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Salt Effects and Ion Pairs in Solvolysis and Related Reactions. IV. Salt Effects in Acetolysis of Neophyl and *p*-Methoxyneophyl Halides and Arylsulfonates

BY ARNOLD H. FAINBERG AND S. WINSTEIN

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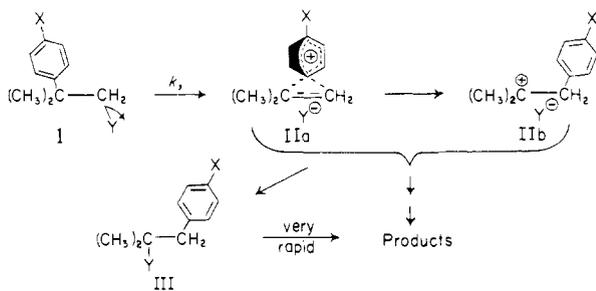
The effects of several salts, including lithium and diphenylguanidinium acetates, lithium *p*-toluenesulfonate, *p*-toluenesulfonic acid and lithium and diphenylguanidinium perchlorates, on the rates of acetolysis of neophyl chloride, bromide, *p*-toluenesulfonate and *p*-bromobenzenesulfonate, as well as *p*-methoxyneophyl *p*-toluenesulfonate have been investigated. For the neophyl system, in which acetolysis proceeds very predominantly by way of an anchimerically assisted ionization involving aryl participation, the observed first-order titrimetric solvolysis rate constant, k_t , is equal to the ionization rate constant, k_i . Therefore, the salt effects observed for these compounds involve effects on ionization rate only and do not involve special effects of salts on the behavior of intermediates; these salt effects are designated "normal." The effect of lithium perchlorate on the acetolysis rates of the aryl sulfonates is accurately described by the linear relation between k_t and the molar concentration of lithium perchlorate over the range 0–0.06 *M*, $k_t = k_t^0[1 + b(\text{LiClO}_4)]$. The dependence of the b values for the various salts on the nature of the salts, on structure of the compounds and on temperature is discussed.

In the study of the general pattern of salt effects on solvolysis in acetic acid as a solvent, we have studied the effects of several salts in the case of neophyl and *p*-methoxyneophyl halides and arylsulfonates I. These materials have a structure which makes them unique control substances for the exploration of salt effects, and this is the reason for their choice.

In other work, it has been shown that acetolysis of neophyl and *p*-methoxyneophyl derivatives I proceeds predominantly by way of an anchimerically assisted ionization involving aryl participation.^{1,2} Ion-pair return³ of cationic intermediates II to the covalent condition would give rise to very reactive tertiary derivatives III which will survive only briefly. Therefore, the observed first-order titrimetric solvolysis rate constant, k_t , measures⁴ the ionization rate constant, k_i . Any salt effects observed relate to the effect on ionization rate and do not involve special effects of salts on the behavior of intermediates. Such salt effects will be designated as "normal."

Results

In Table I are summarized the first-order rate constants for solvolysis of neophyl chloride, bromide, *p*-toluenesulfonate and *p*-bromobenzenesulfonate, in acetic acid containing various added salts. The latter included lithium acetate, diphenylguanidinium acetate (DPGHOAc), lithium *p*-toluenesulfonate, *p*-toluenesulfonic acid, lithium perchlorate and diphenylguanidinium perchlorate

(1) S. Winstein, *et al.*, THIS JOURNAL, **74**, 1113 (1952).

(2) R. Heck, unpublished work.

(3) S. Winstein, E. Clippinger, A. Fainberg, R. Heck and G. C. Robinson, THIS JOURNAL, **78**, 328 (1956).(4) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

(DPGHClO₄). The observed kinetics in all cases were first order within experimental error, the overall average deviation for all of the rate constants reported being less than ±1%. The table also lists the values of the thermodynamic quantities of activation, ΔH^\ddagger and ΔS^\ddagger .

Linear Lithium Perchlorate Salt Effects.—The effect of lithium perchlorate on the acetolysis rates of the arylsulfonates was investigated over a range of salt concentrations. In all three cases, these effects are accurately described by a linear relation between the solvolysis rate constant, k_t , and the molar concentration of lithium perchlorate up to concentrations of lithium perchlorate as high as 0.06 or 0.1 *M*. This is illustrated in Fig. 1 for the

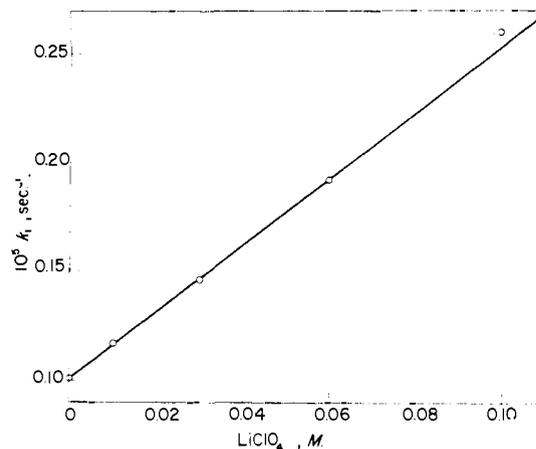


Fig. 1.—Plot of k_t for acetolysis of neophyl *p*-toluenesulfonate at 50.0° vs. $[\text{LiClO}_4]$.

acetolysis of neophyl *p*-toluenesulfonate at 50°. The points at 0, 0.01, 0.03 and 0.06 *M* lithium perchlorate define a good straight line, which can be expressed analytically in the form of equation 1

$$k_t = k_t^0[1 + b(\text{LiClO}_4)] \quad (1)$$

k_t^0 is the solvolysis rate constant at zero salt concentration, and b is the slope of the linear plot. Physically, b is the % increase in rate constant over k_t^0 per 0.01 *M* increment of lithium perchlorate. Over the range of 0 to 0.06 *M* lithium perchlorate, the average fit of equation 1 to the data for neophyl *p*-toluenesulfonate at 50.0° is ±0.3% of k_t . At higher concentrations, the observed rate starts in-

TABLE I
 SUMMARY OF ACETOLYSIS RATES

Compound	[RX] × 10 ² , M	Other solute	Concn. × 10 ² , M	10 ⁵ k (sec. ⁻¹)			ΔH^\ddagger at 50° kcal./ mole	ΔS^\ddagger at 50°, e. u.
				25.0°	50.0°	75.0°		
C ₆ H ₅ C(CH ₃) ₂ CH ₂ Cl	4.70	LiOAc	6.84	0.0250 ± 0.0004 ^a	0.000047 ^e	0.00136 ± 0.0001	29.4	-10
	3.16	LiOAc	50.0	.0313 ± .0004 ^a				
	3.96	LiOAc	100.0	.0367 ± .0003 ^a				
	3.34	{LiOAc LiClO ₄ }	{3.45 3.43}	.0308 ± .0003 ^a				
	3.18	DPG·HOAc	6.77	.0304 ± .0002 ^a				
	3.25	{DPG·HOAc DPG·HClO ₄ }	{3.79 2.99}	.0328 ± .0002 ^a				
C ₆ H ₅ C(CH ₃) ₂ CH ₂ Br	3.55	LiOAc	6.84	.272 ± .005 ^a	.00066 ^e	.0166 ± 0.0003	28.2	-8.7
	3.49	LiOAc	50.0			.0208 ± .0003		
	3.45	LiOAc	100.0			.0247 ± .0002		
	3.35	{LiOAc LiClO ₄ }	{3.45 3.43}			.0198 ± .0002		
	3.52	DPG·HOAc	6.77			.0195 ± .0005		
	3.43	{DPG·HOAc DPG·HClO ₄ }	{3.79 2.99}			.0227 ± .0004		
C ₆ H ₅ C(CH ₃) ₂ CH ₂ OTs	1.03			.00309 ^e	.101 ± 0.001 ^e	2.00 ± 0.02 ^b	26.04 ^c	-5.5 ^c
	1.96	LiClO ₄	1.00		.117 ± .002	2.29 ± .03	25.95	-5.5
	2.41	LiClO ₄	3.00		.146 ± .001	2.73 ± .03	25.52	-6.4
	2.20	LiClO ₄	6.00		.192 ± .001	3.53 ± .03	25.38	-6.3
	2.15	LiClO ₄	10.0		.260 ± .003	4.63 ± .03	25.11	-6.5
	2.12	LiClO ₄	30.0		.668 ± .006	10.97 ± .13	24.37	-6.9
	2.77	HOTs	10.0		.115 ± .002	2.19 ± .03	25.7	-6.3
	2.35	LiOTs	10.0		.140 ± .001	2.64 ± .02	25.6	-6.1
C ₆ H ₅ C(CH ₃) ₂ CH ₂ OBs	2.14			.0119 ^e	.364 ± .001	6.84 ± .03	25.58	-4.4
	2.17	LiClO ₄	3.00		.485 ± .004	8.78 ± .06	25.23	-4.9
	1.98	LiClO ₄	6.00		.621 ± .005	11.0 ± .1	25.05	-5.0
	2.02	LiClO ₄	10.0		.819 ± .007	14.29 ± .08	24.93	-4.8
	2.13	LiOTs	10.0		.483 ± .004	8.80 ± .11	25.30	-4.7
2.02	LiOAc	10.0		.437 ± .015	7.62 ± .10	24.9	-6	
<i>p</i> -CH ₃ OC ₆ H ₄ C(CH ₃) ₂ CH ₂ OTs	2.18			.537 ± 0.004	11.9 ± 0.1 ^d	169 ^e	23.09 ^d	-5.2 ^d
	2.16	LiClO ₄	1.00	.611 ± .005	13.1 ± .1		22.81	-5.9
	2.14	LiClO ₄	3.00	.775 ± .005	16.3 ± .2		22.66	-5.9
	2.19	LiClO ₄	6.00	1.040 ± .005	20.6 ± .2		22.22	-6.8
	2.10	LiClO ₄	10.0	1.41 ± .01	27.3 ± .5		22.06	-6.7
	2.16	HOTs	10.0	0.595 ± .016	13.2 ± .2		23.1	-5.0
1.91	LiOTs	10.0	0.730 ± .010	15.0 ± .4		22.5	-6.5	

^a At 100.0°. ^b [RX] 0.0202 M. ^c Extrapolation to 50.0° of data previously reported at other temperatures gives 10⁵k = 0.104, ΔH^\ddagger = 25.76, ΔS^\ddagger = -6.3 [S. Winstein, *et al.*, THIS JOURNAL, 74, 1113 (1952)]. ^d Previously observed by R. Heck² at 50.0°, 10⁵k = 12.1, ΔH^\ddagger = 23.24, ΔS^\ddagger = -4.4. ^e Extrapolated from the data at other temperatures.

creasing more rapidly than predicted, the extrapolated value being 3% low at 0.10 M lithium perchlorate, and 17% low at 0.30 M lithium perchlorate.

The above pattern of lithium perchlorate salt effects is observed for neophyl *p*-toluenesulfonate at 75.0°, for neophyl *p*-bromobenzenesulfonate at 50.0 and 75.0° and for *p*-methoxyneophyl *p*-toluenesulfonate at 25.0 and 50.0°. In Table II are summarized the values of k_t^0 and b for the linear fits, together with the number of experimental points employed in fitting equation 1, the salt range covered by the linear fit and the average value of the fit, expressed as per cent. of k_t . In all cases, the data, involving rate increases of up to 90%, were fitted to better than 1% over the range of 0 to 0.06 M lithium perchlorate; the extrapolated values at 0.10 M lithium perchlorate were never more than 2 to 4% low.

For salt effects in solvolysis in media of considerably higher dielectric constant (70–90% aqueous acetone, D = 38.9–25.3) than that of acetic acid (D = 6.22⁵ at 25.0°), Hughes, Ingold and co-workers⁶ have previously employed equation 2. In the

latter, D is the dielectric constant of the solvent, T

$$\log k_t = \log k_t^0 + \frac{0.912 \times 10^{16} \sigma \mu}{D^2 T^2} \quad (2)$$

is its absolute temperature, μ is the ionic strength of added salt, or molar concentration for uni-univalent salts and σ is the dipole moment of the transition state dipole, a parameter determined from the experimental data. This equation was derived as a limiting approximation for dilute solutions. It predicts a linear dependence of $\log k_t$ on the molar concentration of uni-univalent added salt. This dependence was, however, very inadequately tested.⁷

For fitting the lithium perchlorate salt effects in acetolysis, the logarithmic relation 2 is inferior to the linear relation 1. Thus, in Fig. 2, the plot of $\log k_t$ for the acetolysis of neophyl *p*-toluenesulfonate vs. the molar concentration of added lithium perchlorate is markedly curved over the entire region investigated. The superiority of the linear plot of Fig. 1 is shown analytically in Table III, in which the linear and linear logarithmic fits (least squares fits over the range 0–0.06 M lithium perchlorate) are compared.

(7) This form was tested by Hughes, Ingold, *et al.*,⁶ for a single case only, that of the effect of two concentrations of sodium azide on the hydrolysis of *p*-*t*-butylbenzhydrol chloride in 90% aqueous acetone. In this case, the linear log fit of equation 2 was superior to that of the form 1, linear in k .

(5) Interpolated from data, at other temperatures, of W. Dannhauser and R. H. Cole, THIS JOURNAL, 74, 6105 (1952).

(6) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

TABLE II
 SUMMARY OF SALT EFFECTS IN ACETOLYSIS

Compound	Other solute	Temp., °C.	$10^4 k_1^0$ (sec. ⁻¹)	<i>b</i>	Linear fit		
					No. of points	Av. fit, % of k_1	Salt range, <i>M</i>
C ₆ H ₅ C(CH ₃) ₂ CH ₂ Cl	LiOAc	100.0	0.024 ^f	0.56	3	±1.3	0.068 to 1.0
	DPG·HOAc	100.0	.024	3.9	2		0 to 0.068
	LiClO ₄	100.0	.024	7.6	2		0 to 0.034
	DPG·HClO ₄	100.0	.024	7.2	2		0 to 0.030
C ₆ H ₅ C(CH ₃) ₂ CH ₂ Br	LiOAc	75.0	.016 ^f	0.56	3	±0.9	0.068 to 1.0
	DPG·HOAc	75.0	.016	3.2	2		0 to 0.068
	LiClO ₄	75.0	.016	6.4	2		0 to 0.034
	DPG·HClO ₄	75.0	.016	9.8	2		0 to 0.030
C ₆ H ₅ C(CH ₃) ₂ CH ₂ OTs	LiClO ₄	50.0	.101	15.0	4	±0.3	0 to 0.06 ^a
	LiClO ₄	75.0	2.00	12.5	4	±0.8	0 to 0.06 ^b
	HOTs	50.0	0.101	1.4	2		0 to 0.1
	HOTs	75.0	2.00	1.0	2		0 to 0.1
	LiOTs	50.0	0.101	3.9	2		0 to 0.1
	LiOTs	75.0	2.00	3.2	2		0 to 0.1
C ₆ H ₅ C(CH ₃) ₂ CH ₂ OBs	LiOAc	50.0	0.364	2	2		0 to 0.1
	LiOAc	75.0	6.84	1.1	2		0 to 0.1
	LiClO ₄	50.0	0.364	11.6	3	±0.6	0 to 0.06 ^c
	LiClO ₄	75.0	6.84	10.0	3	±0.5	0 to 0.06 ^c
	LiOTs	50.0	0.364	3.3	2		0 to 0.1
	LiOTs	75.0	6.84	2.9	2		0 to 0.1
<i>p</i> -CH ₃ OC ₆ H ₄ C(CH ₃) ₂ OTs	NaOAc ^d	50.0	12.1	0.5	2		0 to 0.03
	LiClO ₄	25.0	0.537	15.4	4	±0.9	0 to 0.06 ^e
	LiClO ₄	50.0	11.9	12.2	4	±0.6	0 to 0.06 ^e
	LiOTs	25.0	0.537	3.6	2		0 to 0.10
	LiOTs	50.0	11.9	2.6	2		0 to 0.10
	HOTs	25.0	0.537	1.1	2		0 to 0.10
	HOTs	50.0	11.9	1.1	2		0 to 0.10

^a Extrapolated value is 3.1% low at 0.10 *M* LiClO₄, 16.6% low at 0.30 *M* LiClO₄. ^b Extrapolated value is 2.1% low at 0.10 *M* LiClO₄, 13.4% low at 0.30 *M* LiClO₄. ^c Extrapolated value at 0.10 *M* LiClO₄ is low by 4.0% at 50° and by 4.3% at 75°. ^d Based on data of R. Heck.² ^e Extrapolated value at 0.10 *M* LiClO₄ is low by 3.1% at 25° and by 3.2% at 50°. ^f Linear extrapolation to zero concentration of LiOAc.

 TABLE III
 COMPARISON OF LINEAR WITH LINEAR LOGARITHMIC FITS
 OF SALT EFFECTS IN ACETOLYSIS OF NEOPHYL *p*-TOLUENE-
 SULFONATE AT 50.0°

[LiClO ₄], <i>M</i>	Linear in k_1 ^a	Error in k_1 , %	Linear in log k_1 ^a
0	0.0		+ 2.8
.01	- 0.7		- 1.4
.03	+ 0.3		- 2.6
.06	+ 0.1		+ 1.6
.10	- 3.1		+ 14
.30	-16.6		+366

^aBased on the least squares fit of the data over the range 0–0.06 *M* LiClO₄.

Linear dependence of solvolysis rate on salt concentration in solvents of relatively low dielectric constant has also been reported by Salomaa.⁸ He observed such dependence of solvolysis rate of α -haloethers in binary mixtures of several alcohols with dioxane and benzene on concentration of added hydrogen chloride, lithium chloride, lithium perchlorate and mercuric chloride. While a number of the solvent mixtures Salomaa employed were of lower dielectric constant than that of acetic acid, several were as high as 10 to 15. Even in solvents of still higher dielectric constant, we have observed linear salt effects. For example, the solvolysis rate constants of benzhydryl chloride⁹ in eth-

(8) P. Salomaa, *Ann. Univ. Turkuensis*, **A14** (1953).

(9) A. H. Fainberg, unpublished work.

anol ($D = 24.3$) and methanol ($D = 32.7$) and for benzhydryl bromide in ethanol are linearly dependent on concentration of added lithium perchlorate from 0 to 0.125 *M*.

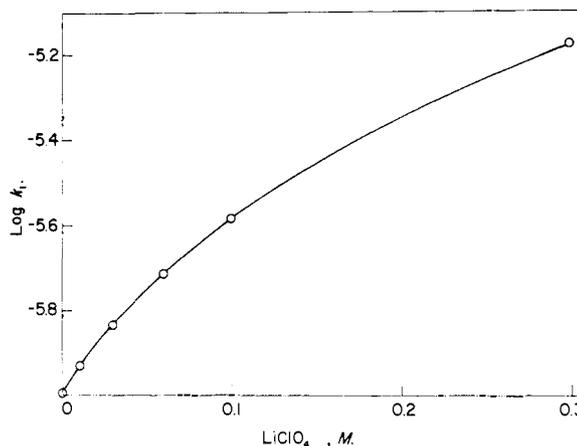


Fig. 2.—Plot of log k_1 for acetolysis of neophyl *p*-toluenesulfonate at 50.0° vs. [LiClO₄].

Other Salts.—Table II lists *b* values for the effect of several other "salts," including lithium acetate, lithium *p*-toluenesulfonate and *p*-toluenesulfonic acid, on the solvolysis rates of the arylsulfonates. The analytical form of equation 1 demonstrated for lithium perchlorate was as-

sumed to hold in these cases as well. For neophyl chloride and bromide, the acetolysis rate constants at zero salt concentration were obtained by linear extrapolation of the rate constants for 0.068, 0.500 and 1.00 *M* lithium acetate. In calculating *b* values for the effect of lithium and diphenylguanidinium perchlorate on the acetolysis rates of the neophyl halides, the additional assumption was made that the effects of two salts are additive. The analytical form employed was that of equation 3.

$$k_t = k_t^0[1 + b_1(\text{salt 1}) + b_2(\text{salt 2})] \quad (3)$$

Comparison of the *b* values for the various salts employed, summarized in Table IV, points up the very marked specificity of these normal salt effects in acetolysis. Thus, for the arylsulfonates, lithium *p*-toluenesulfonate is only *ca.* one fourth as effective as lithium perchlorate, while lithium acetate and *p*-toluenesulfonic acid are still less effective. For the halides, diphenylguanidinium acetate is from one half to one third as effective as lithium or diphenylguanidinium perchlorate, while lithium acetate is less than one tenth as effective.

TABLE IV
SALT ORDER IN ACETOLYSIS OF NEOPHYL COMPOUNDS

Salt	<i>b</i>				
	RCI	RBr	ROBs	ROT _s	<i>p</i> -MeO-ROT _s
HOTs				1.4	1.1
LiOAc	0.56	0.56	2		
LiOTs			3.3	3.9	2.6
DPGHOAc	3.9	3.2			
LiClO ₄	7.6	6.4	11.6	15.0	12.2
DPGHClO ₄	7.2	9.8			

Even in solvents of much higher dielectric constant than that of acetic acid, a certain amount of specificity in salt effects on solvolysis is common. Such effects have been noted, for example, in the solvolysis of *t*-butyl nitrate in 60 and 75 wt. % aqueous dioxane,¹⁰ of benzhydryl and substituted benzhydryl chlorides in aqueous acetone mixtures,⁶ in methanol,^{9,11} in ethanol⁹ and of *t*-butyl chloride and bromide in a number of aqueous acetone compositions.¹²

Structure and Temperature.—Both addition of salt to a solvent and gross change of solvent are medium changes. Therefore, it is interesting to examine the data of Table IV for possible parallelism between the responses of various structures to salt and solvent effects. Changing R in the solvolyzing material RX from neophyl to *p*-methoxyneophyl reduces the magnitude of the salt effects somewhat. Similarly, this structural change reduces sensitivity to gross solvent variation. On the other hand, this parallelism is not observed when the leaving group X of RX is changed. For example, the magnitude of the salt effects on the neophyl halides was *ca.* half that on the *p*-toluenesulfonate. In contrast, the neophyl halides were found⁹ to be somewhat more sensitive to solvent

variation than the *p*-toluenesulfonate. The lack of parallelism in this case is not surprising, since specific salt effects might be expected to depend not only on the nature of the salt but also on the leaving group X.

The salt effects observed for the arylsulfonates uniformly decrease in magnitude with increase in temperature. The function of temperature most closely fit by the data is the inverse square of absolute temperature. In all cases, the rate increase involved in going from 0 to 0.1 *M* lithium perchlorate is accounted for chiefly by a decrease of 0.6 to 1.0 kcal./mole in ΔH^\ddagger , this being partly balanced by a much smaller compensating change in the entropy term.

Experimental

Neophyl Chloride.—The material used had the properties: b.p. 95.1–95.2° (10 mm.), n_D^{20} 1.5249, n_D^{25} 1.5228, d_4^{25} 1.0379; reported¹³ b.p. 97° (13 mm.), n_D^{20} 1.5250. The purity, by solvolysis, was 99.1 ± 0.3%.

Neophyl Bromide.—Neophyl bromide was prepared by the procedure of Berr.¹⁴ To a filtered solution of neophyl Grignard reagent in ether, prepared from 169 g. (1.00 mole) of neophyl chloride, was added 160 g. (1.00 mole) of bromine, the temperature being held below 5° during the addition. The ether layer was extracted with aqueous sodium bisulfite, with aqueous sodium bicarbonate and then dried over anhydrous potassium carbonate. Fractional distillation gave 155 g. of neophyl bromide (0.73 mole, 73% yield), b.p. 110° (4.5 mm.), n_D^{25} 1.5433, d_4^{25} 1.2710. This material was found to contain 0.6% of a "fast" bromide with a solvolysis rate constant of *ca.* 5×10^{-5} sec.⁻¹ in 80% ethanol at 25.0°. Solvolysis in formic acid demonstrated the presence of 4.0% of an inert material, a 96.0% formolysis infinity value being obtained. Purification was attempted by treatment with 90% aqueous methanol for a month at room temperature. After isolation by extraction with pentane and fractional distillation, the material (in pentane) was then passed through a column packed with alumina. Fractional distillation of the eluate gave neophyl bromide, b.p. 97.1° (6.0 mm.), n_D^{20} 1.5470, n_D^{25} 1.5448, d_4^{25} 1.2789; reported¹³ b.p. 89–90° (3.5 mm.), n_D^{25} 1.5445. The average of 14 solvolysis infinities was $98.3 \pm 0.3\%$, showing that a portion, but not all, of the inert impurity had been removed. However, of the material which solvolyzed, *ca.* 1.3% of it was "fast" bromide, which apparently was formed by rearrangement of the neophyl bromide during the chromatography or distillation. The effect of the presence of this impurity was eliminated in the solvolysis runs by taking the first point in each kinetic run after 1.5–2% reaction had occurred.

Anal. Calcd. for C₁₀H₁₃Br: C, 56.35; H, 6.15. Found: C, 56.45; H, 6.22.

***p*-Toluenesulfonates.**—The neophyl and *p*-methoxyneophyl *p*-toluenesulfonates were available from other work.^{1,2}

Neophyl *p*-Bromobenzenesulfonate.—This material, m.p. 80.7–81.7°, was prepared by R. Heck from neophyl alcohol in the usual manner.

Anal. Calcd. for C₁₇H₁₆BrO₃S: C, 52.04; H, 4.64. Found: C, 51.77; H, 4.94.

Solvents.—Acetic acid containing 0.01 *M* acetic anhydride was prepared as described elsewhere.¹⁵ Solutions of lithium perchlorate in acetic acid of various concentrations were prepared by dilution of stock solutions of higher concentration (0.990 and 0.600 *M*). These stock solutions were prepared by dissolving the calculated amount of lithium perchlorate trihydrate (water content checked gravimetrically by quantitative dehydration) in anhydrous acetic acid and treating with an amount of acetic anhydride calculated

(10) G. R. Lucas and L. P. Hammett, *THIS JOURNAL*, **64**, 1928 (1942).

(11) O. T. Benfey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2494 (1952).

(12) F. Spieth and A. R. Olson, *THIS JOURNAL*, **77**, 1412 (1955).

(13) F. C. Whitmore, C. A. Weisberger and A. C. Shabica, Jr., *ibid.*, **65**, 1470 (1943).

(14) C. Berr, Ph.D. Thesis, U.C.L.A., 1952, p. 200.

(15) S. Winstein and A. H. Fainberg, *THIS JOURNAL*, **78**, in press (1956).

to give 0.01 *M* excess. Lithium perchlorate in these high concentrations was found to catalyze the reaction of acetic anhydride with water (as does strong acid), so that it was not necessary to heat the solution to hasten completion of the dehydration.

Acetic acid, 0.100 *M* in *p*-toluenesulfonic acid and 0.01 *M* in acetic anhydride, was similarly prepared from the monohydrate of *p*-toluenesulfonic acid and acetic anhydride.

Acetic acid, 0.100 *M* in lithium *p*-toluenesulfonate and 0.01 *M* in acetic anhydride, was prepared by dissolving the calculated amounts of lithium carbonate, *p*-toluenesulfonic acid monohydrate and pure acetic anhydride in acetic acid and holding the solution at near reflux for 24 hours. The resulting solution was very slightly on the acid side.

Acetic acid containing diphenylguanidinium perchlorate and/or acetate was prepared by dissolving the calculated amounts of diphenylguanidinium perchlorate¹⁶ (m.p. 161.5–

162.5°) and/or diphenylguanidine in anhydrous acetic acid.

Kinetic Measurements.—The usual sealed ampoule technique was used. The halides were followed by an extraction procedure¹⁵ and Volhard analysis for halide ion. The arylsulfonates were followed by acidimetric titration¹⁷ with *ca.* 0.02–0.04 *M* sodium acetate in acetic acid, using brom phenol blue indicator. The presence of high concentrations (0.10 *M*) of lithium perchlorate, lithium *p*-toluenesulfonate and *p*-toluenesulfonic acid was found to diminish appreciably the sharpness of the end-points; the addition of 10–25 ml. of dioxane to the solution being titrated helped only slightly.

The data reported in Table I were based on an average of six points per run, followed past 60–90% reaction.

(17) S. Winstein, E. Grunwald and L. L. Ingraham, *THIS JOURNAL*, **70**, 821 (1948).

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(16) C. Hanson, Thesis, U.C.L.A., 1943, p. 27.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. V. Special Salt Effect in Acetolysis of 2-Anisylethyl *p*-Toluenesulfonates

BY ARNOLD H. FAINBERG AND S. WINSTEIN

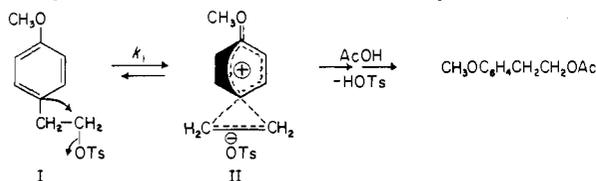
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The effects of lithium perchlorate on acetolysis rate of *o*- and *p*-anisylethyl *p*-toluenesulfonates have been contrasted with those observed with the phenylethyl, neophyl and *p*-methoxyneophyl esters. With the *o*- and *p*-anisylethyl derivatives, lithium perchlorate exerts both "special" and "normal" salt effects. The former designation refers to a very steep rise in trimetric rate constant, k_t , from the base value, k_t^0 , due to low concentrations of lithium perchlorate. The latter refers to the linear increase in k_t at somewhat higher lithium perchlorate concentrations, the magnitude of this effect being approximately equal to that observed with the neophyl analogs. The special salt effect may be characterized by the quantities: (i), k_{ext}^0 , an extrapolated rate constant at zero salt concentration, which includes the special but excludes the normal salt effect; (ii), $(LiClO_4)_{1/2}$, the salt concentration which produces one-half of the total special salt effect equal to $2-3 \times 10^{-4}$ *M* in the present cases; (iii), (k_{ext}^0/k_t^0) , a measure of the magnitude of the special salt effect, equal to *ca.* 3 in the present work. Regarding the origin of the special salt effects, the indications are that these are concerned with suppression of ion-pair return. On this basis, k_{ext}^0 is a better approximation than k_t^0 to the ionization rate. The use of k_{ext}^0 for acetolysis rate modifies substantially EtOH:AcOH rate ratios, useful in certain discussions of mechanism.

In the previous paper¹ were reported the effects of various salts on rates of acetolysis of neophyl and *p*-methoxyneophyl arylsulfonates, substances which are ideal for the elucidation of the pattern of normal salt effects on rates of ionization. The reason for this is that ionization is anchimerically assisted and any ion pair return accompanying acetolysis is without effect on the observed solvolysis rate, since the product of ion pair return is, for practical purposes, instantaneously solvolyzed. The present paper deals mainly with the effect of lithium perchlorate on acetolysis rate of 2-*o*- and *p*-anisylethyl *p*-toluenesulfonates. The acetolysis of these substances resembles that of the *p*-methoxyneophyl analog in one respect; ionization involves anisyl participation,² *p*-anisylethyl toluenesulfonate (I), for example, giving rise to ion pair II. However, ion pair return,³ if it occurs in acetolysis of I or its

o-methoxy isomer, will cause a corresponding decrease in solvolysis rate. Any salt effect on acetolysis rate would include, not only the salt effect on ionization rate, but also the salt effect on ion pair return. The main purpose of the measurements reported in the present paper was to disclose any possible contrast between salt effects in acetolysis of I and its *o*-methoxy isomer, on the one hand, and the neophyl analogs on the other.

In Table I are summarized the first-order rate constants at two temperatures for the solvolysis of 2-phenylethyl, 2-*o*-anisylethyl and 2-*p*-anisylethyl *p*-toluenesulfonates in ethanol and in acetic acid containing various concentrations of lithium perchlorate. The observed kinetics for the 2-phenylethyl ester, as well as for the 2-anisylethyl esters in ethanol and in acetic acid containing the higher concentrations of lithium perchlorate, were first order within the average deviations listed with these rate constants. However, the slight downward drifts in rate during solvolysis of the 2-anisylethyl esters in pure acetic acid previously noted² were confirmed in the present work; such drifts were also noted in the acetolyses involving the lower concentrations of lithium perchlorate. These rate depressions are obviously common ion effects, dealt with for other systems in a previous paper in this series.³ In the present work they were treated empirically, as described in the Experimental section, to obtain the initial rate constants reported in



(1) A. H. Fainberg and S. Winstein, *THIS JOURNAL*, **78**, 2763 (1956).

(2) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

(3) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *ibid.*, **78**, 328 (1956).