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

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. VII. Salt Effects in Acetolysis of Some Secondary Arylsulfonates

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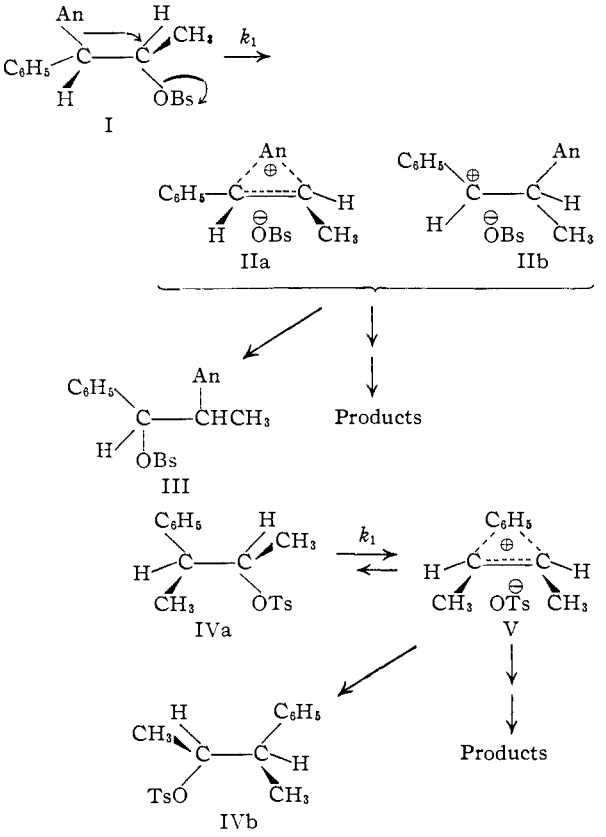
The effects of several salts, including lithium acetate, lithium *p*-toluenesulfonate, *p*-toluenesulfonic acid and lithium perchlorate, on the rates of acetolysis of pinacolyl *p*-toluenesulfonate and *p*-bromobenzenesulfonate, 1-phenyl-1-*p*-anisyl-2-propyl *p*-bromobenzenesulfonate, cyclohexyl *p*-toluenesulfonate and 3-phenyl-2-butyl *p*-toluenesulfonate have been investigated. In all cases only the normal salt effect pattern was observed. The results support the generalization that it is a necessary condition for the titrimetric rate constant to be reduced by ion-pair return before special salt effects will appear. However, they also show that the presence of ion-pair return is not a sufficient condition for the appearance of the special salt effect.

The salt effects observed in acetolysis of arylsulfonates, reported in previous papers in this series, illustrated depression of rate due to common ion rate depression[1] and acceleration of rate due to both normal[2] and special[3,4] salt effects. The present paper reports the results of a survey of the salt effects in acetolysis of a series of secondary arylsulfonates.

The compounds investigated include pinacolyl *p*-toluenesulfonate and *p*-bromobenzenesulfonate, cyclohexyl *p*-toluenesulfonate, 1-phenyl-1-*p*-anisyl-2-propyl *p*-bromobenzenesulfonate(I) and 3-phenyl-2-butyl *p*-toluenesulfonate (IV). The 1-phenyl-1-*p*-anisyl-2-propyl *p*-bromobenzenesulfonate(I)



(racemate "B"), the more reactive of the two diastereoisomers, presumably possesses the *erythro* configuration, and its acetolysis involves essentially exclusively anisyl participation, judging by the product results of Curtin and Bradley[5] and the kinetic work of Heck.[6] The 3-phenyl-2-butyl toluenesulfonate (IV) was the *threo* modification,[7] the one that acetolyzes mainly through the internally compensated bridged ion V. The comparison of the polarimetric and titrimetric acetolysis rates of the optically active form of this diastereomer has been reported previously.[8]

Results.—In Table I are summarized the pertinent acetolysis rate constants. The observed kinetics for 1-phenyl-1-*p*-anisyl-2-propyl *p*-bromobenzenesulfonate(I) were first order within the average deviations listed with the rate constants. However, with the other compounds upward drifts in rate during the runs were noted, particularly in runs with added lithium perchlorate. These data were treated empirically, as described in the Experimental Section, to obtain the initial rate constants reported in the table. Also listed are the values of the thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Linear Salt Effects.—With none of the present compounds was the special salt effect pattern observed. Only the normal salt effect pattern was in evidence, rate rising linearly with lithium perchlorate concentration out to concentrations of 0.06 or 0.10 *M*. This is illustrated graphically in Fig. 1 for *threo*-3-phenyl-2-butyl *p*-toluenesulfonate(IV), whose acetolysis rate departs from the linear fit only at the highest lithium perchlorate concentration. In the present work, it is again obvious that the linear fit of equation[2] 1 is superior to a linear logarithmic fit. This comparison is

$$k_t = k_t^0 [1 + b_t(\mathrm{LiClO_4})] \qquad (1)$$

shown graphically in Fig. 2 for acetolysis of cyclohexyl *p*-toluenesulfonate. Whereas the linear fit is seen to hold quite exactly past concentrations of lithium perchlorate of 0.06 *M*, the logarithmic plot is curved all the way. The least squares fits of the data by equation 1 are summarized in Table II.

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

(2) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956).

(3) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956).

(4) A. H. Fainberg, G. C. Robinson and S. Winstein, *ibid.*, **78**, 2777 (1956).

(5) (a) D. Curtin, private communication; (b) D. Curtin, page 40 of Abstracts, 13th National Organic Symposium of the American Chemical Society, Ann Arbor, Mich., June 15–18, 1953.

(6) R. Heck, unpublished work.

(7) (a) D. J. Cram, THIS JOURNAL, **71**, 3863 (1949); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952).

(8) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952).

TABLE I

SUMMARY OF ACETOLYSIS RATES

Compound	[RX] × 10^2, M	Other solute	Concn. × 10^2, M	10^5k (sec.$^{-1}$) 25.0°	50.0°	75.0°	$\Delta H^{\pm}$ at 50°, kcal./mole	$\Delta S^{\pm}$ at 50°, e.u.
$(CH_3)_3CCH(OTs)CH_3$	2.25			0.0191[e]	0.635 ± 0.002	12.8	26.20	−1.4
	2.41	$LiClO_4$	3.00		1.27	24	25.6	−1.8
	2.61	$LiClO_4$	6.00		1.93	37	25.75	−0.6
	2.49	HOTs	10.0		0.825 ± 0.010	17.2 ± 0.3	26.5	0.0
	2.44	LiOAc	10.0		0.785 ± 0.02	15.9 ± 0.2	26.2	−0.9
$(CH_3)_3CCH(OBs)CH_3$	2.21			0.0697[e]	2.34[a]	47.4	26.26[a]	+1.4[a]
	2.25	$LiClO_4$	3.00		4.0	72	25.2	+1.1
	2.18	LiOAc	10.0		2.75 ± 0.08	58.3 ± 0.4	26.7	+3.0
Cyclohexyl OTs	3.16			0.00457[e]	0.179	4.14 ± 0.3[b]	27.44[b]	−0.1[b]
	3.11	$LiClO_4$	1.00		.245	5.3	26.84	−1.3
	1.57	$LiClO_4$	3.00		.38	7.7	26.24	−2.3
	1.62	$LiClO_4$	6.00		.58	11.7	26.22	−1.5
	3.41	$LiClO_4$	10.0		.89	16.8	25.63	−2.5
	1.57	$LiClO_4$	30.0		2.63	47.3	25.19	−1.7
1-Phenyl-1-*p*-anisyl-2-propyl OBs "B"	2.06			1.60 ± 0.02[c]	36.1 ± 0.2[c]	520[e]	23.21[c]	−2.6[c]
	2.00	$LiClO_4$	3.00	2.37 ± .03	49.3 ± 0.7		22.59	−3.9
	2.04	$LiClO_4$	6.00	3.21 ± .03	64.6 ± 0.8		22.33	−4.2
	2.06	$LiClO_4$	10.0	4.47 ± .02	87.1 ± 1.1		22.10	−4.3
	2.03	HOTs	10.0	1.86 ± .02	41.2 ± 1.7		23.1	−2.7
	2.08	LiOTs	10.0	2.26 ± .07	48.3 ± 0.5		22.8	−3.3
	2.05	LiOAc	10.0	1.90 ± .09	40.4 ± 0.9		22.8	−3.8
3-Phenyl-2-butyl OTs (I)	2.06			0.00740[e]	0.256 ± 0.001[d]	5.31 ± 0.05[d]	26.49[d]	−2.3[d]
	2.30	$LiClO_4$	1.00		.354	6.7	25.65	−4.2
	2.04	$LiClO_4$	3.00		.53	10.3	25.89	−2.7
	2.13	$LiClO_4$	6.00		.83	15.3	25.42	−3.3
	1.98	$LiClO_4$	10.0		1.36	24.0	25.01	−3.5

[a] Previously reported[9] at 50.0°, 10^5k = 2.37; at 70.0°, $\Delta H^{\pm}$ = 26.3, $\Delta S^{\pm}$ = +1.5. [b] Extrapolation to 50.0° of data previously reported[10] at other temperatures gives 10^5k = 0.187, $\Delta H^{\pm}$ = 27.56, $\Delta S^{\pm}$ = +0.4. [c] Previously observed by R. Heck[6] at 25.0°, 10^5k = 1.56; at 50.0°, 10^5k = 36.4, $\Delta H^{\pm}$ = 23.4, $\Delta S^{\pm}$ = −1.8. [d] Interpolation of data previously reported[6] at other temperatures gives, at 50.0°, 10^5k = 0.249, $\Delta H^{\pm}$ = 26.33, $\Delta S^{\pm}$ = −2.9. [e] Extrapolated from the data at other temperatures.

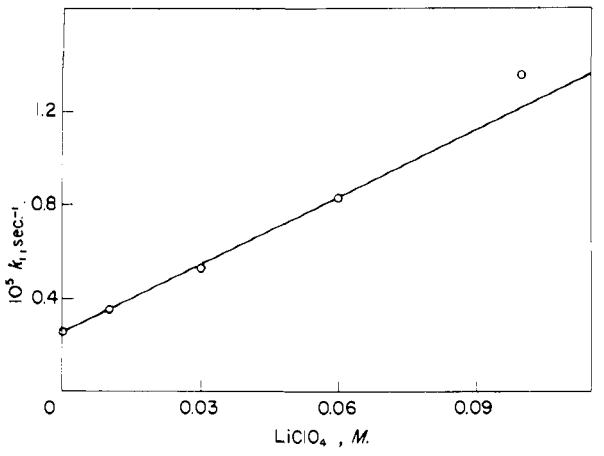


Fig. 1.—Plot of k_t for acetolysis of *threo*-3-phenyl-2-butyl *p*-toluenesulfonate at 50.0° *vs.* [$LiClO_4$].

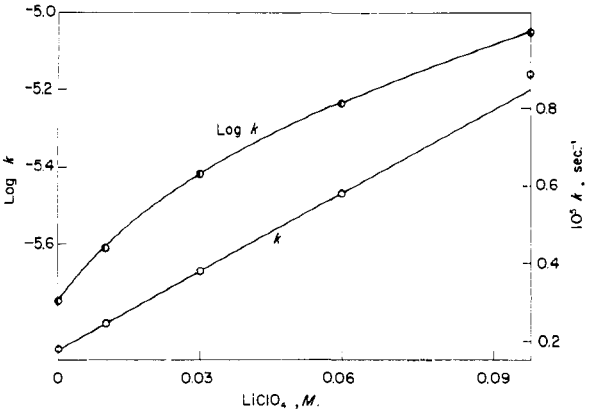


Fig. 2.—Effect of lithium perchlorate on acetolysis of cyclohexyl *p*-toluenesulfonate at 50.0°.

Table II also lists b values for the effect of several other "salts," including lithium, sodium and potassium acetate, lithium and sodium *p*-toluenesulfonate, *p*-toluenesulfonic acid and diphenylguanidinium acetate (DPGHOAc) on the solvolysis rates of the arylsulfonates. As before,[2] the analytical form of equation 1, demonstrated to hold for lithium perchlorate, was assumed to hold in these cases as well.

Examination of the b values for the various salts employed, summarized in Table II, discloses that the salt order observed for the present compounds is in good agreement with the order previously noted[2] for the neophyl and *p*-methoxyneophyl esters. Thus, lithium *p*-toluenesulfonate is *ca.* one third

(9) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, THIS JOURNAL, **74**, 1113 (1952).

(10) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948).

(11) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).

(12) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).

(13) E. Clippinger, unpublished work.

TABLE II

SUMMARY OF SALT EFFECTS IN ACETOLYSIS

Compound	Other solute	Temp., °C.	$10^5 k_0$ (sec.$^{-1}$)	b	No. of points	Linear fit Av. fit % of k	Salt range M
$(CH_3)_3CCH(OTs)CH_3$	$LiClO_4$	50.0	0.635	33.7	3	±0.4	0 to 0.06
	$LiClO_4$	75.0	12.8	30.5	3	±1.4	0 to .06
	LiOAc	50.0	0.635	2.4	2		0 to .1
	LiOAc	75.0	12.8	2.4	2		0 to .1
	HOTs	50.0	0.635	3.0	2		0 to .1
	HOTs	75.0	12.8	3.4	2		0 to .1
$(CH_3)_3CCH(OBs)CH_3$	$LiClO_4$	50.0	2.34	24	2		0 to 0.03
	$LiClO_4$	75.0	47.4	17	2		0 to .03
	LiOAc	50.0	2.34	1.8	2		0 to .10
	LiOAc	75.0	47.4	2.3	2		0 to .10
	KOAc	70.0	27.4	1.0	2		0 to .025
Cyclohexyl OTs	$LiClO_4$	50.0	0.179	37.2	4	±0.2	0 to 0.06[a]
	$LiClO_4$	75.0	4.14	29	3	±0.4	0 to .03[b]
	DPG·HOAc	74.9	4.27	4.6	2		0 to .095[c]
	DPG·HOAc	99.7	64.2	3.6	2		0 to .10[c]
	KOAc	75.0	4.14[d]	4.5[d]	2		0 to .10
1-Phenyl-1-*p*-anisyl-2-propyl OBs "B"	$LiClO_4$	25.0	1.60	16.5	3	±0.6	0 to 0.06[e]
	$LiClO_4$	50.0	36.1	12.8	3	±0.9	0 to .06[e]
	LiOAc	25.0	1.60	1.8	2		0 to .10
	LiOAc	50.0	36.1	1.2	2		0 to .10
	LiOTs	25.0	1.60	4.1	2		0 to .10
	LiOTs	50.0	36.1	3.4	2		0 to .10
	HOTs	25.0	1.60	1.6	2		0 to .10
	HOTs	50.0	36.1	1.4	2		0 to .10
3-Phenyl-2-butyl OTs (I)	$LiClO_4$	50.0	0.256[f]	37.3	4	±0.8	0 to 0.06[h]
	$LiClO_4$	75.0	5.31[f]	31.2	4	±1.1	0 to .06[h]
	NaOAc	74.9	5.15[f,i]	2.6[i]	2		0 to .12
	NaOAc	74.9	22.6[g,i]	4.1[i]	2		0 to .12
	NaOTs	74.9	5.15[f,i]	0.1[i]	2		0 to .09
	NaOTs	74.9	22.6[g,i]	1.3[i]	2		0 to .09
exo-Norbornyl OBs	$LiClO_4$	25.0	9.1[j]	38[j]			
cis-5-Methyl-2-cyclohexenyl chloride[11]	$LiClO_4$[k]	30.0	0.80	28.3	7	±3.3	0 to .15

[a] Extrapolated value is 5.3% low at 0.10 M $LiClO_4$, 21% low at 0.3 M $LiClO_4$. [b] Extrapolated value is 4.1% low at 0.10 M $LiClO_4$, 18% low at 0.3 M $LiClO_4$. [c] Based on data of S. Winstein, *et al.*[10] [d] Based on data of J. D. Roberts and V. C. Chambers.[12] [e] Extrapolated value at 0.10 M $LiClO_4$ is low by 5.2% at 25°, and by 5.8% at 50°. [f] Titrimetric. [g] Polarimetric. [h] Extrapolated value at 0.10 M $LiClO_4$ is low by 12% at 50°, and by 10% at 75°. [i] Based on data of S. Winstein and K. C. Schreiber.[8] [j] Reported by E. Clippinger.[13] [k] All solvent mixtures also contained 0.0518 M NaOAc.

as effective as lithium perchlorate, while lithium acetate and *p*-toluenesulfonic acid are still less effective.

There is definite indication of a lack of additivity of arylsulfonic acid and lithium perchlorate effects. In the absence of lithium perchlorate, arylsulfonic acid effects are very small. However, it is just possible to detect a slight upward drift in rate constant due to developing arylsulfonic acid with the substances which are especially sensitive to salt effects. The drifts in these cases reach 1–2% increase in integrated rate constant per 0.01 M reaction, the magnitude of this drift being consistent with the observations of the effect of added arylsulfonic acid. Apparently, the effect of arylsulfonic acid is enhanced by lithium perchlorate, since the upward drifts in rate constant during a run are larger in the presence of lithium perchlorate.

In most of the cases listed in Table II, the magnitude of the salt effects decreased with increasing temperature, in line with previous observations.[2-4] Again, the increase in rate arising from the operation of the salt effects appeared to be due mainly to decreases in $\Delta H^{\ddagger}$, these being usually opposed by much smaller changes in the entropy term.

Normal Salt Effects.—1-Phenyl-1-*p*-anisyl-2-propyl *p*-bromobenzenesulfonate(I) acetolyzes with anisyl participation[5,6] just as do the anisylethyl derivatives reported previously.[3] However, ion pair return in this case would lead to the very rapidly solvolyzing rearranged derivative III, and thus the titrimetric rate constant really measures the ionization rate constant k_1. Effectively, the same situation obtains for the pinacolyl arylsulfonates. Here too, because of methyl shift, ion-pair return would lead to a rapidly solvolyzing tertiary derivative, and the titrimetric rate is again equal to the ionization rate. Thus, for both of these compounds, as for the neophyl derivatives,[2] the observed salt effects involve effects on ionization rates only.

Viewing the addition of salt to a solvent as a change of medium, some parallelism was previously noted[2] between the responses of various structures to salt and solvent effect. The present work affords further evidence for this parallelism. Thus, making allowance for the effect of difference in

leaving group discussed below, the change of R in the solvolyzing material RX from 1-phenyl-1-*p*-anisyl-2-propyl to *p*-methoxyneophyl[2] reduces the magnitude of the salt effects. Similarly, this structural change reduces sensitivity to gross solvent variation.[14] The increased sensitivity of the pinacolyl esters to normal salt effects, as compared with the 1-phenyl-1-*p*-anisyl-2-propyl system, is likewise paralleled by the greater sensitivity of the former to gross solvent variation.[14]

As before,[2] this parallelism is not observed for change of leaving group. Thus, normal salt effects on *p*-toluenesulfonates are *ca.* one third larger than on the corresponding *p*-bromobenzenesulfonates, whereas such change of leaving group has only a minor effect on sensitivity to gross solvent variation.

The present failure to observe special salt effects[3,4] in acetolysis of the 1-*p*-anisyl-1-phenyl-2-propyl and pinacolyl derivatives supports the generalization[3,4,15] that it is necessary for the titrimetric rate constant to be reduced by ion pair return before special salt effects will appear. However, while the available data suggest that ion pair return is a necessary condition for the appearance of special salt effects, they also show that ion pair return is not a sufficient condition for their appearance. This is illustrated by the case of *threo*-3-phenyl-2-butyl toluenesulfonate (IV). Here, ion pair return is sufficient to make the polarimetric–titrimetric rate ratio substantial,[8] yet only the normal salt effect pattern is observed. Another case in point is that of *exo*-norbornyl bromobenzenesulfonate, in acetolysis of which ion pair return[13,16] is very important. Nevertheless, the work of E. Clippinger[13] has shown that only the normal salt effect pattern is observed with this material. Reference to this case is made in Table II, which lists a *b* value of 38 for the effect of lithium perchlorate in acetolysis at 25°. Still another illustrative example is the acetolysis of *cis*-5-methyl-2-cyclohexenyl chloride recently reported by Goering, Nevitt and Silversmith.[11] We find that their reported lithium perchlorate effects are fitted well by equation 1, the results of this treatment being summarized in Table II. Only the normal salt effect pattern is visible, although ion pair return is important in acetolysis.

While the special salt effects are concerned with reduction of ion pair return, the normal salt effects are concerned with increase of ionization rate in such cases as the neophyl and 1-*p*-anisyl-1-phenyl-2-propyl derivatives. However, in cases where ion pair return is a factor, salt effects with the normal linear pattern may include some effect on ion pair return and thus be concerned partly with reduction of such return. It is helpful to express the titrimetric rate constant, k_t, as a fraction, F, of the ionization rate constant, k_1 (equation 2). With a linear lithium perchlorate effects on k_1, k_t may be expressed as in equation 3. Since one would expect that changes which increase k_1 will also have some increasing effect[8] on F, we might anticipate that F will rise somewhat as ($LiClO_4$) increases. This increase could occur in such a way as to leave the linear approximation of equation 1 for k_t a good one. However, b_t would be larger than b_1 because of some reduction of ion pair return by salt addition.

$$k_t = Fk_1 \quad (2)$$

$$k_t = Fk_1^\circ[1 + b_1(LiClO_4)] \quad (3)$$

There is an alternative way to discuss the decrease in ion pair return that can be included in a normal salt effect pattern. It may be profitable to express the normal linear specific salt effects on ionization rate in terms of a second-order salt-promoted ionization superimposed on the first-order unpromoted ionization as in equation 4.

$$k_1 = k_1^\circ + k_{salt}(salt) \quad (4)$$

This is the form which Salomaa[17] chose to express the linear salt effects he observed with α-haloethers in dioxane– and benzene–alcohol mixtures. In this formulation, k_{salt} is equal to the $k_1^0 b_1$ of equation 3. From this point of view, the second term on the right-hand side of equation 4 represents ionization promoted by a salt ion pair. However, such a description is still non-committal regarding the intimate or solvent-separated[1,15,18] nature of the two ionic components of the salt with respect to each other and with respect to the ionizing organic molecule, RX. With such a description of the ionization process, the titrimetric rate constant, k_t, may be expressed as in equations 5 and 6, F_0 and F_{salt} being the fractions of unpromoted and salt-promoted ionization, respectively, leading to product. Even with no variation of F_0 and F_{salt} with salt concentration, it is apparent that the application of equation 1 to data which might be treated by equation 6 will lead to a b_t larger than b_1 because F_{salt} must tend to be larger than F_0.

$$k_t = F_0 k_1^0 + F_{salt} k_1^\circ b_1(salt) \quad (5)$$

$$k_t = F_0 k_1^0[1 + (F_{salt}/F_0) b_1(salt)] \quad (6)$$

The above considerations suggest that the high lithium perchlorate b_t values observed with 3-phenyl-2-butyl and *exo*-norbornyl arylsulfonates, somewhat out of line with the sensitivity of these compounds to solvent variation,[8,13,14] include some effect on ion pair return. The situation with respect to cyclohexyl *p*-toluenesulfonate is less clear, inasmuch as ion pair return has not been shown to occur in this case. However, some could conceivably occur, and its suppression could be responsible for a portion of the relatively high b_t value observed for this compound.

Quantitative studies of the extent of modification of ion pair return by both special and normal salt effects will be reported in later papers of this series.

Experimental Part

Arylsulfonates.—Pinacolyl *p*-toluenesulfonate, $n^{20}D$ 1.5007, $n^{25}D$ 1.4987, freezing point below *ca.* 20°, was prepared from pinacolyl alcohol in the usual manner by R. Heck.

Anal. Calcd. for $C_{13}H_{20}O_3S$: C, 60.90; H, 7.86. Found: C, 60.73; H, 7.92.

Pinacolyl *p*-bromobenzenesulfonate, m.p. 52–53°, has been described previously.[19]

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

(15) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, (a) THIS JOURNAL, **76**, 2597 (1954); (b) *Chem. and Ind.*, 664 (1954).

(16) S. Winstein and D. Trifan, THIS JOURNAL, **74**, 1154 (1952).

(17) P. Salomaa, *Ann. Acad. Turkuensis*, **A14**, (1953).

(18) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

(19) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

Cyclohexyl *p*-toluenesulfonate, m.p. 43.6–44.2°, was obtained from Holness.[20]

1-*p*-Anisyl-1-phenyl-2-propyl *p*-bromobenzenesulfonate, m.p. 71–72°, was the material studied by R. Heck[6] and prepared by him from the diastereoisomeric "B" alcohol kindly provided by Professor D. Curtin of the University of Illinois and Mr. A. Bradley of Columbia University.

threo-3-Phenyl-2-butyl *p*-toluenesulfonate, m.p. 47.6–48.2°, was prepared in the usual manner from alcohol kindly supplied as the acid phthalate by Professor D. J. Cram of this Department.

Solvents.—The preparation of acetic acid, 0.01 *M* in acetic anhydride, with and without added salts, has previously been described.[2,21]

Kinetic Measurements.—The usual sealed ampoule technique was employed. Formation of arylsulfonic acid was followed by titration with sodium acetate in acetic acid, as previously described.[2,22]

The new data in Table I were based on an average of 6 points per run followed past 70–90% reaction. The observed kinetics were clearly first order within experimental error only for the 1-phenyl-1-*p*-anisyl-2-propyl ester. Upward drifts during the run were the rule for the other compounds. These drifts are summarized in Table III, which lists the per cent. increase in the integrated rate constant over the extrapolated initial value per 0.01 *M* reaction. In these cases, the initial rate constants were obtained by linear extrapolation to zero reaction of plots of integrated rate constant *vs.* per cent. reaction. These are listed in Table I.

TABLE III

UPWARD DRIFTS IN RATE CONSTANTS DURING ACETOLYSIS

$(LiClO_4)$, *M*	Temp., °C.	—% Increase in k_t per 0.01 *M* reaction— Pinacolyl OTs	Pinacolyl OBs	Cyclohexyl OTs	3-Phenyl-2-butyl OTs
0	50	0	2.7	1.5	0
	75	2.6	1.4	1	0
0.01	50			11	6.4
	75			9	10
.03	50	7	9	12	11
	75	10	9	11	8.5
.06	50	8.5		11	11
	75	6		7	11
.10	50			8	6
	75			9	8
.30	50			8	
	75			7	

(20) S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

(21) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

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

LOS ANGELES 24, CALIFORNIA

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

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. VIII. Special Salt Effects in Acetolysis of Cholesteryl and 2-(2,4-Dimethoxyphenyl)-ethyl Arylsulfonates

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Special salt effects are especially striking in acetolysis of cholesteryl toluenesulfonate and bromobenzenesulfonate and 2-(2,4-dimethoxyphenyl)-ethyl bromobenzenesulfonate. As lithium perchlorate concentration is increased, the special stage of the salt effect appears to end at *ca.* 10^{-3} *M*. At higher concentrations, the normal linear salt effect pattern is observed. The magnitude of the special salt effects, measured by $k_{ext.}^0/k_t^0$, are similar to those observed in several other cases. However, the values of $(LiClO_4)_{1/2}$, the concentration of lithium perchlorate which produces half of the special salt effect, are of the order of $4–8 \times 10^{-5}$ *M*. Thus, the cholesteryl and dimethoxyphenylethyl esters show the sharpest separation between special and normal salt effects. With cholesteryl toluenesulfonate, it has been shown that the normal salt effects are specific with regard to the nature of the salts. The observed salt order is $LiClO_4 \cong HClO_4 > DPGHClO_4 > DPGHOAc > LiOAc$. Also, there is specificity in the value of $(salt)_{1/2}$ in the special salt effects, the salt order for increasing values of $(salt)_{1/2}$ being the same as the one for decreasing normal salt effects. On the other hand, there is no specificity in the magnitude of the special salt effects; all the salts lead to the same $k_{ext.}^0$, the rate constant inclusive of special and exclusive of normal salt effects. The present results support the view that the special salt effects are concerned with reduction of ion pair return. The lack of specificity in the magnitude of the special salt effect shows that the same fraction of ion pair return is eliminated in the special salt effect by all the salts.

In an earlier study[2] of the acetolysis of cholesteryl toluenesulfonate, it was observed that the first order acetolysis rate constant was increased substantially and approximately identically by 0.01 *M* and 0.02 *M* sodium acetate, 0.01 *M* potassium acetate and 0.01 *M* lithium perchlorate. At the time,[2] these results made it clear that the accelerations in rate were not due to bimolecular substitution by acetate ion but to salt effects. In the light of more recent observations[3] on salt effects, the pattern of these salt effects appeared special[4] rather than normal.[5] Similar indications of special salt effects in acetolysis of 2,4-dimethoxyphenylethyl *p*-bromobenzenesulfonate were observed by R. Heck.[6] Further study has disclosed that special salt effects on acetolysis rates of both cholesteryl and 2,4-dimethoxyphenylethyl arylsulfonates are very marked at especially low salt concentrations. This paper reports the results of the investigation of the pattern of such salt effects in acetolysis of both systems.

Results

Cholesteryl *p*-Toluenesulfonate and *p*-Bromobenzenesulfonate.—From the pertinent rate constants collected in Table I it can be seen that the rate constant of 130×10^{-6} sec.$^{-1}$, which is steady[2,7] for cholesteryl *p*-toluenesulfonate at the 0.005 *M* concentration level employed, is increased

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