tion of the aqueous layer and re-extraction of the pentane layer with the second 10-ml. portion of water was deferred until after all of the points were pulled, it having been demonstrated that the reaction was effectively quenched by the first extraction. In this way, the first point could be pulled within 20 to 30 seconds of mixing, and subsequent points could be pulled every 15 to 20 seconds.

A microphone feeding a tape recorder was employed for the time measurement in the fast rates, the quench time for each point being announced orally. The elapsed times between points were later obtained from the tape on playback, using a stopwatch. Accuracy was ensured by reading a time signal into the tape before and after each run, and employing this interval as a calibration time check. In this way, timing accuracy of ±0.2% was readily attained.

The new data reported in Table I were based on an average of six points per run followed past 50 to 90% reaction. The average deviation for all of the rates which were constant was ±1.0%; in only four cases did the average deviation reach ±2%: 50% HCOOH–H_2O at 25.0°, 16 M H_2O in AcOH at 50.0°, and 50% AcOH–HCOOH at 25.0 and 50.0°. The observed kinetics were first order within experimental error for all of the solvent compositions employed except 80 and 90 vol. % aqueous dioxane at both 25.0 and 50.0°. In the former solvent, the integrated first order rate constant calculated from the true zero time rose 2.6% for the reaction of the first 0.01 M *t*-butyl chloride at both temperatures; in the latter solvent, the corresponding rise was 5.6%.

Equilibrium in Acetolysis of *t*-Butyl Chloride.—The acetolysis of *t*-butyl chloride comes to an equilibrium position far short of completion unless the acetolysis is carried out in the presence of excess base.[1a,57,58] The indications in the present work were that solvolysis of *t*-butyl chloride fell slightly short of completion in acetic acid, formic acid and acetic–formic acid mixtures, even in the presence of a twofold excess of lithium acetate. As shown in Table IV, in the solvolysis of 0.034 M *t*-butyl chloride in acetic acid containing 0.068 M lithium acetate, the experimental infinity, taken after ten half-lives and accurate to ±1%, was found to be 6.2% smaller than the analytically determined initial concentration of *t*-butyl chloride. A much higher concentration (1 M) of lithium acetate was found to suppress the back reaction completely, as did the addition of 2 M water. The addition of formic acid was only partly effective. Even in pure formic acid containing 0.068 M lithium formate, a measurable equilibrium was observed.

TABLE IV

PER CENT. CHLORIDE ION AFTER 10 SOLVOLYSIS HALF-LIVES UNDER VARIOUS CONDITIONS

Solvent	Temp., °C.	(*t*-BuCl), M	(Lithium salt), M	% Cl^- after 10 half-lives
AcOH + 0.01 M Ac_2O	50.0	0.034	0.068	93.8
AcOH + 0.01 M Ac_2O	50.0	.032	1.000	100
AcOH + 2 M H_2O	50.0	.033	0.068	99
75% AcOH–HCOOH	50.0	.038	.065	95.6
50% AcOH–HCOOH	25.0	.035	.065	97.3
50% AcOH–HCOOH	50.0	.035	.065	97.1
25% AcOH–HCOOH	0.0	.051	.065	96
25% AcOH–HCOOH	25.0	.051	.065	97.6
HCOOH	25.0	.042	.068	97.8

In computing the rate constants for these solvolyses, the initial analytically determined concentrations of *t*-butyl chloride were employed in place of the experimentally determined infinities. In all cases, the drop in the integrated rate constants as the equilibrium position was approached was not perceptible until 60 to 70% of reaction; later points were not averaged.

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[57] J. Stiegman and L. P. Hammett, THIS JOURNAL, **59**, 2540 (1937).

[58] W. G. Young, S. Winstein and H. L. Goering, *ibid.*, **73**, 1958 (1951).

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

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. VI. Additional Examples of Special Salt Effects in Acetolysis[1]

BY ARNOLD H. FAINBERG, GENE C. ROBINSON AND S. WINSTEIN

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trans-2-*p*-Anisylcyclopentyl *p*-bromobenzenesulfonate, *trans*-2-anisylcyclohexyl *p*-bromobenzenesulfonate, 1-*p*-anisyl-2-propyl *p*-toluenesulfonate and *erythro*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate are shown to exhibit the same special salt effect of lithium perchlorate in acetolysis as was previously demonstrated for 2-*o*- and 2-*p*-anisylethyl *p*-toluenesulfonates. The numerical quantities characterizing the magnitude of both the normal and special salt effects are tabulated and compared.

In the preceding paper[2] in this series, it was shown that, in the acetolysis of 2-*o*- and *p*-anisylethyl *p*-toluenesulfonates, lithium perchlorate exerts a special salt effect superimposed on the normal salt effect previously demonstrated[3] for the neophyl esters. In this special salt effect, a steep rise in the titrimetric rate constant, k_t, from the base value, k_t°, is produced by low concentrations of lithium perchlorate. This phenomenon, apparently connected with the reduction of ion pair return,[2,4] has been noted in a number of other cases.[5] In the present paper is reported a study of such salt effects in acetolysis of *trans*-2-*p*-anisylcyclopentyl *p*-bromobenzenesulfonate, *trans*-2-*p*-anisylcyclohexyl *p*-bromobenzenesulfonate, 1-*p*-anisyl-2-propyl *p*-toluenesulfonate, and *erythro*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate. For all of these substances, acetolysis involves predominantly or exclusively anchimerically assisted ionization[5d,6,7] to a bridged carbonium ion, the anisyl group participating as in the 2-anisylethyl cases.[8]

In Table I are summarized the first-order rate

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[1] Research sponsored by the Office of Ordnance Research, U. S. Army.

[2] A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2767 (1956).

[3] A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956).

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

[5] (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 and Industry*, 664 (1954); (c) G. C. Robinson, E. Clippinger and S. Winstein, p. 21-N, Abstracts of Papers, 125th meeting, A.C.S., Kansas City, Mo., March, 1954; (d) G. C. Robinson, unpublished work.

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

[7] R. Heck, unpublished work.

[8] S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

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°	$\Delta H^{\ddagger}$ at 50°, kcal./mole	$\Delta S^{\ddagger}$ at 50°, e.u.
trans-2-*p*-Anisylcyclopentyl OBs	2.53			0.545 ± 0.009	13.10 ± 0.09[a]	199[d]	23.70[a]	−3.1[a]
	2.64	$LiClO_4$	0.100	0.632 ± .008	15.25 ± .12		23.72	−2.7
	2.59	$LiClO_4$	1.00	1.20 ± .01	25.9 ± .4		22.89	−4.2
	2.49	$LiClO_4$	3.00	2.01 ± .05	42.2 ± .8		22.66	−3.4
	2.46	$LiClO_4$	6.00	2.88 ± .01	58.8 ± .8		22.45	−4.0
	2.46	$LiClO_4$	10.0	4.09 ± .06	82.3 ± .8		22.33	−3.7
trans-2-*p*-Anisylcyclohexyl OBs	3.09			0.00527[d]	0.232[b]	5.92	28.32[b]	+3.2[b]
	2.45	$LiClO_4$	0.100		0.263	6.65	28.24	+3.2
	3.16	$LiClO_4$	1.00		0.435	10.3	27.7	+2.4
	2.71	$LiClO_4$	3.00		0.739 ± .005	16.1 ± 0.1	26.9	+1.1
	2.55	$LiClO_4$	6.00		1.120 ± .008	22.8 ± .3	26.30	+0.1
	2.0–2.5	$LiClO_4$	10.0		1.57 ± .02	32.5 ± .5	26.45	+1.2
	2.54	$LiClO_4$	30.0		4.25 ± .04	81.0 ± .8	25.71	+0.9
1-*p*-Anisyl-2-propyl OTs	3.11			0.0460[d]	1.918 ± .007[c]	19.5 ± .3	24.31[c]	−6.0[c]
	3.20	$LiClO_4$	0.100		1.52 ± .02	24.4 ± .3	24.16	−5.9
	3.14	$LiClO_4$	1.00		3.19 ± .04	47.7 ± .4	23.55	−6.4
	3.43	$LiClO_4$	3.00		5.18 ± .05	74 ± 3	23.1	−7
	3.20	$LiClO_4$	6.00		7.54 ± .02	105 ± 2	22.87	−6.8
	3.28	$LiClO_4$	10.0	0.481 ± 0.005	10.65 ± .07	151[d]	23.07	−5.5
	3.45	$LiClO_4$	30.0	1.37 ± 0.01	28.3 ± .4	379[d]	22.56	−5.1
erythro-3-*p*-Anisyl-2-butyl -OBs	1.00[e]			3.45 ± 0.07[e]				
	1.04			3.40 ± .010				
	0.98	$LiClO_4$	0.100	5.37 ± .017				
	1.01	$LiClO_4$	0.500	7.68 ± .020				
	1.06	$LiClO_4$	1.00	10.2 ± .2				
	1.01	$LiClO_4$	3.00	16.5 ± .6				
	1.00	$LiClO_4$	6.00	22.2 ± .7				
	1.02	$LiClO_4$	10.0	30.0 ± 1.8				

[a] Previously observed by R. Heck[7] at 50.0°, $10^5k = 13.0$, $\Delta H^{\ddagger} = 23.52$, $\Delta S^{\ddagger} = -3.7$. [b] Interpolation at 50.0° of data reported by R. Heck[7] at other temperatures gives $10^5k = 0.234$, $\Delta H^{\ddagger} = 28.29$, $\Delta S^{\ddagger} = +3.1$. [c] Interpolation at 50.0° of data previously reported[6] gives $10^5k = 1.24$, $\Delta H^{\ddagger} = 24.17$, $\Delta S^{\ddagger} = -6.3$. [d] Extrapolated from the data at other temps. [e] In EtOH.

TABLE II

SUMMARY OF LITHIUM PERCHLORATE EFFECTS IN ACETOLYSIS

Compound	Temp., °C.	$10^5k^{\circ}_{ext.}$ (sec.$^{-1}$)	b	$(LiClO_4)_{1/2}$ × 10^3, M	$k^{\circ}_{ext}/k^{\circ}_t$	Linear fit No. of points	Av. fit, % of k_t.	Salt range, M
trans-2-*p*-Anisylcyclopentyl OBs	25.0	1.12	26.5	5	2.1	3	±0.3	0.03 to 0.10
	50.0	24.7[c]	23.3	4	1.9	3	+0.4	.03 to .10
trans-2-*p*-Anisylcyclohexyl OBS	50.0	0.40[d]	29	3	1.7	3	±1.3	.03 to .10[a]
	75.0	9.0	26	3	1.5	4	±1.0	.03 to .30
1-*p*-Anisyl-2-propyl OTs	50.0	2.85[e]	27.4	3	2.4	3	±0.1	.03 to .10[b]
	75.0	41	26.5	3	2.1	3	±0.8	.03 to .10[b]
erythro-3-*p*-Anisyl-2-butyl OBs	25.0	1.06	18.3	4	3.1	3	±0.2	.03 to .10

[a] Extrapolated value is 9% low at 0.30 M $LiClO_4$. [b] Extrapolated value at 0.30 M $LiClO_4$ is 7% low at 50°, 3% low at 75°. [c] $\Delta H^{\ddagger} = 23.05$ kcal./mole; $\Delta S^{\ddagger} = -3.8$ e.u. [d] $\Delta H^{\ddagger} = 27.2$ kcal./mole; $\Delta S^{\ddagger} = +1.$ e.u. [e] $\Delta H^{\ddagger} = 23.20$ kcal./mole; $\Delta S^{\ddagger} = -7.7$ e.u.

constants at two temperatures for the solvolysis of these compounds in acetic acid containing various concentrations of lithium perchlorate. The observed kinetics for the *trans*-2-*p*-anisylcyclopentyl, 1-*p*-anisyl-2-propyl and *erythro*-3-*p*-anisyl-2-butyl esters were first order within the average deviations listed with these rate constants. Good first-order kinetics were also observed for the *trans*-2-*p*-anisylcyclohexyl ester for lithium perchlorate concentrations of 0.03 M and higher. At lower concentrations, and in the absence of salt, small upward drifts in rate during the course of these runs were noted. These drifts were treated empirically, as described in the Experimental section, to obtain the initial rate constants listed in Table I. The table also lists the values of the thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

All four of the compounds listed in Table I show the special salt effect in addition to the normal salt effect, although these effects are not as sharply separated as they were for the 2-anisylethyl esters. This is illustrated for *erythro*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate in Fig. 1, in which k_t for acetolysis at 25.0° is plotted against molar concentration of added lithium perchlorate. As the plot shows, k_t is linear in lithium perchlorate concentration over the range 0.03 to 0.10 M. Linear extrapolation of this portion of the plot back to zero salt concentration gives k°_{ext}, the titrimetric rate constant in pure acetic acid, which includes the special salt effect of lithium perchlorate, but excludes its normal salt effect. Values of k°_{ext} and of b, the slope of the linear portion, as calculated with equation 1, are listed in Table II for all four

$$k_t = k^\circ_{\text{ext}}\,[1 + b(\text{LiClO}_4)] \qquad (1)$$

compounds. Also listed are the salt ranges in which linearity was found, the number of experimental points in these ranges, and a measure of the linearity of the fit, in terms of per cent. of k_t. In all cases the fits were linear to within ±1% of k_t over the range 0.03 to 0.10 M lithium perchlorate.

Values of b, the measure of the magnitude of the normal salt effect (physically the per cent. increase in rate constant over k°_{ext} per 0.01 M increment of lithium perchlorate), tend to run somewhat higher for these secondary arylsulfonates than for the previously discussed[2,3] primary esters. As before,[2,3] they decrease with increasing temperature.

It is of interest to examine the relative contributions of the thermodynamic quantities of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, to the increase in rate by the normal salt effect. As a measure of the latter we may employ the increase from k°_{ext} to k_t for solvolysis in acetic acid containing 0.1 M lithium perchlorate. For the p-anisylcyclopentyl and cyclohexyl esters, as well as for the two 2-anisylethyl esters previously reported,[2] this rate increase is chiefly accounted for by a decrease of 0.7–0.9 kcal./mole in $\Delta H^{\ddagger}$, in close analogy with the results previously observed[3] for the neophyl esters. However, in the case of 1-p-anisyl-2-propyl p-toluenesulfonate, the normal salt effect rate increase is chiefly due to an increase in the entropy term.

The magnitude of the special salt effect, measured by the ratio of the rate constants, $k^\circ_{\text{ext}}/k^\circ_t$, listed in Table II, ranges from 1.5 for *trans*-2-p-anisylcyclohexyl p-bromobenzenesulfonate at 75.0° to 3.1 for *erythro*-3-p-anisyl-2-butyl p-bromobenzenesulfonate at 25.0°. Except for the latter, these values are appreciably smaller than those previously observed[2] (2.9 to 3.3) for the 2-anisylethyl esters. Again, values of this ratio decrease as temperature increases.

The relative contributions of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to the special salt effect rate increase, as measured by the change from k°_t to k°_{ext}, show some regularity of behavior. In all cases thus far studied which involve the special salt effect, including the 2-anisylethyl esters previously reported,[2] this rate increase is accounted for chiefly by a decrease of 0.7 to 1.2 kcal./mole in $\Delta H^{\ddagger}$, this being partly balanced by a smaller compensating change in the entropy term.

The most striking difference between the special salt effects herein reported and those previously observed[2] for the 2-p-anisylethyl esters is shown by the values of $(\text{LiClO}_4)_{1/2}$ listed in Table II. Values of this quantity, defined[2] as the concentration of lithium perchlorate at which the titrimetric rate constant equals $(k^\circ_{\text{ext}} + k^\circ_t)/2$, ranged from 2 to 3.4 × 10^{-4} M for the 2-p-anisylethyl esters. In contrast, the corresponding values for the present series are ten to twenty-five times larger; in other words, much higher salt concentrations are required for the operation of the special salt effect for these compounds. It is this difference that is principally responsible for the poorer separation between the normal and special salt effects for the compounds herein described, as compared with the 2-anisylethyl esters.

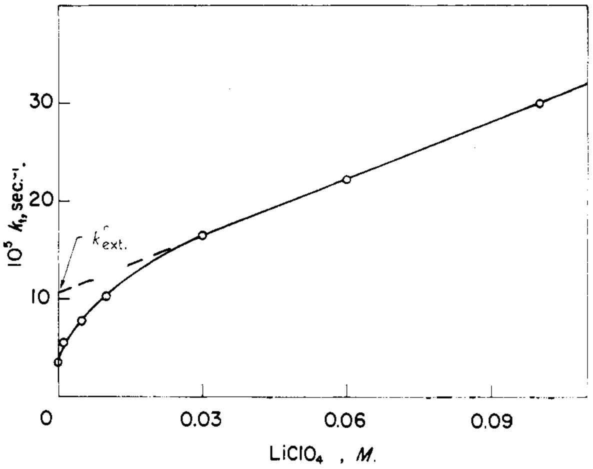

Fig. 1.—Plot of k_t for acetolysis of *erythro*-3-p-anisyl-2-butyl p-bromobenzenesulfonate at 25.0° *vs.* [LiClO$_4$].

Experimental Part

Compounds.—*trans*-2-p-Anisylcyclopentyl p-bromobenzenesulfonate, m.p. 100–101°, and *trans*-2-p-anisylcyclohexyl p-bromobenzenesulfonate, m.p. 123–125°, were available from other work.[7] The 1-p-anisyl-2-propyl p-toluenesulfonate was the same material as that employed in previous work.[6] *erythro*-3-p-Anisyl-2-butyl p-bromobenzenesulfonate, m.p. 67–69°, was prepared in the usual way from 3.0 g. (0.0166 mole) of *erythro*-3-p-anisyl-2-butanol,[5d,6] m.p. 58–60°, in 3.5 g. (53%) yield.

Anal. Calcd. for $C_{17}H_{19}O_4BrS$: C, 51.13; H, 4.80. Found: C, 51.31; H, 5.13.

Solvents.—The preparation of acetic acid 0.01 M in acetic anhydride and containing various concentrations of lithium perchlorate has been described previously.[3,9]

Kinetic Measurements.—The usual sealed ampoule technique was employed. Development of arylsulfonic acid was followed by titration with sodium acetate in acetic acid, as previously described.[3,10]

The new data in Table I were based on an average of six points per run, followed past 70–90% reaction. The observed kinetics were first order within experimental error for all the runs reported except those listed in Table III.

TABLE III

UPWARD DRIFT IN ACETOLYSIS RATE CONSTANTS OF *trans*-2-p-ANISYLCYCLOHEXYL OBs

	% Increase in k_t per 0.01 M reaction	
(LiClO$_4$), M	50°	75°
0	3	1
0.001	4	2.4
.010	5	2.5

For these runs, a linear extrapolation to zero reaction of a plot of the integrated rate constant *vs.* per cent. reaction gave the initial rate constants listed in Table I.

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[9] A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2770 (1956).

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