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Salt Effects and Ion Pairs in Solvolysis and Related Reactions. X. The 2-p-Anisyl-1-propyl System[1,2]

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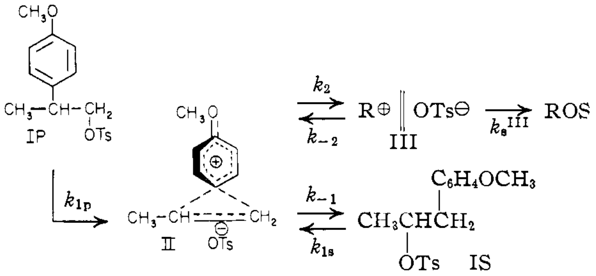
Due to ion pair return accompanying solvolysis, 2-p-anisyl-1-propyl p-toluenesulfonate (IP) rearranges to the 1-p-anisyl-2-propyl isomer (IS) during acetolysis. Therefore, the first-order acetolysis rate constant drifts upward in a run. By a kinetic analysis of the acetolysis of the primary isomer IP, making use of the first-order rate constants (k_s) for acetolysis of the secondary isomer (IS), rate constants for rearrangement (k_r) and solvolysis (k_p) may be obtained. The ($k_r + k_p$) values represent ionization rate constants (k_{1p}). Lithium perchlorate salt effects on k_p exhibit the combination of steep special and more shallow normal linear patterns observed in other cases. On the other hand, the salt effects on ionization rate constant k_{1p} exhibit only the normal linear pattern. The 2-anisyl-1-propyl system is another one like 3-anisyl-2-butyl, where it is very clear that the special salt effect is not concerned with ionization rate, but with modification of ion pair return. As in the case of the 3-anisyl-2-butyl system, the special salt effect does not close the gap between k_p and k_{1p} for the 2-anisyl-1-propyl toluenesulfonate. Again, this is interpreted on the basis that the special salt effect eliminates external ion pair return (from solvent-separated ion pair III), but permits internal return (from the intimate ion pair II). It is then possible to calculate the importance of internal and external ion pair return during acetolysis of IP. Since common intermediates are involved in acetolysis of both isomers IP and IS, these are expected to respond identically to lithium perchlorate in the special salt effect. An important check on the mechanistic scheme is afforded by the observed identity in the response of the two isomers in the special salt effect. While it was not possible to obtain directly the ionization rate constants (k_{1s}) of the secondary isomer IS, values of k_{1s} may be generated from the expected identity of (k_{1s}/k_s) and (k_{1p}/k_p). As in the comparison of the 3-anisyl-2-butyl and 3-phenyl-2-butyl systems, the substitution of the p-methoxyl group into the 2-phenyl-1-propyl system has a major effect on the distribution of ion pair return between internal and external ion pair return. Internal return is much reduced in importance, while return from solvent-separated ion pair is introduced strongly.

In the study of special salt effects[1-5] in acetolysis, the 2-anisyl-1-propyl system[6] (IP) appeared to be a potentially instructive one. From the fragmentary previous[6] work on this system and the investigation of the 2-phenyl-1-propyl[6] analog, it was clear that ion pair return[7] would occur in acetolysis of 2-anisyl-1-propyl p-toluenesulfonate IP. Also, it was probable such return was essentially exclusively to the secondary isomer IS. Further, special salt effects could be anticipated in the acetolysis of IP, since these did appear[4] in acetolysis of the IS isomer, and solvolysis of both isomers IP and IS could be expected to proceed very largely through the same intermediates. Thus, it appeared feasible to obtain the ionization rate constant k_{1p} of 2-anisyl-1-propyl toluenesulfonate by kinetic methods[6] and to ascertain how much ion pair return was eliminated by the special salt effect. Such an analysis has been accomplished in the present study, the results of which are presented and discussed in this article.



Determination of k_r- and k_p-Values.—Integrated first-order rate constants $\bar{k}$ for the acetolysis of 2-p-anisyl-1-propyl p-toluenesulfonate (IP), calculated from equation 1, where a is the initial concentration of the ester and x is the concentration of reacted material at time t, rose markedly during a run. A representative run is illustrated in

$$\ln [a/(a - x)] = \bar{k}t \qquad (1)$$

Table I, showing the rise in the integrated first-order rate constant from 0.515 to 0.889 × 10^{-5} sec.$^{-1}$ over the range of 6 to 83% reaction during acetolysis of 0.0324 M material.

TABLE I

SOLVOLYSIS AND REARRANGEMENT OF 0.0324M 2-p-ANISYL-1-PROPYL p-TOLUENESULFONATE IN AcOH + 0.01M Ac_2O AT 50.0°

Elapsed time,[a] 10^{-2} sec.	Ml. of titrant[b] per aliquot	Integ. 10^5 $\bar{k}$, sec.$^{-1}$	f[c]	Instant. 10^5 k, sec.$^{-1}$	F_p[d]	10^5 ($k_r + k_p$), sec.$^{-1}$
0	0	(0.46)[e]		0.46	1.000	
126.3	0.415	.515	1.923	.566	0.856	1.74
204.9	.70	.548	1.881	.626	.775	1.79
272.1	.95	.573	1.848	.668	.718	1.79
627.3	2.25	.667	1.714	.815	.519	1.71
715.5	2.55	.685	1.688	.840	.485	1.70
800.7	2.845	.707	1.664	.871	.443	1.72
880.5	3.09	.720	1.644	.888	.420	1.71
969.9	3.37	.740	1.622	.914	.385	1.73
1051	3.58	.747	1.604	.921	.376	1.68
1134	3.845	.774	1.587	.959	.324	1.77
1465	4.605	.821	1.527	1.012	.252	1.76
1593	4.825	.829	1.507	1.016	.246	1.71
1786	5.15	.854	1.479	1.043	.210	1.73
1992	5.46	.889	1.453	1.083	.156	1.82
∞	6.58				Mean	1.74 ± 0.03

[a] Corrected to true zero time. [b] 0.02491 M NaOAc in AcOH. [c] $f = (k - k_p)/(\bar{k} - k_p)$. [d] Mole fraction of the primary ester in the residual toluenesulfonate. [e] Extrapolated from a plot of integrated $\bar{k}$ vs. % reaction, employing a calculated curve; see kinetic appendix.

The addition of lithium perchlorate in several concentrations ranging from 0.01 to 0.10 M to the acetolysis solution was found to raise the initial

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(1) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson: (a) THIS JOURNAL, **76**, 2597 (1954); (b) *Chemistry & Industry*, 664 (1954).

(2) Presented in summary at VIth Reaction Mechanism Conference, Swarthmore, Pa., Sept. 12, 1956.

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

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

(5) S. Winstein and E. Clippinger, *ibid.*, **78**, 2784 (1956).

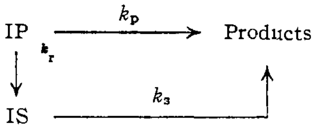
(6) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

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

solvolysis rate of the primary isomer markedly, and to reduce the magnitude of the upward drifts during the runs. However, even at 0.10 *M* lithium perchlorate, a small but steady upward drift was noted during the run.

In contrast with the primary derivative IP, 1-*p*-anisyl-2-propyl toluenesulfonate (IS) displayed extremely steady first-order acetolysis rate constants.[4] Also, while the addition of lithium perchlorate[4] gave rise to much enhanced rates of acetolysis, the rate constants were steady in a run to within experimental error (*ca.* ±1%).

The available information on medium effects[8] and common ion rate depression[7] due to added toluenesulfonic acid in acetolysis, as well as the behavior of the secondary isomer IS,[4,9] show that the upward drift in first-order rate constant for acetolysis of the 2-anisyl-1-propyl toluenesulfonate (IP) must be ascribed entirely to rearrangement to the secondary isomer IS accompanying acetolysis. As in acetolysis of 2-phenyl-1-propyl *p*-bromobenzenesulfonate,[6] it is helpful to treat the acetolysis of IP on the basis of the following simplified kinetic scheme.



In the above kinetic scheme, k_r is the first-order rate constant for rearrangement of primary ester IP, and k_p and k_s are first-order solvolysis rate constants for IP and IS, respectively. The values of k_r and k_p may be determined by the type of treatment employed previously in handling simultaneous rearrangement and solvolysis of α,α-dimethylallyl chloride[10] and 2-phenyl-1-propyl bromobenzenesulfonate.[6]

By a predominantly analytical method of successive approximations described in the kinetic appendix, values of the instantaneous rate constant k, or $(\mathrm{d}x/\mathrm{d}t)/(a - x)$, were calculated from the integrated rate constants. These furnish an analysis of the residual *p*-toluenesulfonate at any time t with the aid of equation[6] 2, where F_p denotes the mole fraction of the primary ester in the residual toluenesulfonate at time t. The necessary k_s values for solvolysis of 1-*p*-anisyl-2-propyl *p*-toluenesulfonate (IS), listed in Table II, have been reported previously.[4] The necessary k_p values for solvolysis of 2-*p*-anisyl-1-propyl *p*-toluenesulfonate (IP), also listed in Table II, are the values of the instantaneous rate constant at zero time, obtained by an extrapolation procedure described in the kinetic appendix. The trend of F_p values in acetolysis of the primary derivative IP in the absence of lithium perchlorate is illustrated in Table I, F_p decreasing from unity initially to 0.156 at 83% reaction.

$$k = (\mathrm{d}x/\mathrm{d}t)/(a - x) = k_pF_p + k_s(1 - F_p) \quad (2)$$

TABLE II

SOLVOLYSIS AND IONIZATION RATE CONSTANTS IN ACETOLYSIS OF 2-*p*-ANISYL-1-PROPYL *p*-TOLUENESULFONATE AT 50.0°

[RX] 10^2M	(LiClO$_4$) 10^2M	$10^5 k_s$[4], sec.$^{-1}$	$10^5 k_p$, sec.$^{-1}$	$10^5 k_r$, sec.$^{-1}$	$10^5(k_r + k_p)$, sec.$^{-1}$ Observed	Calcd.[b]
3.14		1.198[a]	0.46	1.29	1.75 ± 0.06	1.79
3.24		1.198[a]	0.46	1.28	1.74 ± .03	1.79
3.17	1.00	3.19	1.25	0.80	2.05 ± .06	2.00
3.22	3.00	5.18	1.96	.47	2.43 ± .04	2.43
3.24	6.00	7.54	2.72	.39	3.11 ± .08	3.08
3.33	10.0	10.65	3.81	.12	3.93 ± .03	3.94

[a] Previously[4] listed erroneously as 1.918 due to typographical error. [b] Calculated values from the relation, $10^5(k_r + k_p) = 1.79[1 + 12.0\ (\mathrm{LiClO_4})]$.

The concentration of primary toluenesulfonate IP at any time in a solvolysis run is given by $(a - x)F_p$, and this should show a first-order decrease with time with an apparent rate constant of $(k_r + k_p)$, according to equation 3. On application of

$$(k_r + k_p)t = \ln\,[a/(a - x)F_p] \quad (3)$$

this equation to the experimental data, very constant values of $(k_r + k_p)$ were obtained for all of the runs. For example, in the run without added salt shown in Table I, the mean value of $(k_r + k_p)$ was $(1.74 \pm 0.03) \times 10^{-5}$ sec.$^{-1}$. Table II summarizes the values of $(k_r + k_p)$ for all of the runs.

Examination of the values of k_r and k_p in Table II discloses that the $(k_r + k_p)/k_p$ ratio without added lithium perchlorate is 3.8. This is approximately the same as the rough estimate made previously for the 2-anisyl-1-propyl bromobenzenesulfonate.[6]

As derived previously,[6] the ratio (S/P) of secondary isomer IS to primary isomer IP in the residual toluenesulfonate in acetolysis of originally pure IP is given by equation 4. When k_s is greater than $(k_r + k_p)$, (S/P) approaches the value $k_r/(k_s - k_r - k_p)$ in a run. However, when $(k_r + k_p)$ is greater than k_s, the residual toluenesulfonate approaches pure secondary isomer IS as reaction proceeds. It is interesting that in the present case the balance between $(k_r + k_p)$ and k_s is so close that the latter situation obtains in the absence of lithium perchlorate, but the former applies in the presence of 0.01–0.10 *M* lithium perchlorate.

$$\frac{S}{P} = \left[\frac{k_r}{k_s - k_r - k_p}\right][1 - e^{-(k_s - k_r - k_p)t}] \quad (4)$$

Special and Normal Salt Effects.—The plot of k_p *vs.* lithium perchlorate concentration in Fig. 1 illustrates that the inclusion of lithium perchlorate in the acetolysis of 2-*p*-anisyl-1-propyl *p*-toluenesulfonate (IP) gives rise to a combination of special[3] and normal[8] salt effects on k_p similar to that previously noted[4] for 1-*p*-anisyl-2-propyl *p*-toluenesulfonate (IS) as well as for a number of other compounds.[1-5] Thus, the plot of k_p *vs.* lithium perchlorate concentration in Fig. 1 is linear over the range of 0.03 to 0.10 *M*. Linear extrapolation to zero salt concentration gives $k_p{}^0{}_{\mathrm{ext}}$, the titrimetric rate constant which includes the special salt effect of lithium perchlorate, but excludes its normal salt effect. The least squares fit of these

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

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

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

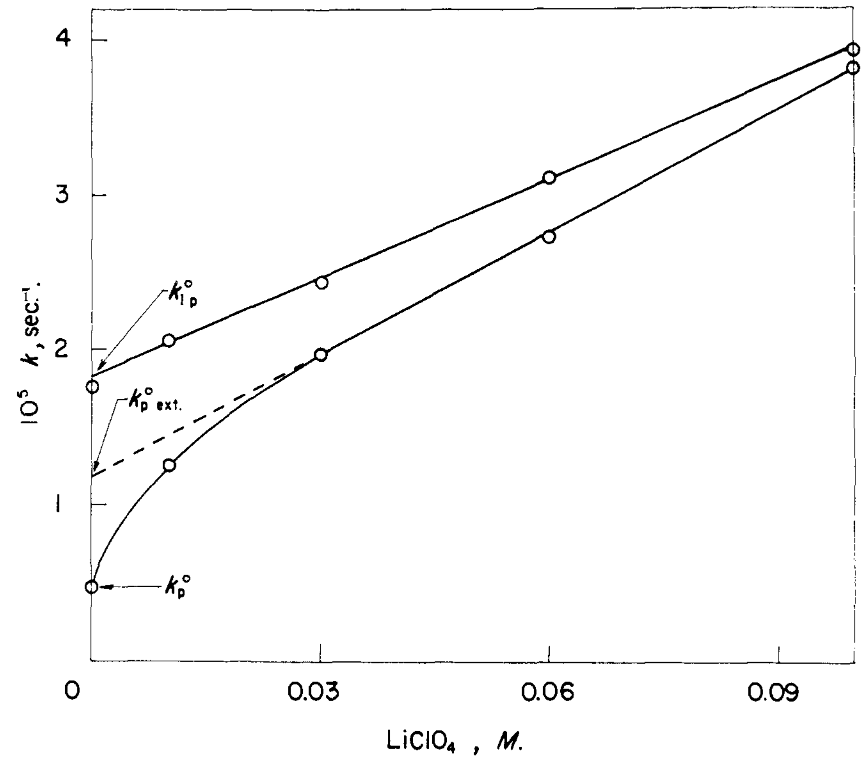

Fig. 1.—Graphical analysis of effect of lithium perchlorate on acetolysis of 2-*p*-anisyl-1-propyl *p*-toluenesulfonate at 50.0°.

data to equation 5 gives $k_p{}^0{}_{ext} = 1.16 \times 10^{-5}$

$$k = k^{\circ}[1 + b(\text{LiClO}_4)] \qquad (5)$$

sec.$^{-1}$ and $b = 22.9$ (Table III).

TABLE III

SUMMARY OF LINEAR SALT EFFECTS

		$10^5 k_{p\ ext}$	$10^5 k_{1p}$
$10^5 k^0$		1.16	1.79
b		22.9	12.0
Linear fit	No. of points	3	5
	Av. fit (% of k)	±0.5	±1.3
	Salt range, M	0.03–0.1	0–0.1

As we have discussed extensively elsewhere,[10–12] rearrangement and acetolysis of 2-anisyl-1-propyl toluenesulfonate (IP) must involve a common rate-determining ionization step. Thus, rearrangement is due to ion pair return. Since the observed kinetics show that secondary isomer IS is produced from primary starting material IP, but primary isomer IP does not arise from the secondary toluenesulfonate IS, ion pair return must produce exclusively the secondary ester IS. On this basis, k_{1p}, the ionization rate constant for the primary toluenesulfonate IP is equal to $(k_r + k_p)$. The effect of lithium perchlorate on $(k_r + k_p)$ is in fact the effect on k_{1p}.

The plot of k_{1p} *vs.* lithium perchlorate concentration in Fig. 1 shows that the pattern of salt effects on k_{1p} is the normal one. The k_{1p} points lie on a good straight line, the least squares fit of the data to equation 5 being summarized in Table III. For k_{1p}, the b-value is 12. That the linear relation 5 gives an excellent fit of the $(k_p + k_r)$ values is shown in Table II, which lists the $(k_p + k_r)$ values predicted by the least squares fit for comparison with the observed ones.

Special Salt Effect and Ion Pair Return.—The present work has added another system where it has been possible to observe salt effects on both ionization rate constants and titrimetric acetolysis rate constants. As in the case of 3-anisyl-2-butyl bromobenzenesulfonate[11] acetolysis, it is very clear that the special salt effect is not concerned with ionization rate, but with modification of ion pair return.

It is obvious from the graphical presentation in Fig. 1 that the special salt effect does not close the gap between k_p and k_{1p}. Not only is $k_p{}^0{}_{ext}$ substantially smaller than $k_{1p}{}^0$, but the values on the $k_{p\ ext}$, k_p line remain lower than the k_{1p} values even at the higher salt concentrations. Just as in acetolysis of 3-anisyl-2-butyl bromobenzenesulfonate,[11] only part of the ion pair return is eliminated in the special salt effect. Again, the best working hypothesis is that the special salt effect eliminates external ion pair return from the solvent-separated ion pair III, but permits internal return from the intimate ion pair II On this basis, we can estimate the importance of return from the intimate ion pair II and the solvent-separated ion pair III in the absence and in the presence of lithium perchlorate.

By the same arguments employed previously,[7] the absence of common ion rate depression in acetolysis of the present systems makes it evident that the solvent-separated ion pair III is the furthest stage of ionization-dissociation which needs to be reckoned with. For a reaction scheme involving intimate and solvent-separated ion pairs II and

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[11] S. Winstein and G. C. Robinson, THIS JOURNAL, 80, 169 (1958).
[12] S. Winstein and K. C. Schreiber, *ibid.*, 74, 2165 (1952).

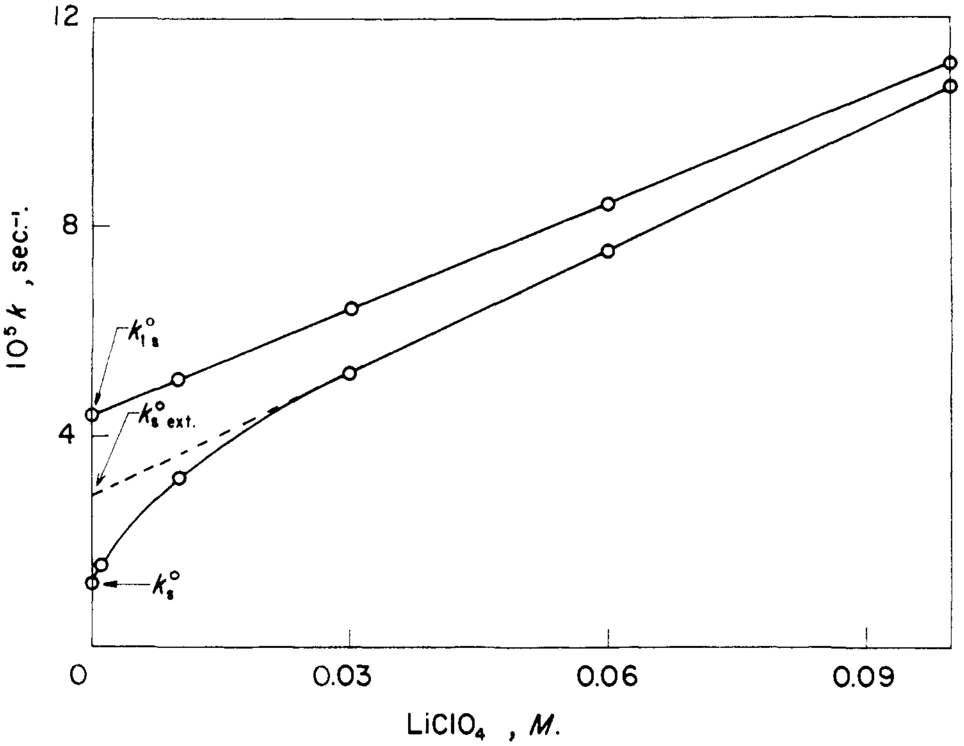

Fig. 2.—Analysis of the effect of lithium perchlorate on acetolysis of 1-*p*-anisyl-2-propyl *p*-toluenesulfonate at 50.0°.

III, with formation of solvolysis product from solvent-separated ion pair III, one may derive[7] expressions 6 and 7 for k_p and $k_{p\ \mathrm{ext}}$. These enable one to calculate k_{-1}/k_2 as well as $k_s^{III}/(k_{-2} + k_s^{III})$.

Apparent values of $k_s^{III}/(k_{-2} + k_s^{III})$ represent the fraction of solvent-separated ion pair III which yields solvolysis product rather than engaging in return. These values listed in Table IV are seen to rise relatively rapidly to 1.00 as lithium perchlorate is added. The values of $k_2/(k_{-1} + k_2)$ represent the fraction of intimate ion pair II which goes on to solvent-separated ion pair III rather than entering into internal return. As shown in Table IV, these values rise relatively slowly as lithium perchlorate is added.

TABLE IV

ANALYSIS OF SALT EFFECTS ON ION PAIR RETURN IN ACETOLYSIS OF 2-ANISYL-1-PROPYL AND 1-ANISYL-2-PROPYL TOLUENESULFONATES AT 50°

(LiClO$_4$), *M*	0	0.003	0.01	0.03
k_{1p}/k_p	3.89	2.37	1.60	1.24
$k_{p\ \mathrm{ext}}/k_p$	2.52	1.59	1.14	1.00
$k_{s\ \mathrm{ext}}/k_s$	2.38	1.56	1.14	1.00
$k_2/(k_{-1} + k_2)$	0.648	0.670	0.715	0.807
$k_s^{III}/(k_{-2} + k_s^{III})$	0.188	0.359	0.665	1.00
F_0	0.65	0.66	0.68	0.73

$$k_p = \frac{k_{1p}}{1 + \dfrac{k_{-1}/k_2}{k_s^{III}/(k_{-2} + k_s^{III})}} \quad (6)$$

$$k_{p\ \mathrm{ext}} = \frac{k_{1p}}{1 + (k_{-1}/k_2)} \quad (7)$$

$$k_{1p} = k^0_{1p}\,[1 + b_{1p}(\mathrm{LiClO_4})] = k^0_{1p} + k^0_{1p}b_{1p}(\mathrm{LiClO_4}) \quad (8)$$

$$k_{p\ \mathrm{ext}} = F_0k^0_{1p} + k^0_{1p}b_{1p}(\mathrm{LiClO_4}) \quad (9)$$

Even the relatively slow increase in the $k_2/(k_{-1} + k_2)$ values may yield an exaggerated notion of the effect of salt on internal return. This is because normal salt effects are sufficiently large at the concentrations of lithium perchlorate employed in the special salt effect that much of the ionization is salt-promoted[8,13] and such ionization is undoubtedly attended by less internal return than is ordinary ionization. The maximum correction for this effect can be made by assuming that there is no ion pair return connected with the salt-promoted ionization. On this basis, one obtains from equations 8 and 9 the value of F_0, the fraction of unpromoted ionization which leads to product. These values of F_0, entered in Table IV, increase less rapidly with lithium perchlorate concentration than do the values of $k_2/(k_{-1} + k_2)$.

Comparison with Secondary Isomer IS.—An important check on certain portions of the mechanistic scheme employed in accounting for salt effects on the behavior of 2-anisyl-1-propyl *p*-toluenesulfonate (IP) may be obtained by comparison of the special salt effects in acetolysis of IP with those in the case of the secondary isomer IS. On the basis of the mechanism employed, expressions for k_s and $k_{s\ \mathrm{ext}}$ may be derived[7] in the form of equations 10 and 11. Division of equation 11 by 10 leads to equation 12 for $k_{s\ \mathrm{ext}}/k_s$. The value of the latter quantity at zero salt concentration, namely, $k_s^0{}_{\mathrm{ext}}/k_s^0$, is the measure of the full magnitude of the special salt effect. Since common intermediates are visualized in acetolysis of both the secondary and primary isomers IS and IP, $k_{s\ \mathrm{ext}}/k_s$ is expected to be equal to $k_{p\ \mathrm{ext}}/k_p$, as can be seen by dividing equation 7 by 6. In other words, both isomers are expected to respond identically to lithium perchlorate in the special salt effect.

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[13] A. H. Fainberg and S. Winstein, THIS JOURNAL, **78**, 2780 (1956).

$$k_s = \frac{k_{1s}}{1 + \dfrac{k_{-1}/k_2}{k_s^{\text{III}}/(k_{-2} + k_s^{\text{III}})}} \quad (10)$$

$$k_{s\ \text{ext}} = \frac{k_{1s}}{1 + (k_{-1}/k_2)} \quad (11)$$

$$(k_{p\ \text{ext}}/k_p) = (k_{s\ \text{ext}}/k_s) = \frac{k_{-1} + k_2[k_s^{\text{III}}/(k_{-2} + k_s^{\text{III}})]}{k_{-1} + k_2} \quad (12)$$

$$(k_{1p}/k_p) = (k_{1s}/k_s) = 1 + \frac{(k_{-1}/k_2)}{k_s^{\text{III}}/(k_{-2} + k_s^{\text{III}})} \quad (13)$$

Examination of the special salt effects in acetolysis of 1-anisyl-2-propyl toluenesulfonate (IS), reported earlier[4] and now illustrated graphically in Fig. 2, discloses that they correspond closely to those observed with the primary isomer IP. Thus, the $k_s^0{}_{\text{ext}}/k_s^0$ and $(\text{LiClO}_4)_{1/2}$ values at 50° reported[4] for the secondary isomer IS were 2.4 and 3×10^{-3} M, respectively. These are nearly identical with the $k_p^0{}_{\text{ext}}/k_p^0$ and $(\text{LiClO}_4)_{1/2}$ values now observed with the primary isomer IP, namely, 2.5 and 3×10^{-3} M, respectively. The identity of $k_{s\ \text{ext}}/k_s$ and $k_{p\ \text{ext}}/k_p$ values at lithium perchlorate concentrations from 0 to 0.03 M is shown explicitly in Table IV.

TABLE V

SUMMARY OF DERIVED RATE CONSTANTS (k_{1s}) OF IONIZATION OF 1-p-ANISYL-2-PROPYL p-TOLUENESULFONATE (IS) IN ACETIC ACID AT 50.0°

(LiClO_4), M	$10^5 k_{1s}$, sec.$^{-1}$ Calcd.[a]	 Lin.[b]
0	4.40	(4.40)
0.003	4.60	4.60
.010	5.08	5.07
.030	6.44	6.42
.060	8.44	8.44
.100	10.99	11.13

[a] Derived from k_s values assuming $k_{1s}/k_s = k_{1p}/k_p$. [b] Based on the linear relation, $10^5 k_{1s} = 4.40[1 + 15.3(\text{LiClO}_4)]$.

TABLE VI

EFFECT OF p-METHOXYL SUBSTITUTION ON SALT EFFECTS AND ION PAIR BEHAVIOR IN ACETOLYSIS

Compound	Temp., °C.	(k_1^0/k_t^0)	Special salt effect $k^0_{\text{ext}}/k^0_t)$	 $(\text{LiClO}_4)_{1/2}$, $10^3 M$	Ion pair return, % From II[a]	 From III[b]
2-Phenyl-1-propyl OBs[6]	75	6	1.0	..	83	*ca.* 0
2-p-Anisyl-1-propyl OTs	50	3.8	2.5	3	35	81
1-p-Anisyl-2-propyl OTs[4]	50	(3.8)[c]	2.4	3	(35)[c]	(81)[c]
threo-3-Phenyl-2-butyl OTs[12]	50	4.6	1.0	..	78	*ca.* 0
threo-3-p-Anisyl-2-butyl OBs[11]	25	4.1 (4.6)[d]	2.6 (2.9)[d]	2	37	81

[a] $100k_{-1}/(k_{-1} + k_2)$. [b] $100k_{-2}/(k_{-2} + k_s^{\text{III}})$. [c] Derived values based on the primary isomer, 2-p-anisyl-1-propyl toluenesulfonate. [d] For toluenesulfonate.

The identity of special (but not normal) salt effects in acetolysis of the structurally isomeric toluenesulfonates confirms: (i) that special salt effects are concerned with altering the behavior of intermediates in solvolysis; and (ii) that the same series of intermediates subject to the same salt effects is involved in acetolysis of both isomers IP and IS.

Although it was not possible in the present work to observe directly the rate of ionization of the secondary isomer IS, it is possible to estimate the value of k_{1s} indirectly because the mechanism of acetolysis of IS is identical with that of the primary isomer IP beyond the rate-determining ionization step. Inspection of equations 6 and 10 shows, as is explicitly stated in equation 13, that k_{1s}/k_s should equal k_{1p}/k_p. Since k_{1p}/k_p values are known, k_{1s} values may be generated from the corresponding known k_s values.

In Table V are listed the generated values of k_{1s}, the rate constant for ionization of 1-anisyl-2-propyl toluenesulfonate (IS), at lithium perchlorate concentrations from 0 to 0.10 M. Also, the values of k_{1s} are shown graphically in Fig. 2. These k_{1s} values conform very closely to the normal linear salt effect pattern of equation 5, the b-value being 15.3. Table V shows explicitly how well equation 5 reproduces the generated k_{1s} values.

Effect of p-Methoxyl Substitution on Ion Pair Behavior.—The comparison of the 2-anisyl-1-propyl system with the 2-phenyl-1-propyl[6] analog with respect to ion pair return accompanying acetolysis is similar to the 3-anisyl-2-butyl[11]–3-phenyl-2-butyl[12] comparison. In fact, it is profitable to list both comparisons together, as is done in Table VI.

From Table VI it is clear that the 2-anisyl-1-propyl toluenesulfonate system resembles the 3-anisyl-2-butyl[11] analog rather closely with respect to the importance of return during acetolysis from intimate and solvent-separated ion pairs II and III. The substitution of a p-methoxyl group into the 2-phenyl-1-propyl or 3-phenyl-2-butyl system decreases slightly the over-all importance of ion pair return. However, it has a major effect on the distribution of ion pair return between internal and external ion pair return[7] (from II and III, respectively). Internal return is much reduced in importance, while return from solvent-separated ion pair III is introduced strongly.

It is helpful to visualize the effects of p-methoxyl substitution with the aid of the schematic free energy plot in Fig. 3. The introduction of a p-methoxyl group, which decreases $\Delta F_1^{\pm}$, the free energy of activation for ionization, also decreases $\Delta F_2^{\pm} - \Delta F_{-1}^{\pm}$, the difference between free energies of activation for progression to the solvent-separated ion pair III and for internal return, respectively. Intuitively, one would predict that $\Delta F_{-1}^{\pm}$ increases, while $\Delta F_2^{\pm}$ may decrease. The introduction of the p-methoxyl group evidently increases $\Delta F_s^{\text{III}\pm} - \Delta F_{-2}^{\pm}$ markedly. Probably the most important reason for this is the effect on $\Delta F_s^{\text{III}\pm}$, the free energy of activation for collapse of ion pair III to solvolysis product. Stabilization of the carbonium ion portion of the ion pair III probably results in a larger $\Delta F_s^{\text{III}\pm}$.

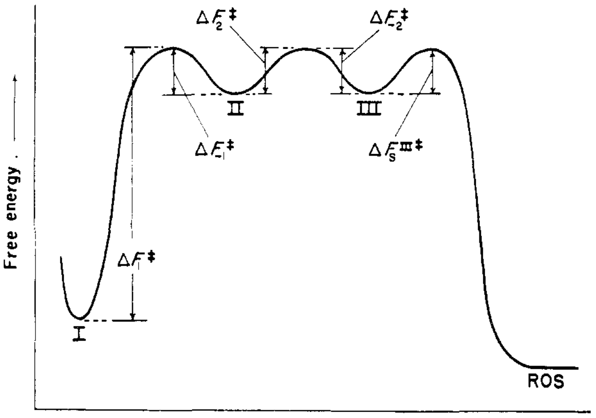

Fig. 3.—Schematic free energy diagram.

Kinetic Appendix

In carrying out the kinetic analysis of the simultaneous solvolysis and rearrangement of a substance such as 2-anisyl-1-propyl toluenesulfonate (IP), it is necessary to obtain values of the instantaneous first-order solvolysis rate constant k at each experimental point. The procedure employed previously for α,α-dimethylallyl chloride[10] and 2-phenyl-1-propyl bromobenzenesulfonate[6] involved preparation of a large scale plot of $(a - x)$ *vs.* t and the determination of slopes with the aid of a tangent meter. Such a purely graphical procedure suffers from the disadvantage that it is rather subjective and insufficiently sensitive in the treatment of small rate changes. Using equation[10] 14, which expresses $(a - x)$ as a function of time, we have instead obtained the instantaneous rate constants k analytically from the corresponding integrated rate constants $\bar{k}$ by a method of successive approximations.

$$(a - x) = \frac{a}{k_s - k_p - k_r}[(k_s - k_p)e^{-(k_r + k_p)t} - k_r e^{-k_s t}] \quad (14)$$

$$k = k_p + f(\bar{k} - k_p) \quad (15)$$

The first-order integrated rate constants $\bar{k}$, calculated from the true zero of reaction time *via* equation 1, are plotted against percentage reaction, as in Fig. 4. A preliminary linear extrapolation to zero reaction gives a first approximation to $\bar{k}^0 = k^0 = k_p$. It is convenient to define by equation 15 the quantity f which relates each instantaneous rate constant k to the corresponding integrated rate constant $\bar{k}$. The first approximations to k are made with equation 15 taking f to be constant in a run and equal to 2.00 (first approximation to f). From this set of values are obtained the first approximations to F_p (equation 2) and to $(k_r + k_p)$ (equation 3).

Using these first approximations to k_r and k_p, and the experimental value of k_s, an "ideal" set of values of $(a - x)$ are calculated *via* equation 14 at times corresponding to the experimental times. From these "ideal" data are calculated an "ideal" set of F_p's *via* equation 3, and thence a set of "ideal" k's *via* equation 2. In addition, a set of "ideal" $\bar{k}$'s are generated *via* equation 1. A comparison of each k with its corresponding $\bar{k}$ *via* equation 15 gives rise to a set of f's relating these quantities; this constitutes the second approximation to f.

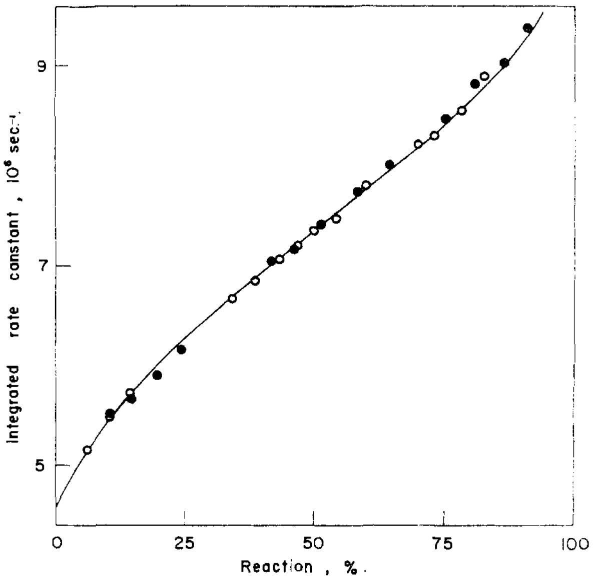

Fig. 4.—Plot of integrated rate constant $\bar{k}$ *vs.* % reaction for acetolysis of 2-*p*-anisyl-1-propyl *p*-toluenesulfonate at 50.0°: circles experimental data; curve calculated for k_r = 0.46 × 10^{-5} sec.$^{-1}$, $k_r + k_p$ = 1.76 × 10^{-5} sec.$^{-1}$, and k_s = 1.198 + 10^{-5} sec.$^{-1}$.

At this point, a plot of the "ideal" $\bar{k}$'s *vs.* percentage reaction is constructed. The resulting curve is superimposed on the plot of the experimental $\bar{k}$ *vs.* percentage reaction, as in Fig. 4. With the aid of this curve, a much superior extrapolation to $\bar{k}^0 = k^0 = k_p$ can be made. This second approximation to k_p, together with the set of second approximations to f, are now employed to calculate the second approximation to $(k_r + k_p)$ as described above.

If necessary, the whole process described above can then be repeated as many times as is necessary to attain the accuracy inherent in the data. In practice, however, it was found that convergence is very rapid, and that the process, with one additional modification, usually did not have to be car-

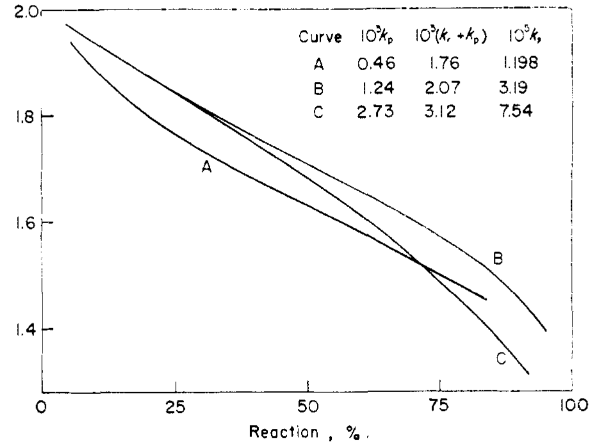

Fig. 5.—Plot of $f = (k - k_p)/(\bar{k} - k_p)$ *vs.* % reaction.

ried beyond the second approximation. This modification resulted from the observation that the factor *f* is mainly a function of the percentage reaction, and only to a much lesser degree of the relative magnitudes of k_s, k_r and k_p. Thus, from Fig. 5, in which *f* is plotted against percentage reaction for several combinations of values of k_s, k_r and k_p, it is obvious that a much superior first approximation to *f* can be made by taking average values from this plot in place of using the constant value of 2. When this was done, the correction involved in going from the first to the second approximation became very much smaller, and the need for a third approximation was usually obviated.

Experimental Part

2-*p*-Anisyl-1-propyl *p*-Toluenesulfonate.—2-*p*-Anisyl-1-propanol, b.p. 80° (0.15 mm.), $n^{25}\text{D}$ 1.5278, prepared by lithium aluminum hydride reduction of the corresponding aldehyde, was converted in the usual way to the *p*-toluenesulfonate, m.p. 34–35°.

Anal. Calcd. for $C_{17}H_{20}O_4S$: C, 63.72; H, 6.29. Found: C, 63.79; H, 6.44.

Kinetic Measurements.—The anhydrous acetic acid, and the solutions of lithium perchlorate in acetic acid, were the same as those previously described.[4] The usual sealed ampoule technique was employed, the development of *p*-toluenesulfonic acid being followed by titration with standard sodium acetate in acetic acid using brom phenol blue indicator.[14] Solvolysis was followed to 80–95% completion. Experimental infinity titers agreed with those calculated within an average of 0.2%.

To obtain reaction time intervals from the so-called "true" zero time, the elapsed time interval from immersion in the 50° thermostat was corrected by subtracting an empirically determined "warm-up time" of 66 seconds. This figure was obtained from solvolysis of materials solvolyzing with steady first-order rate constants of 10^{-4} sec.$^{-1}$ or higher.

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

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE WM. H. NICHOLS CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

The Configurational Correlation of Optically Active Biphenyls with Centrally Asymmetric Compounds. The Absolute Configuration of 6,6′-Dinitro-2,2′-diphenic Acid[1]

BY PAUL NEWMAN,[2] PHILIP RUTKIN AND KURT MISLOW[3]

RECEIVED JULY 1, 1957

Incomplete reduction of (±)-4′,1″-dinitro-1,2,3,4-dibenz-1,3-cycloheptadiene-6-one (DNDBCH-6-one) with *S*(+)-pinacolyl alcohol and *S*(+)-2-octanol, in the presence of aluminum *t*-butoxide in dioxane, gives, in each case, a mixture of (+)-DNDBCH-6-one and (−)-DNDBCH-6-ol. These results can be accounted for readily on the basis of a simple model for the transition state of the reduction. Accordingly, (+)-DNDBCH-6-one has been assigned the *S*-configuration, and, since (+)-DNDBCH-6-one has been prepared from (−)-6,6′-dinitro-2,2′-diphenic acid, the latter compound also has been shown to possess the *S*-configuration. This method of correlation should be applicable to any optically stable hindered 2,2′-diphenic acid, regardless of the nature of the blocking substituents in the 6,6′-positions. Pseudo-first order rate constants have been obtained for the above transformations, and the difference in free energy of the competing diastereomeric transition states has been estimated.

The optical resolution of 6,6′-dinitro-2,2′-diphenic acid[4] provided the first example of enantiomerism resulting from restricted rotation about a single bond (conformational enantiomerism, *Atropisomerie*), a phenomenon which has since been amply documented in many diverse cases.[5] The problem of the absolute configuration of such compounds has remained a major one in stereochemistry: although an enormous body of configurational correlations exists in the field of centrally asymmetric compounds,[6] the area of optically active biphenyls has remained virtually untouched.[7]

The absolute configuration of optically active biphenyls could, in principle, be determined by the

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[1] Configurational Studies in the Biphenyl Series. I. Preliminary reports of portions of the work described in this and the following papers: (a) K. Mislow, *Trans. N. Y. Acad. Sci.*, [2] **19**, 298 (1957); (b) K. Mislow and P. Newman, THIS JOURNAL, **79**, 1769 (1957); (c) K. Mislow, P. Rutkin and A. K. Lazarus, *ibid.*, **79**, 2974 (1957).

[2] Trubek Fellow, 1956–1957.

[3] To whom correspondence regarding the article should be addressed.

[4] G. H. Christie and J. Kenner, *J. Chem. Soc.*, 614 (1922).

[5] *E.g.*, *cf.* G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 202 ff.; R. L. Shriner, R. Adams and C. S. Marvel, in H. Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 343 ff.; M. S. Newman, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 471 ff.

[6] *E.g.*, *cf.* K. Freudenberg, in K. Freudenberg, "Stereochemie," F. Deuticke, Leipzig and Vienna, 1932, pp. 662 ff.; J. A. Mills and W. Klyne, in W. Klyne, "Progress in Stereochemistry," Academic Press, Inc., New York, N. Y., 1954, pp. 177 ff. Recent examples of unusual interest are (a) the chemical correlation of centrally asymmetric carbon with asymmetric quadricoördinate nitrogen, by G. Fodor, J. Toth and I. Vincze, *J. Chem. Soc.*, 3504 (1955), *et seq.* (*cf.* also G. Fodor, *Tetrahedron*, **1**, 86 (1957)), and (b) the correlation (by X-ray methods) of centrally asymmetric carbon with centrally asymmetric tricoördinate sulfur, by R. Hine and D. Rogers, *Chemistry & Industry*, 1428 (1956). The determination of the screw-sense of the polypeptide α-helix (A. Elliott and B. R. Malcolm, *Nature*, **178**, 912 (1956)) by the X-ray method may be regarded as an elegant and important extension in this field.

[7] (a) Through correlating thebaine and phenyldihydrothebaine, J. A. Berson, THIS JOURNAL, **78**, 4170 (1956), recently has succeeded in assigning absolute configurations to phenyldihydrothebaine as well as to simpler biphenylic derivatives of the latter; (b) W. Kuhn and K. Bein, *Z. physik. Chem.*, **24B**, 335 (1934), on the basis of qualitative arguments derived from their theoretical model, assigned the *R*-configuration to (−)-6,6′-dinitro-2,2′-diphenic acid; (c) W. Kuhn and R. Rometsch, *Helv. Chim. Acta*, **27**, 1080, 1346 (1944), assigned the *R*-configuration to (−)-6,6′-dimethyl-2,2′-biphenyldiamine and to (−)-2,2′-dichloro-6,6′-dimethyl-4,4′-biphenyldiamine, on the basis of quantitative, theoretical arguments.