ NOTs	0.0798			
Bu ₄ NCIO ₄	1.01	1.99 ± .01	2.00 ^a	.5
Bu ₄ NOTs	0.197			
Bu ₄ NCIO ₄	1.01	1.79 ± .01	1.80 ^a	.6
Bu ₄ NOTs	0.397			
Bu ₄ NCIO ₄	1.01	1.61 ± .01	1.61 ^a	.0
Bu ₄ NOTs	0.822			
Bu ₄ NCIO ₄	1.01	1.54 ± .01	1.51 ^a	1.9
Bu ₄ NOTs	1.60			
Bu ₄ NOAc	1.00	2.54 ^a	2.50 ^a	1.6

^a Downward drifting rate constant; see Table VII.

^b Calculated from 10⁵k_t = 1.16 [1 + 4.31 (Bu₄NOTs)].

^c Calculated from: k_t/(k_{ext} - k_t) = 0.670 + [364 (Bu₄NCIO₄)]/[1 + 939 (Bu₄NOTs)] with 10⁵k_{ext} = 2.85 [1 + 5(Bu₄NCIO₄) + 4.3(Bu₄NOTs)].

TABLE VII

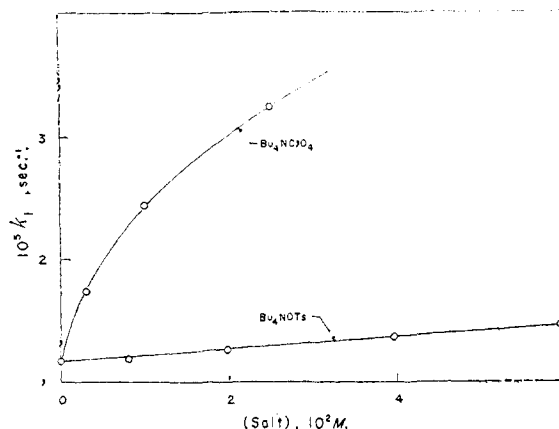
ACETOLYSIS OF 0.0100 M 1-*p*-ANISYL-2-PROPYL *p*-TOLUENESULFONATE WITH 0.0100 M TETRABUTYLAMMONIUM ACETATE AT 50.0°

Time, 10 ⁻³ sec.	(Bu ₄ NOAc), 10 ³ M	(Bu ₄ NOTs), 10 ³ M	Instant. 10 ⁵ k _t		Fit, % of k _t
			Obsd. ^a	Calcd. ^b	
0	1.00	0	2.54	2.50	1.6
1.60	0.961	0.040	2.45	2.46	0.4
3.60	.915	.085	2.40	2.40	0
6.00	.866	.134	2.34	2.34	0
8.20	.822	.178	2.28	2.28	0
12.00	.755	.245	2.20	2.20	0
17.50	.670	.330	2.08	2.09	0.5
21.40	.619	.381	2.01	2.03	1.0
27.80	.544	.456	1.94	1.92	1.0
37.00	.457	.543	1.86	1.81	2.7
47.00	.380	.620	1.80	1.72	4.4
63.50	.287	.713	1.68	1.59	5.4
82.00	.214	.786	1.43	1.49	4.2

^a Estimated graphically from a plot of log [a/(a-x)] vs. time. ^b Calculated from k_t/(k_{ext} - k_t) = 0.670 + [410(Bu₄NOAc)]/[1 + 218(Bu₄NOTs)] with 10⁵k_{ext} = 2.85[1 + 6.3(Bu₄NOAc) + 4.3(Bu₄NOTs)].

found to be linear and the plot vs. (Bu₄NOTs)^{1/2} was extensively curved. From the intercept and slope of the straight line plot, values of 364 and 939 were obtained for *b*_s and *c*, respectively. These parameters reproduce the rate data for the tetrabutylammonium salts with an average deviation of less than 1% (Table VI).

The final entry in Table VI is for acetolysis of 1-anisyl-2-propyl toluenesulfonate with added 0.01 M tetrabutylammonium acetate (Bu₄NOAc). Just as for 3-anisyl-2-butyl bromobenzenesulfonate with added lithium acetate, first-order rate constants drift down rapidly in the run because the added acetate is consumed and common ion salt is made

Fig. 3.—Effects of tetra-*n*-butylammonium salts in acetolysis of 1-*p*-anisyl-2-propyl toluenesulfonate at 50°.

available for induced common ion rate depression. Table VII contains an analysis of the run with added Bu₄NOAc. A plot of the quantity *Z* (Bu₄NOAc) vs. (Bu₄NOTs) according to eq. 13 yielded a good straight line, *b*_s- and *c*- values of 410 and 218, respectively, being obtained from the slope and intercept. These parameters reproduce the instantaneous acetolysis rate constants for the run with a mean deviation of 1.6% (Table VII).

Values of *a*, *b*_s and *c*; Rate Ratios and Equilibrium in Ion Pair Exchanges.—In Table VIII are collected the various *a*, *b*_s and *c* parameters whose evaluation has been described above. It is of some interest to examine these further.

Considering first the parameter *a* defined in solvolysis scheme II we see from eq. 10 that it represents the quantity [k_t/(k_{ext} - k_t)] at zero salt concentrations. This is expressed more formally by eq. 14. Therefore, (k_{ext}⁰/k_t⁰) ratios provide an alternative way to evaluate

$$k_t^0/(k_{ext}^0 - k_t^0) = a \quad (14)$$

the *a* parameter. Table VIII shows the good agreement between the *a*-values obtained from the intercepts of plots of [k_t/(k_{ext} - k_t)] vs. (MY), on the one hand, and previously available k_{ext}⁰/k_t⁰ ratios^{7,10} on the other.

The efficiency of the special salt in the special salt effect was characterized previously with the aid of the quantity^{6,8} (MY)_{1/2}, the concentration of salt which introduces one-half of the special salt effect. This quantity was estimated graphically from a plot of k_t vs. (MY). On the basis of the mechanism of the special salt effect in solvolysis scheme II and the defined *a* and *b*_s parameters, (MY)_{1/2} can be shown to be equal to [(*a* + 1)/*b*_s]. In Table VIII are listed the (MY)_{1/2} values given by the *a*- and *b*_s-values obtained from the present work on the kinetic form of the special salt effect and induced depression. For lithium perchlorate as the special salt, the (LiClO₄)_{1/2} values of 3.5 × 10⁻³ M and 1.9 × 10⁻³ M for the 1-anisyl-2-propyl and 3-anisyl-2-butyl systems, respectively, compare very favorably with the values previously estimated graphically, namely, 3 × 10⁻³ and 2.2 × 10⁻³ M, respectively.^{1a,7}

The efficiency of exchange or capture of the solvent-separated ion pair III₂ by the special salt MY

TABLE VIII
 COLLECTED PARAMETERS AND DERIVED QUANTITIES

System Temp., °C.	1-An-2-PrOTs ^a			3-An-2-BuOBs ^b	
	50.0			25.0	
Special salt	LiClO ₄	Bu ₄ NClO ₄	Bu ₄ NOAc	LiClO ₄	LiOAc
Common ion salt	LiOTs	Bu ₄ NOTs	Bu ₄ NOTs	LiOBs	LiOBs
<i>a</i> , graphical	0.670			0.60	
<i>a</i> , $k_t^0/(k_{ext}^0 - k_t^0)$	0.696			0.63	
<i>b</i> _s	475	364	410	829	67
<i>c</i> , ($k_{ey}^{III}/k_{sy}^{III}$)	78.5	939	218	163	345
(MY) _{1/2} , graphical, ^{1a,7} 10 ³ M	3			2.2	
(MY) _{1/2} , (<i>a</i> + 1)/ <i>b</i> _s , 10 ³ M	3.5	4.6	4.1	1.9	24
(k_{ex}^{III}/k_{-2}), [$b_s k_{-1}/(k_{-1} + k_2)$] ^c	166	127	143	307	25
($k_{ex}^{III}/k_{ex}^{III}$), (<i>b</i> _s / <i>a</i>)	709	543	612	1380	112
[$K k_{sy}^{III}/k_{sx}^{III}$], [<i>b</i> _s /(<i>a</i> <i>c</i>)]	9.03	0.58	2.81	8.46	0.32

^a 1-Anisyl-2-propyl *p*-toluenesulfonate. ^b *threo*-3-*p*-Anisyl-2-butyl *p*-bromobenzenesulfonate. ^c [$k_{-1}/(k_{-1} + k_2)$] values at zero salt concentration available from previous work on these systems^{1a,7} were employed in this calculation.

may be expressed in terms of the ratios (k_{ex}^{III}/k_{-2}) or ($k_{ex}^{III}/k_{sx}^{III}$). Reference to the definitions of the *a* and *b*_s parameters shows that the first of these ratios may be evaluated from the values for *b*_s and for [$(k_{-1} + k_2)/k_{-1}$]. The ($k_{ex}^{III}/k_{sx}^{III}$) ratio is simply *b*_s/*a*. The (k_{ex}^{III}/k_{-2}) and ($k_{ex}^{III}/k_{sx}^{III}$) ratios calculated in this manner are summarized in Table VIII.

By reference to the values of (MY)_{1/2}, *b*_s, (k_{ex}^{III}/k_{-2}) or ($k_{ex}^{III}/k_{sx}^{III}$), it is evident that there are no major differences between LiClO₄, Bu₄NClO₄ and Bu₄NOAc in efficiency as special salts. On the other hand, LiOAc is very much less efficient than the other special salts.

The parameter *c*, or $k_{ey}^{III}/k_{sy}^{III}$, which characterizes induced common ion rate depression, has the same meaning for ion pair III_y as the ratio $k_{ex}^{III}/k_{sx}^{III}$ has for III_x. It is obvious from Table VIII that large changes in the relative values of these ratios are produced by changing the special and common ion salt pairs. For example, with the LiClO₄, LiOTs salt pair, LiClO₄ is much more efficient in the capture of III_x than LiOTs is in trapping III_y. On the other hand, with the Bu₄NClO₄, Bu₄NOTs salt pair, Bu₄NOTs competes more effectively for III_y than does Bu₄NClO₄ for III_x.

It is interesting that no serious kinetic disturbance was observed due to induced common ion rate depression by accumulating toluenesulfonic acid (HOTs) or bromobenzenesulfonic acid (HOBs) in special salt-enhanced acetolysis of the 1-anisyl-2-propyl and 3-anisyl-2-butyl systems. Evidently, *c*-values for HOTs and HOBs are very small. This fortunate circumstance is probably to be ascribed mainly to a low degree of ionization of these acids. That they are only slightly ionized may be judged by their unusually low over-all dissociation constants in acetic acid solvent.¹⁷

Although equilibrium for the exchange reaction in eq. 1 is not maintained during solvolysis, one may consider the equilibrium constant *K* defined by eq. 15. This equilibrium constant is equal to

$$\frac{(\text{III}_y)(\text{M}^\oplus\text{X}^\ominus)}{(\text{III}_x)(\text{M}^\oplus\text{Y}^\ominus)} = K = \frac{k_{ex}^{III}}{k_{ey}^{III}} \quad (15)$$

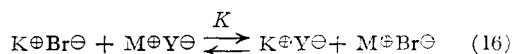
($k_{ex}^{III}/k_{ey}^{III}$), but this ratio is not available. How-

ever, the available parameters permit us to evaluate a quantity which may well approximate *K*.

Reference to the definitions of parameters *a*, *b*_s and *c* shows that (*b*_s/*a**c*) is equal to *K* ($k_{sy}^{III}/k_{sx}^{III}$). Thus, a quantity may be evaluated which differs from *K* by only the factor ($k_{sy}^{III}/k_{sx}^{III}$), the ratio of rate constants for collapse to solvolysis product of the III_y and III_x ion pairs. To the extent this ratio approximates unity, (*b*_s/*a* *c*) approaches *K*.

From Table VIII it is clear that the 1-anisyl-2-propyl and 3-anisyl-2-butyl systems behave similarly as regards the (*b*_s/*a* *c*) approximation to *K*. With LiClO₄ as special salt and LiOTs or LiOBs as common ion salt, (*b*_s/*a* *c*) is 8-9 for both systems. With this salt pair, the equilibrium constant for the ion pair exchange in eq. 1 is favorable. However, (*b*_s/*a* *c*) changes greatly as the salt pair varies, and the equilibrium constant is unfavorable for the Bu₄NClO₄, Bu₄NOTs salt pair, for example. A more quantitative treatment of the *K*-values has been given in outline elsewhere,^{1c} and it will be dealt with in detail in a later paper in this series.

Ion Pair Metathesis and Modifications of the Solvolysis Scheme.—From the kinetic evidence, the special salt effect and induced depression phenomena observed in acetolysis of arenosulfonates involve metathetical interconversions between ion pairs III_x and III_y, by reactions with salt ion pairs M[⊕]Y[⊖] or M[⊕]X[⊖]. Analogous formulations involving electrolyte ion pairs account for various equilibrium phenomena in acetic acid solvent. One interesting example involves the solubility of a salt like potassium bromide and its increase by non-common ion salts such as lithium acetate or formate. It is interesting that Griswold and co-workers¹⁸ were able to account for the solubility increase on the basis of a diversion of K[⊕]Br[⊖] as K[⊕].Y[⊖] ion pairs according to eq. 16. With the aid of an equilibrium constant, *K*, for the metathetical



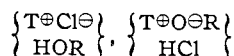
equilibrium in eq. 16, the solubility data could be accounted for quantitatively in some cases.

(17) (a) I. M. Kolthoff and S. Bruckenstein, *THIS JOURNAL*, **78**, 1 (1956); (b) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956).

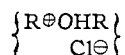
(18) (a) E. Griswold, M. M. Jones and R. K. Birdwhistell, *ibid.*, **75**, 5701 (1953); (b) E. Griswold and W. E. Parker, Abstracts of Papers, American Chemical Society Meeting, Minneapolis, Minn., Sept., 1955.

chlorobenzhydryl chloride in acetone²⁵ or acetic acid²⁶ solvents, rate of racemization exceeds rates of chloride exchange or solvolysis by substantial factors. Rate of ionization is at least as large as that of racemization, so, in this case, rate of ionization is much greater than rate of chloride exchange.

The detailed mechanistic scheme employed by Ingold¹⁹ for trityl chloride in benzene differs in many respects from the one we employ as our best working hypothesis for certain arenosulfonates in acetic acid solvent. For the methanolysis of trityl chloride in benzene with low concentrations of methanol, he visualizes four ion pair intermediates, namely, $T^{\oplus}Cl^{\ominus}$



and $R^{\oplus}O^{\ominus}R$. However, for the latter two species,



and $R^{\oplus}OHR$ were mentioned as alternatives. For the special salt effect of tetrabutylammonium perchlorate, he envisages an attack of the single perchlorate ion on $T^{\oplus}Cl^{\ominus}$ with possible formation of the triple ion $ClO_4^{\ominus}T^{\oplus}Cl^{\ominus}HOR$. On the other hand, for induced depression by tetrabutylammonium chloride, Ingold assumes that a tetrabutylammonium chloride ion pair acts on the triple ion. In the exchange reactions of trityl chloride in benzene, Ingold emphasizes the role of ion quadruplets in the conversion of $T^{\oplus}Cl^{\ominus}$ and $M^{\oplus}Y^{\ominus}$ ion pairs to two new ion pairs, $T^{\oplus}Y^{\ominus}$ and $M^{\oplus}Cl^{\ominus}$. In fact, his mechanism includes two ion quadruplets, their interconversion being slow.

Ingold's mechanistic scheme is supported by long and involved, partly intuitive, arguments, some of which we find it impossible to follow. The mechanism is not supported by a thoroughgoing objective analysis of the expected kinetics. By using the steady state assumption for all the intermediates involved, it is possible to derive the kinetic expressions for rates of exchange or methanolysis which correspond to the proposed schemes, and this we have done. As Swain²⁴ has already pointed out, it is impossible on this basis to understand how rates of exchange of trityl chloride can be independent of the reagent salt concentration and yet dependent on the nature of the reagent salt. Ingold¹⁹ appears to be convinced of this latter fact, and his mechanism purports to account for it. Also, on this basis one does not expect any common ion rate depression (ordinary, not the induced variety) of the methanolysis by added tetrabutylammonium chloride. Nevertheless, serious depression of the uncatalyzed rate of methanolysis by common ion salt is reported by Ingold and his co-workers and discussed in terms of competition between a salt ion pair and a methanol molecule for the $T^{\oplus}Cl^{\ominus}$ ion pair. Ingold's failure to subject his scheme to a conventional steady state treatment makes one suspect that he believes this situation should not be treated by conventional kinetics.²⁷ Also, it is by no means evident that Ingold believes the principle

of microscopic reversibility is everywhere applicable in his mechanism.

We can certainly anticipate changes⁷ in the kinetic patterns and the nature and importance of various carbonium ion intermediates in solvolysis and related reactions as solvent changes grossly. We already have indications of such changes with arenosulfonates and halides as solvent is varied from acetic acid toward more or less dissociating and ion-solvating ones.¹³ However, it is not yet clear just how the situation in benzene containing small amounts of a hydroxylic species such as methanol compares with that in acetic acid solvent. Certainly, the Ingold work needs to be clarified. Also, we are engaged in the investigation of a system which will afford more information regarding the actual ionization rate and, therefore, more insight into the nature of solvolytic and exchange reactions in benzene.

As regards ion quadruplet intermediates for the ion pair exchanges in eq. 1, it is, of course, obvious that two ion pairs must pass through ion quadruplet arrangements during an exchange. We have intentionally omitted ion quadruplets for the sake of simplicity. Since we find it sufficient to employ a solvolysis scheme which has solvolysis product arise from ion pairs and not ion quadruplets, the kinetic form of the solvolysis rate, special salt effect and induced depression is unaffected by inclusion of any number of ion quadruplets as intermediates in the ion pair exchanges. It should be noted that the Ingold mechanisms for reactions of trityl chloride in benzene also have products arising only from ion pairs and not ion quadruplets. Therefore, for a steady state treatment of his scheme, ion quadruplets could just as well be omitted.

In his series of papers,¹⁹ Ingold made only one reference to our prior related work in acetic acid solvent. This was in the form of a footnote²⁸ dealing only with salt effects and suggesting that our special salt effects be ascribed to dissociated anion, e.g., perchlorate, and normal salt effects to salt ion pairs. He did not make it clear whether the salt catalysis was thought to be associated with ionization or some later step, and his suggestion has introduced a note of confusion.²⁹ Most readers have inferred that he had in mind the ionization step. From his suggestion, it is obvious that Ingold was either unaware of, or else disregarded, the contents of several publications at his disposal. In view of the evidence in this and previous papers in this series, it seems unnecessary to discuss his suggestion further.

Experimental Part

Arenosulfonates.—Norbornyl and *threo*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonates were specimens employed previously.^{5b,7} The 1-*p*-anisyl-2-propyl *p*-toluenesulfonate,¹² m.p. 80.4–80.9° (reported¹² 80.0°), after recrystallization, displayed an acetolysis rate constant of $(1.17 \pm 0.01) \times 10^{-4}$ sec.⁻¹ in 0.01 *M* solution at 50.0°.

Anal. Calcd. for $C_{17}H_{20}SO_4$: C, 63.73; H, 6.29. Found: C, 63.59; H, 6.12.

The following procedure was employed to ensure the absence of common ion salts. A solution of 8.5 g. of toluenesulfonate in 175 ml. of ether was washed with a 200-ml. portion of distilled water. The ether solution was extracted

(25) S. Winstein and J. S. Gall, *Tetrahedron Letters*, 2, 31 (1960).

(26) S. Winstein, J. S. Gall, M. Hojo and S. Smith, *This Journal*, 82, 1010 (1960).

(27) C. K. Ingold, *Proc. Chem. Soc.*, 270, (1957).

(28) Reference 19, page 1278.

(29) D. Bethell and V. Gold, *Quart. Revs.*, 12, 173 (1958).

eight more times in the same manner, after which the ether was dried over anhydrous magnesium sulfate and the toluenesulfonate precipitated with pentane. Recrystallization from Skellysolve B gave 6.2 g. of material, m.p. 80.5–81.3°, acetolysis rate constant $(1.16 \pm 0.01) \times 10^{-6} \text{ sec.}^{-1}$ in 0.01 *M* solution at 50.0°. An ether solution (125 ml.) of this purified material (5.5 g.) was then subjected to nine more washes with 200-ml. portions of distilled water. Isolation of the solid and one recrystallization from Skellysolve B yielded 4.7 g. of material, m.p. 80.5–81.3°, acetolysis rate constant $(1.17 \pm 0.01) \times 10^{-6} \text{ sec.}^{-1}$ in 0.01 *M* solution at 50.0°.

Salts.—Lithium bromobenzenesulfonate and lithium perchlorate were prepared and handled in anhydrous acetic acid as described previously.^{6a,9} Solutions of lithium acetate and lithium toluenesulfonate in anhydrous acetic acid were prepared as described previously⁹ from lithium carbonate and toluenesulfonic acid.

Solutions of lithium toluenesulfonate were also prepared from solid material prepared as follows. To a solution of 18.5 g. (0.25 mole) of lithium carbonate in 600 ml. of acetic acid were added 95.1 g. (0.50 mole) of recrystallized *p*-toluenesulfonic acid monohydrate and 77 g. (0.75 mole) of pure acetic anhydride, and the mixture was heated overnight. Upon cooling, crystalline lithium toluenesulfonate separated. This product was recrystallized three times from acetic acid and dried for two days at 2 mm. and 140° over potassium hydroxide to yield 65 g. (73%) of salt.

Anal. Calcd. for $C_7H_7O_3SLi$: C, 47.20; H, 3.96; S, 18.00. Found: C, 46.94; H, 3.90; S, 17.57.

Tetra-*n*-butylammonium perchlorate was prepared by the method of Darwish³⁰ and Smith.³¹ Two recrystallizations from an ethyl acetate–pentane mixture yielded material, m.p. 212–212.5° [reported^{30,32} 213–213.5°, 213° and also³² 203–204°].

(30) D. Darwish, *Thesis*, U.C.L.A., 1958.

(31) S. Smith, *Thesis*, U.C.L.A., 1959.

(32) M. B. Reynolds and C. A. Kraus, *This Journal*, **70**, 1709 (1948).

Anal. Calcd. for $C_{16}H_{36}O_4NCl$: C, 56.20; H, 10.61. Found: C, 56.47; H, 10.50.

Tetra-*n*-butylammonium acetate containing one mole of acetic acid of crystallization was prepared according to a method devised by Smith.³¹ Five recrystallizations from ethyl acetate yielded material, m.p. 116.5–117.5°, equivalent weight by titration with perchloric acid in acetic acid solvent, 358 (calcd. 361.6).

Tetrabutylammonium toluenesulfonate was prepared as follows. To 53.4 g. (0.145 mole) of tetra-*n*-butylammonium iodide in 200 ml. of ethanol and 150 ml. of water was added excess freshly prepared silver oxide. The mixture was stirred until the supernatant liquid gave a negative test for iodide ion. After filtration and careful neutralization of the solution with toluenesulfonic acid monohydrate, the solvent was removed under reduced pressure to give 52 g. (87%) of crude material, m.p. 68–72°. The product was crystallized at low temperatures from ethyl acetate, yielding 35 g. of salt, m.p. 72–73°. Three more recrystallizations from ethyl acetate, followed by drying at 1.5 mm. over phosphorus pentoxide for several days, gave 28 g. of hygroscopic material, m.p. 73.5–74.5° (sealed tube).

Anal. Calcd. for $C_{22}H_{44}O_2NS$: C, 66.78; H, 10.48; S, 7.75. Found: C, 66.58; H, 10.51; S, 7.57.

Kinetic Procedure.—Anhydrous acetic acid designed to contain 0.01 *M* acetic anhydride was prepared in the usual way from reagent grade solvent. Karl Fischer titration on the final dried solvent always showed less than 0.002% water. Checks of the water content from time to time never showed more than a negligible increase in the percentage of water over periods of many months.

The titration methods and the rate measurements have been amply described.^{9,33}

(33) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Intermediates and Transition States in Reactions of Allylic and Homoallylic Systems. II. Factors Affecting the Distribution of Products from Allylic Carbonium Ions

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The distributions of products arising on methanolysis of the isomeric α -phenyl- γ -methyl- and α -methyl- γ -phenylallyl *p*-nitrobenzoates have been determined by a combination of kinetic and ultraviolet spectrophotometric techniques and were found to be identical; of the ethereal products each ester furnished 39% of α -phenyl- γ -methylallyl methyl ether and 61% of α -methyl- γ -phenylallyl methyl ether. Substitution of a *p*-methyl group into the phenyl ring of the γ -phenyl ester had no discernible effect on the product distribution; α -methyl- γ -*p*-tolylallyl *p*-nitrobenzoate underwent methanolysis to furnish the corresponding solvolysis products of which α -*p*-tolyl- γ -methylallyl methyl ether constituted $37.5 \pm 1.5\%$. However when the solvolysis of α -phenyl- γ -methylallyl *p*-nitrobenzoate was conducted in 60 per cent. aqueous dioxane, α -phenyl- γ -methylallyl alcohol constituted only *ca.* 16% of the solvolysis product mixture.

Introduction

The first paper in this series¹ described the uncatalyzed first-order solvolysis of α -phenyl- γ -methyl- (RX) and α -methyl- γ -phenylallyl *p*-nitrobenzoate (R'X) in aqueous dioxane.² The former compound was found to be the more reactive by a factor of *ca.* 300 and to furnish, in addition to solvolysis products, the isomeric α -methyl- γ -phenylallyl *p*-nitrobenzoate. These results were interpreted in terms of a scheme involving an ion pair intermediate, common to the reactions of both allylic esters.

(1) R. A. Sneen, *J. Am. Chem. Soc.*, **82**, 4261 (1960).

(2) In this as well as in the accompanying paper, the symbols RX and R'X will always refer to α -phenyl- γ -methyl- and α -methyl- γ -phenylallyl *p*-nitrobenzoate, respectively.

