5-Methoxyl Participation in Acetolysis.
Ion and Ion-Pair Intermediates[1]

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Abstract: Two varieties of O-methyl-2-methyltetrahydrofuranium ion pairs as well as the corresponding dissociated ion are identified as common intermediates in the acetolysis of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) p-bromobenzenesulfonates. Diagnostic probes for detecting intervention of these intermediates included investigation of common ion rate depression, anion exchange, and the effect of salts such as lithium perchlorate on the titrimetric (k_t) and ionization (k_1) rate constants. As a consequence of ion pair return, IP and IS rearrange into each other during acetolysis. The kinetics require the intervention of a symmetrical intimate cyclic tertiary oxonium ion pair. A consideration of the geometry of the MeO-5 transition state leading to ionization also implies the occurrence of two unsymmetrical intimate ion pair species. The possibility of product arising from the intimate ion pairs is considered, and the available evidence suggests that this route is unimportant. The fraction of intimate and solvent-separated ion pairs showing internal return and external ion pair return, respectively, is comparable to the results for other long-lived bridged cation intermediates. The data for IP and IS fit a lithium perchlorate special salt effect mechanism which involves a metathetical diversion of solvent-separated ion pairs $R^+\|X^-$ by salt ion pair M^+Y^-.

O-Methyl cyclic tertiary oxonium ions have been employed to explain the kinetics and the product observations for the solvolysis of δ-methoxyalkyl arenesulfonates.[2] However, as we have pointed out earlier, the mechanistic details are a good deal more complicated than this simple interpretation. A cursory reconnaissance of the effect of the inclusion of salts such as lithium perchlorate on the acetolysis kinetics indicated clearly that it is necessary to distinguish between several kinds of cyclic tertiary oxonium ion intermediates.[2c] Since systems showing MeO-5 participation are a structural extreme among RX substrates in solvolysis, these preliminary results also suggested that such systems represent an important calibration point for our understanding of ion pairs and dissociated ions in solvolysis.[3] This present paper deals with our more extensive investigation of MeO-5 participation and the accompanying formation of ion pairs and dissociated ions in acetolysis. The 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) p-bromobenzenesulfonate system was selected for the study because these isomers, which by coincidence solvolyze at almost identical rates, form the same O-methyl-2-methyltetrahydrofuranium ion structure.[2a] On the basis of this, it appeared feasible to obtain ionization rate constants by kinetic methods[4] and to evaluate ion and ion pair return by examining the effects of various added salts on the kinetics.[3] Such an investigation

has been accomplished and the results are here presented and discussed.

Results

Acetolysis Kinetics and Common Ion Rate Depression. Table I summarizes the pertinent titrimetric rate constants, k_t, for the study of the effects of added salts on the acetolysis of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) p-bromobenzenesulfonates. As noted previously,[2a] acetolysis of IP and IS, followed titrimetrically, obeyed good first-order kinetics. Satisfactory first-order behavior was observed with acetic acid containing added salts, except for the inclusion of lithium p-toluenesulfonate and for the very low concentrations of lithium perchlorate. In the latter two cases the first-order rate constants drifted downward during the course of a kinetic run. For the drifting rates, the rate constants listed in Table I are initial values which were obtained as the slope near zero reaction from a first-order plot of ln $(a - x)$ vs. t using eq 1, where a is the initial concentration of sulfonate ester and x is the concentration of reacted material at time t.

$$\ln [a/(a - x)] = k_t t \qquad (1)$$

Even though there was no noticeable downward drift in k_t during acetolysis of either IP or IS, a composite consideration of the salt effect pattern for a whole spectrum of compounds (see Table VI) placed both in the division showing common ion rate depression.[3b] For this reason both isomers were meticulously scrutinized for the occurrence or absence of common ion rate depression. Other work in these laboratories has shown that maximum depression of rate can be achieved with very low concentrations of arenesulfonate salts.[3d,5,6] Further, it is evident that an arenesulfonate sample, although analytically pure, can contain enough of some ionic sulfonate salt to cause nearly full common ion rate depression.[5,6] Consequently,

(1) (a) Research supported by the National Science Foundation. (b) Paper XXXII in the series, "Salt Effects and Ion Pairs in Solvolysis and Related Reactions"; paper XXVIII in the series, "The Role of Neighboring Groups in Replacement Reactions."

(2) (a) E. L. Allred and S. Winstein, *J. Am. Chem. Soc.*, **89**, 3391 1967; (b) S. Winstein, E. L. Allred, and P. Klinedinst, Jr., Foreign Papers at the 8th Mendeleev Congress of Pure and Applied Chemistry, Moscow, USSR, March 1959, p 48; (c) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

(3) S. Winstein, *et al.*: (a) *Chem. Ind.* (London), 664 (1954); (b) *J. Am. Chem. Soc.*, **78**, 328 (1956); (c) *ibid.*, **80**, 169 (1958); (d) *ibid.*, **83**, 885, 4986 (1961); (e) *ibid.*, **86**, 2072 (1964); (f) *ibid.*, **86**, 2720 (1964); (g) Special Publication No. 19, The Chemical Society, London, 1965, p 109.

(4) (a) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **80**, 459 (1958); (b) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

(5) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).

(6) P. Klinedinst, unpublished work.

Table I. Summary of Acetolysis Rates of 4-Methoxy-1-pentyl (IP) and 5-Methoxy-2-pentyl (IS) p-Bromobenzenesulfonates with Added Salts at 25.20°

ROBs	(ROBs), 10^2 M	Salt	(Salt) 10^2 M	$10^5 k_t$, sec^{-1}
IP	0.97	...	...	1.85 ± 0.03[a]
	1.02	...	...	1.84 ± 0.03[b]
	0.97	LiOBs	0.100	1.71 ± 0.02[c]
	0.99	LiOTs	2.00	2.21 - 0.61[d]
	0.98	LiClO₄[e]	0.0020	2.40[d]
	0.98	LiClO₄	0.0060	3.04[d]
	0.98	LiClO₄	0.0100	3.53[d]
	0.99	LiClO₄	0.0250	4.28[d]
	0.98	LiClO₄	0.0500	4.68[d]
	0.99	LiClO₄	0.100	4.76[d]
	3.12	LiClO₄	0.500	5.11 ± 0.07
	3.18	LiClO₄	1.00	5.50 ± 0.06
	3.25	LiClO₄	2.00	6.07 ± 0.05
	3.35	LiClO₄	3.00	6.52 ± 0.05
	3.40	LiClO₄	4.00	6.96 ± 0.06
	3.33	LiClO₄	5.00	7.39 ± 0.09
	0.98	LiOBs / LiClO₄	1.00 / 0.100	2.61[d]
IS	0.98	...	...	1.86 ± 0.03[a]
	0.99	...	...	1.86 ± 0.03[b]
	0.99	LiOBs	0.100	1.73 ± 0.01[c]
	1.00	LiOTs	2.00	2.14 - 0.61[d]
	0.98	LiClO₄[e]	0.0020	2.46[d]
	0.98	LiClO₄	0.0060	3.09[d]
	0.97	LiClO₄	0.0100	3.53[d]
	0.99	LiClO₄	0.0250	4.34[d]
	0.99	LiClO₄	0.0500	4.77[d]
	1.00	LiClO₄	0.100	4.85[d]
	3.06	LiClO₄	0.500	5.30 ± 0.05
	3.32	LiClO₄	1.00	5.75 ± 0.05
	3.30	LiClO₄	2.00	6.49 ± 0.03
	3.28	LiClO₄	3.00	7.03 ± 0.05
	3.38	LiClO₄	4.00	7.76 ± 0.05
	3.38	LiClO₄	5.00	8.35 ± 0.04
	0.98	LiOBs / LiClO₄	1.00 / 0.100	2.67[d]

[a] Common ion rate depression study, first water washing treatment, five times. See Experimental Section. [b] Common ion rate depression study, second water washing, ten times. [c] Common ion rate depression study, ROBs from second water washing treatment. [d] Downward drifts in rate were noted for low concentrations of lithium perchlorate. The reported constant is an initial value estimated from a plot of log $(a - x)$ vs. time. [e] The product used for the lithium perchlorate study was not specially treated by water washing (see a and b). However, it was recrystallized three times from a 40:60 ether–pentane solvent. Indications are that this removed essentially all common ion salts.

both IP and IS were treated specially to remove any trace amounts of occluded ionic bromobenzenesulfonate salts. A bromobenzenesulfonate sample was purified by three low-temperature recrystallizations from ether–pentane solvent and then dissolved in the solvent and subjected to exhaustive washing with five different portions of distilled water. After drying, the bromobenzenesulfonate was recrystallized and a rate measurement was made in acetic acid covering from ca. 2 to 90% reaction. The remaining sample was subjected again to exhaustive extraction with ten separate portions of water. Again, after recrystallization, another rate measurement was made. The rate constants after each washing treatment were numerically the same for both IP and IS as indicated in Table I. Very little, if any, downward drift outside of experimental deviations could be detected. However, when the products from the second water extraction were solvolyzed in acetic acid containing 0.001 M lithium p-bromobenzenesulfonate, the rate constants were

diminished by ca. 8% for both bromobenzenesulfonates. This rate depression was shown to be outside of experimental error by comparing duplicate rate experiments. It is clear that both esters do show a small amount of rate depression by the addition of the common anion.

Exchange and Special Salt Effects. The exchange of toluenesulfonate anion for bromobenzenesulfonate anion were relatively efficient in acetolysis of IP and IS. For example, addition of 0.02 M lithium p-toluenesulfonate caused the rate constant values to drift downward from initial values about 5–8% higher than for IP and IS without added salt. At ca. 60% reaction the conversion was nearly complete for both isomers since the instantaneous rate constants were fairly steady at the values estimated for the toluenesulfonates, roughly one-third of the initial values. This behavior is illustrated in Table II and graphically in Figure 1 by first-order plots of log $(a - x)$ vs. time.

Table II. Acetolysis of 0.0099 M 4-Methoxy-1-pentyl p-Bromobenzenesulfonate (IP) with Added 0.0200 M LiOTs at 25.20°

Time, sec	% reaction	0.0110 M NaOAc,[a] ml	$10^5 k_t$, sec^{-1} Integ	$10^5 k_t$, sec^{-1} Instant.[b]
000	0.70	0.032	...	2.21
965	3.04	0.140	2.46	2.12
2,613	6.09	0.280	2.12	1.79
4,506	9.57	0.440	2.08	1.57
6,470	12.51	0.575	1.96	1.45
10,562	16.53	0.760	1.65	1.27
16,270	21.36	0.982	1.43	1.14
24,595	26.97	1.240	1.25	0.98
41,680	34.42	1.720	1.11	0.77
68,036	48.07	2.210	0.95	0.72
97,726	57.43	2.640	0.87	0.68
129,830	64.28	2.955	0.79	0.61
176,925	73.96	3.400	0.76	0.61
258,996	85.27	3.920	0.74	...
∞		4.597		

[a] Per 5.14-ml aliquot. [b] Evaluated as the slope at time t from a first-order plot of ln $(a - x)$ vs. t. The slope was determined with the aid of a tangent meter.

As is illustrated for IS by a plot of titrimetric rate constant vs. lithium perchlorate concentration in Figure 2, both IP and IS display the steep special salt effect pattern[3c,d,7,8] at lower concentrations and develop the normal linear pattern[7,9] at higher concentrations of lithium perchlorate. Further, it is evident by greatly expanding the scale for lithium perchlorate concentration (Figure 3) that both isomers respond identically with the special salt effect of lithium perchlorate. The ratio k^0_{ext}/k_t^0 measures the magnitude of the special salt effect. The rate constant k^0_{ext} is obtained by a short extrapolation of the linear part of the k_t vs. [LiClO₄] plot to zero salt concentration, and includes the special but not the normal salt effect. For IP and IS the k^0_{ext}/k_t^0 ratios are 2.75 and 2.76, respectively, and numerically are similar to values observed in a number of other cases.[7,8,10] Another means for

(7) A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78, 2767 (1956).
(8) A. H. Fainberg, G. C. Robinson, and S. Winstein, ibid., 78, 2777 (1956).
(9) A. H. Fainberg and S. Winstein, ibid., 78, 2763 (1956).
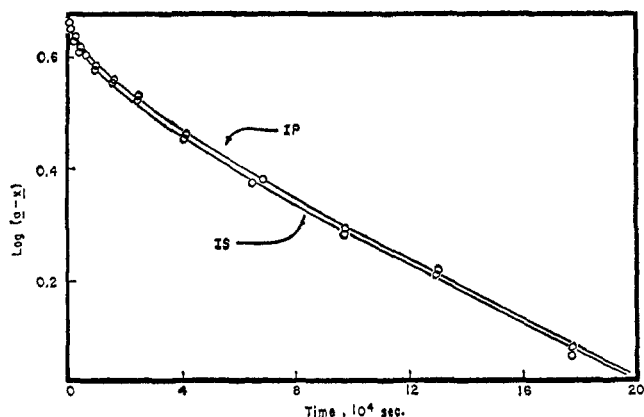(10) S. Winstein and E. Clippinger, ibid., 78, 2784 (1956).

Figure 1. Acetolysis of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) p-bromobenzenesulfonates with 0.0200 M LiOTs at 25.20°.
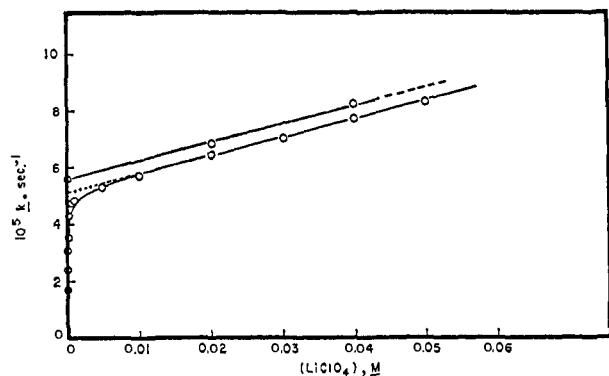

Figure 2. Effects of lithium perchlorate on acetolysis of 5-methoxy-2-pentyl p-bromobenzenesulfonate (IS) at 25.20°.
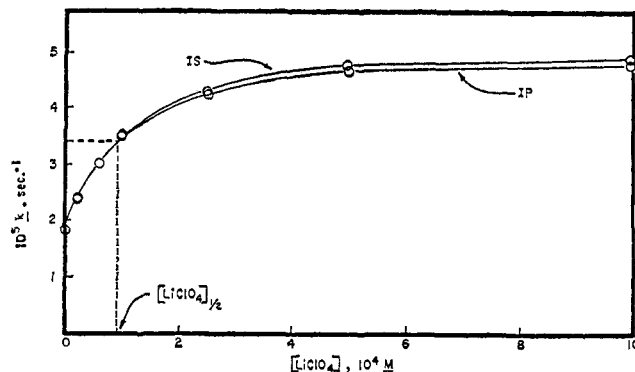

Figure 3. Special salt effect of lithium perchlorate on acetolysis of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) p-bromobenzenesulfonates at 25.20°.

characterizing the special salt effect has been the quantity $(LiClO_4)_{1/2}$, the concentration of lithium perchlorate which produces one-half of the total special salt effect.[7] For the IP–IS system the value for $(LiClO_4)_{1/2}$ is 9×10^{-5} M which compares to values of ca. 4–8×10^{-5} M for cholesteryl and 2-(2,4-dimethoxyphenyl)ethyl arenesulfonates.[10] The latter two systems show the sharpest differentiation between the special and normal salt effects yet reported. The normal part of the lithium perchlorate salt effect can be characterized with the aid of the b_t values from the fit of the data to the linear relation given in eq 2. The b_t value represents the per cent increase in rate constant per 0.01 M increment of lithium perchlorate.[7] The secondary IS isomer exhibits a larger normal salt effect than the primary IP compound, the b_t values being 12.5 and 9.0, respectively. As noted previously,[3c,7,9,11] values of b_t tend to be somewhat higher for secondary arenesulfonates than for the primary esters.

$$k_t = k^0_{ext}[1 + b_t(LiClO_4)] \qquad (2)$$

The slight downward drift in acetolysis of IP and IS at low lithium perchlorate concentrations (ca. 10^{-5} to 10^{-4} M) is suggestive that a common ion effect due to accumulating p-bromobenzenesulfonic acid is operating.[3d] This was confirmed by comparing the initial rate constants of a bromobenzenesulfonate solution containing only lithium perchlorate and a solution

containing lithium p-bromobenzenesulfonate in addition to the same lithium perchlorate concentration. When 0.01 M lithium p-bromobenzenesulfonate was included in a solution 0.001 M in lithium perchlorate, the initial rate constants for both isomers were lower than for 0.001 M lithium perchlorate alone by a factor of 1.8. Thus, in this system the induced common ion variety of rate depression is much more serious than is direct common ion rate depression.[3d]

Equilibration of IP and IS during Acetolysis. Rearrangement studies of IP and IS during acetolysis were accomplished by examination of the bromobenzenesulfonate remaining in solution after varying lengths of time. The unreacted bromobenzenesulfonate was recovered in 90–95% yield by pouring the acetic acid solution into ice–water and immediately extracting with an ether–pentane solvent. Degradation of the bromobenzenesulfonate to hydrocarbon involved reductive oxygen–carbon cleavage of the sulfonate group by lithium aluminum hydride in ether. After reduction, the aluminum salts were removed, and the ether mixture was analyzed by gas chromatography. This simple degradation method was complicated, however, by the fact that reduction of pure samples of IP and IS gave mixtures of three products, methyl 2-pentyl ether, methyl 1-pentyl ether, and 2-methyltetrahydrofuran.[12] Nevertheless, it was still feasible to use this method for analytical purposes because the product ratios from the two isomeric bromobenzenesulfonates were widely different and very reproducible. The reproducibility was checked by comparison of a total of three separate reductions each for pure samples of IP and IS using a standard set of reaction conditions; it was found to be ca. ±0.15%. To avoid any unpredictable variation, the same filtered, homogeneous solution of lithium aluminum hydride in ether was used for all reductions. Table III summarizes the standardization results.

By using the data of Table III in eq 3 and 4, it is possible to calculate the per cent of IP and IS in the recovered p-bromobenzenesulfonate at any time t. In eq 3, F_{IP} and $(1 - F_{IP})$ are the mole fractions of IP and IS, respectively, in the recovered p-bromobenzenesulfonate sample; $0.9639F_{IP}$ and $0.1720(1 - F_{IP})$ are the respective fractions of IP and IS which give methyl 2-pentyl ether (P'); and $f_{P'}$ is the experimentally

(11) A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 78, 2780 (1956).

(12) The details and probable meaning of these highly interesting results will be discussed in a subsequent paper.

Table III. Standardization of the Lithium Aluminum Hydride Reduction of 4-Methoxy-1-pentyl (IP) and 5-Methoxy-2-pentyl (IS) *p*-Bromobenzenesulfonates

Products[a]	Total product ratio, mole %[b] For IP[c]	Total product ratio, mole %[b] For IS[c]
Methyl 2-pentyl ether (P')	96.39 ± 0.14	17.20 ± 0.15
Methyl 1-pentyl ether (S')	0.43 ± 0.08	72.66 ± 0.17
2-Methyltetrahydrofuran	3.18 ± 0.12	10.14 ± 0.13

[a] The identity of these ethers was confirmed by comparison of retention times with pure authentic samples. [b] These ratios as determined by gas chromatography are wt %. The reported values have been corrected. [c] The numerical values are the average of three separate reductions each for IP and IS. Three separate gas chromatographic determinations were made for each reduction run.

per cent of IP and IS in the mixed bromobenzenesulfonate M. Both IP and IS tend toward the same 69:31 mixture as illustrated graphically by Figure 4 with a plot of per cent acetolysis *vs.* per cent IS isomer.

$$ROBs{-}IP \xrightarrow{k_{mp}} ROBs{-}M \tag{5}$$

$$ROBs{-}IS \xrightarrow{k_{ms}} ROBs{-}M \tag{6}$$
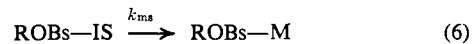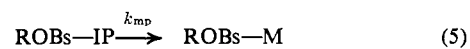
$$k_{mp} = (2.303/t) \log 69/(69 - \% \, IS) \tag{7}$$

$$k_{ms} = (2.303/t) \log 31/(31 - \% \, IP) \tag{8}$$

In acetic acid solvent without added lithium perchlorate, four separate values for the mixing rate of both

Table IV. Summary of the Rearrangement during Acetolysis of 4-Methoxy-1-pentyl *p*-Bromobenzenesulfonate (IP) at 25.20°

Time, sec	Added LiClO₄, M	% acetolysis	Ratio of prodt from LiAlH₄ reduct, mole %[a] Methyl 2-pentyl ether	Ratio of prodt from LiAlH₄ reduct, mole %[a] Methyl 1-pentyl ether	Ratio of prodt from LiAlH₄ reduct, mole %[a] 2-Methyl-tetrahydro-furan	% IS isomer calcd from Eq 3	% IS isomer calcd from Eq 4	% IS isomer calcd from Av	10⁵k_{mp}, sec⁻¹
0[b]	...	0	94.95	1.80	3.25	1.8	1.9	1.9	...
9,060	...	15	79.56	15.62	4.76	21.2	21.1	21.2	4.05
20,040	...	30	66.56	27.68	5.76	37.7	37.7	37.7	3.94
40,440	...	50	52.70	39.87	7.43	55.2	54.6	54.9	3.93
40,560	...	50	52.95	40.92	6.13	54.9	56.1	55.5	4.02
									Av 3.98 ± 0.05
11,310	0.020	50	91.08	4.23	4.69	6.7	5.3	6.0	0.54[c]
9,750	0.040	50	91.91	3.04	5.05	5.7	3.6	4.6	0.42[c]

[a] These numerical values are wt % as determined by gas chromatography. The reported values have been corrected to mole %. The reported numbers for each experiment are an average of three separate gas chromatographic determinations. [b] A control experiment to determine the amount of rearrangement of IP during work-up and recovery. [c] Corrected for the 1.9% rearrangement obtained in the work-up of the control run.

Table V. Summary of the Rearrangement during Acetolysis of 5-Methoxy-2-pentyl *p*-Bromobenzenesulfonate (IS) at 25.20°

Time, sec	Added LiClO₄, M	% acetolysis	Ratio of prodt from LiAlH₄ reduct, mole %[a] Methyl 2-pentyl ether	Ratio of prodt from LiAlH₄ reduct, mole %[a] Methyl 1-pentyl ether	Ratio of prodt from LiAlH₄ reduct, mole %[a] 2-Methyl-tetrahydro-furan	% IP isomer calcd from Eq 3	% IP isomer calcd from Eq 4	% IP isomer calcd from Av	10⁵k_{ms}, sec⁻¹
9,000	...	15	25.72	64.11	10.17	10.8	11.8	11.3	5.04[b]
20,040	...	30	30.77	60.06	9.17	17.1	17.4	17.3	4.08
39,900	...	50	36.44	55.99	7.57	24.3	23.8	24.1	3.77
40,440	...	50	36.30	54.58	9.12	24.1	25.0	24.6	3.90
									Av 3.92 ± 0.11
10,560	0.020	50	18.12	71.81	10.07	1.2	1.2	1.2	0.37
8,940	0.040	50	17.26	72.13	10.61	0.1	0.7	0.4	0.51

[a] These numerical values are wt % as determined by gas chromatography. The reported values have been corrected to mole %. The reported numbers for each experiment are an average of three separate gas chromatographic analyses. [b] The point for 15% acetolysis was omitted from the average.

determined total mole fraction of P'. Similarly for eq 4, F_{IS} and $(1 - F_{IS})$ are the fractions of IS and IP in the recovered *p*-bromobenzenesulfonate; $0.7266F_{IS}$ and $0.0043(1 - F_{IS})$ are the fractions of IS and IP which result in methyl 1-pentyl ether (S'); and $f_{S'}$ is the total fraction of S' coming from IP and IS. Thus, eq 3 and 4 offer two independent means for determining the per cent IP and IS in the recovered *p*-bromobenzenesulfonate. The rearrangement results for various stages of acetolysis are reported in Tables IV and V. For acetolysis it is possible to evaluate the equilibra-

$$f_{P'} = 0.9639F_{IP} + 0.1720(1 - F_{IP}) \tag{3}$$

$$f_{S'} = 0.7266F_{IS} + 0.0043(1 - F_{IS}) \tag{4}$$

tion or mixing rate constants, symbolized k_{mp} and k_{ms} and defined by eq 5 and 6, with the aid of eq 7 for IP and eq 8 for IS. The numbers 69 and 31 refer to the

arenesulfonates were determined at three different states of solvolysis. As shown in Tables IV and V, the mixing rate constants for first-order approach of bromobenzenesulfonates IP and IS to mixed bromobenzenesulfonate M were essentially the same, the average value being $(3.98 \pm 0.05) \times 10^{-5}$ sec⁻¹ for IP and $(3.92 \pm 0.11) \times 10^{-5}$ sec⁻¹ for IS at 25.20°. It is seen that inclusion of lithium perchlorate in the acetic acid solvent markedly decreases the rate of mixing for both IP and IS. However, even at 0.020 and 0.040 M concentrations of lithium perchlorate, a small but definite amount of rearrangement was observed in the bromobenzenesulfonate recovered after 50% acetolysis. The k_m values in these cases are $0.4{-}0.5 \times 10^{-5}$ sec⁻¹.

Discussion

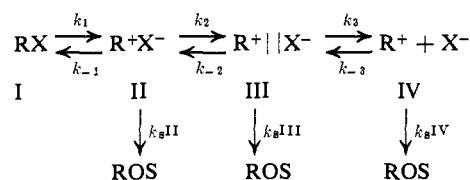During recent years it has become increasingly evident that more than one form of carbonium ion inter-

Table VI. A Comparison of the Salt Effects in Acetolysis of Various Arenesulfonates[a]

| | Temp, °C | Common ion depress. | OBs–OTs exchange | Induced common ion depress. | Special salt effects, $(LiClO_4)_{1/2}$ | | | α^b |
					Presence	$10^5 M$	k^0_{ext}/k_t^0	AcOH
threo-3-Phenyl-2-butyl OTs	50	No	No	...	No	...	1.0	2
exo-Norbornyl OBs	25	No	No	No	No	...	1.0	10
1-*p*-Anisyl-2-propyl OTs	50	No	Yes[c]	Yes[d]	Yes	300	2.4	...
threo-3-*p*-Anisyl-2-butyl OBs	25	No	Yes	Yes	Yes	230	3.1	500
2-*p*-Anisylethyl OTs	50	Yes	...	Yes	Yes	28[d]	2.5	...
4-Methoxy-1-pentyl OBs (IP)	25	Yes	Yes	Yes	Yes	9	2.75	...
5-Methoxy-2-pentyl OBs (IS)	25	Yes	Yes	Yes	Yes	9	2.76	...
2-(2,4-Dimethoxyphenyl)ethyl OBs	50	Yes	Yes	Yes	Yes	8	2.2	$>2 \times 10^4$

[a] See ref 10 for source of data, except as noted. [b] Reference 14; α is an efficiency factor for bromide exchange. It measures the competition between bromide ion and acetic acid. [c] Reference 3d, exchange of bromide ion for *p*-toluenesulfonate ion. [d] Reference 3d.

mediate may intervene between covalent starting material and product in the solvolysis of a variety of RX structures.[3,4a,13] Solvolysis Scheme I is a general

Scheme I

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R^+||X^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R^+ + X^-$$

$$I \qquad II \qquad III \qquad IV$$

$$\downarrow k_sII \qquad \downarrow k_sIII \qquad \downarrow k_sIV$$

$$ROS \qquad ROS \qquad ROS$$

formulation designed for systems where reaction proceeds by way of two varieties of ion pair, II and III, and dissociated carbonium ion IV, and where solvolysis product ROS arises from all three intermediates. According to the best working hypothesis, ion pairs II and III are intimate and solvent-separated species, respectively.
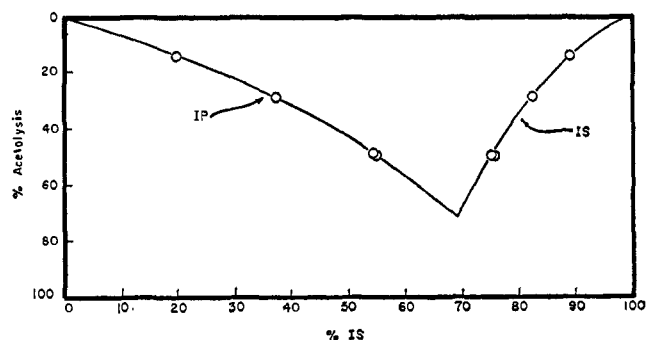

Figure 4. Plot of per cent acetolysis vs. per cent IS isomer from rearrangement studies of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) *p*-bromobenzenesulfonate.

Kinetic probes for detecting intervention of intermediates II, III, and IV during solvolysis include investigation of common ion rate depression,[3b,e] anion exchange,[3b,d] and the effect of foreign salts like lithium perchlorate on the ionization rate constant k_1 and the titrimetric rate constant k_t.[3a,c,d,4a]

Ion and Ion-Pair Intermediates Involved with MeO-5 Participation in Acetolysis. To assist in deciding on the number and kind of cyclic tertiary oxonium ion species involved in the acetolysis of IP and IS *p*-bromobenzenesulfonates, a comparison of the pattern of salt effects with the results for other arenesulfonates

(13) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **86**, 120 (1964).

is helpful. For this consideration, the results for IP and IS are summarized in Table VI along with related data for some representative systems investigated previously.

Since both IP and IS show common ion rate depression, it is unambiguous that ionization–dissociation proceeds to the dissociated O-methyl-2-methyltetrahydrofuranium ion. Moreover, it is evident that this common intermediate undergoes some external ion return[3c,d] in addition to reaction with solvent to give product. Another consequence of common ion rate depression is that its presence, when considered in terms of the general salt effect pattern of the spectrum of compounds in Table VI, helps place the O-methyl-2-methyltetrahydrofuranium ion among the most stable and long-lived of the carbonium ion systems studied.[3b,10,14] Since the compounds (excepting IP and IS) have been arranged in Table VI in general order of increasing ion stability and lifetime, the position occupied by IP and IS places the cyclic tertiary oxonium ion about on a par with the 2-*p*-anisylethyl- and 2-(2,4-dimethoxyphenyl)ethyl-bridged ions.

The occurrence of bromobenzenesulfonate–toluenesulfonate exchange for the IP and IS esters also is consistent with ionization, dissociation, and return from both ion pairs and dissociated ion. It is evident from Figure 1 that both isomers behave exactly alike in the exchange reaction. This further suggests that common intermediates are involved in the solvolysis[2a] and return reactions of the two bromobenzenesulfonates.

It is clear from Figures 2 and 3 that inclusion of lithium perchlorate in acetolysis of IP and IS affords the same sharply differentiated combination of special and normal salt effects on k_{tp} and k_{ts} as observed for a number of other systems (Table VI). Figure 3 shows that the two compounds respond identically with the special salt effect. This identity of the special (but not the normal) salt effect indicates that the action of lithium perchlorate is concerned with altering the behavior of the same intermediate(s).

A comparison of the effects of lithium perchlorate on the titrimetric and ionization rates of IP and IS is especially illuminating with regard to the nature of the intermediates involved. The acetolysis ionization rate constants k_{1p} and k_{1s} for IP and IS, respectively, are simply a sum of the corresponding measured k_m and k_t values as shown in the Kinetics Appendix. As is

(14) E. Clippinger, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1954.

Scheme II
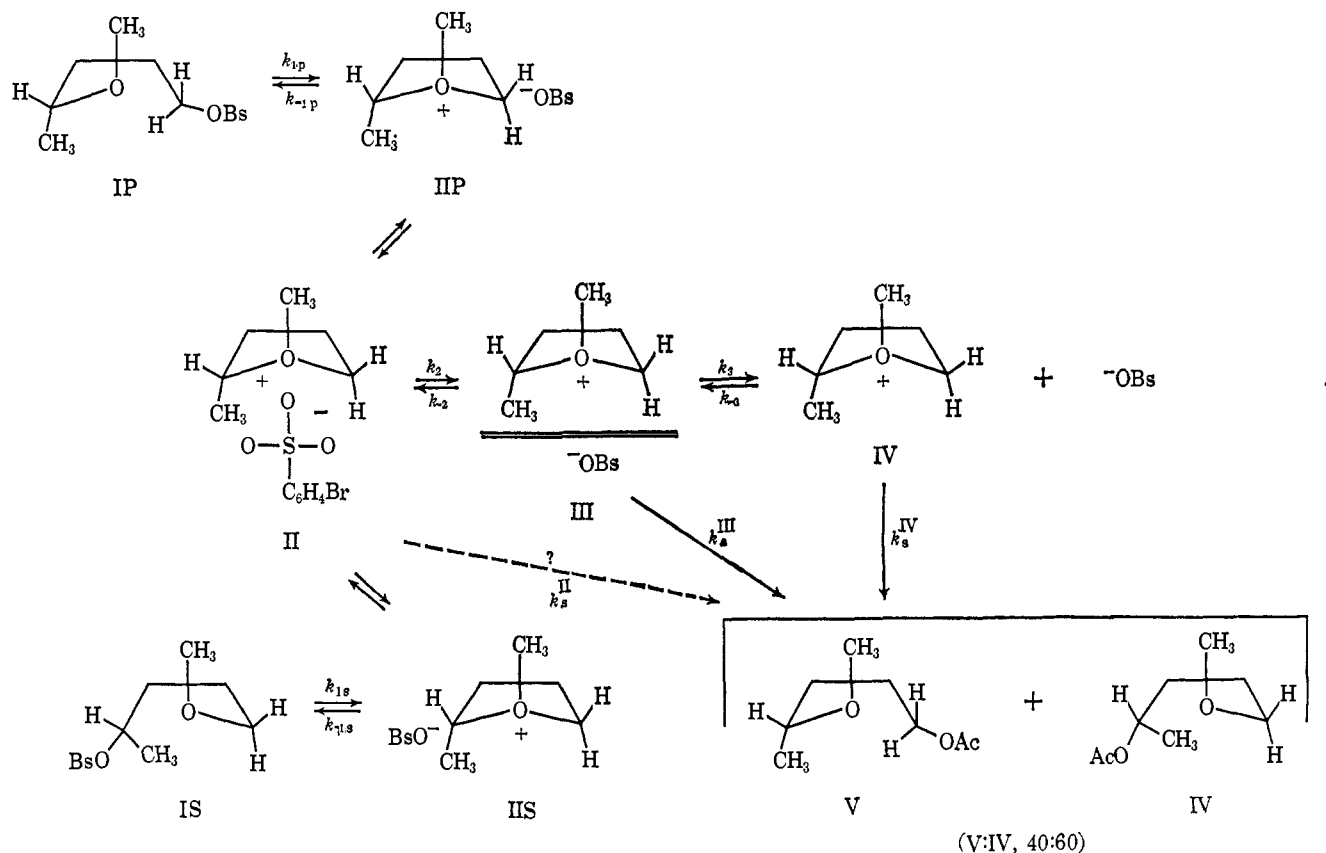
illustrated with k_{1s} vs. lithium perchlorate concentration in Figures 2, k_{1p} and k_{1s} vary linearly with the lithium perchlorate concentration; the lithium perchlorate effect on the ionization rates shows only the normal pattern. These good linear fits of the data serve as a check on the reliability of the k_m and k_t values which go to make up k_1 since there is nothing in the derivation of k_{1p} and k_{1s} which would be expected to produce these linear relations. The most singular feature of these results is that the special salt effect does not completely close the gap between the ionization and titrimetric rates. The k^0_{ext} values are below k_{1p}^0 and k_{1s}^0, and the k_t points are definitely below the k_1 lines out to concentrations beyond 0.05 M lithium perchlorate. It is obvious that a small amount of rearrangement still persists even at concentrations in the normal salt-effect range.

The rearrangement mechanism for IP and IS during acetolysis and the fractional elimination of rearrangement by inclusion of lithium perchlorate bear directly on the question of the kind and number of intermediates. An examination of molecular models reveals that the geometry imposed on the transition state VII formed by the participating methoxyl group precludes

VII
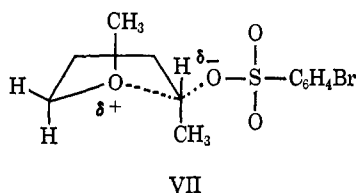
the operation of an independent cyclic rearrangement, or for that matter, any sort of cyclic reaction mecha-

nism. This leaves the interpretation that rearrangement is the result of ionization and is due entirely to ion and/or ion pair return. It is clear from the almost negligible amount of common ion rate depression that external ion return is minor and cannot possibly account for the observed magnitude of the special salt effect. As with other systems showing the special salt effect,[3a,c,d,4a,7,8] lithium perchlorate clearly is altering ion-pair return. Since the amount of rearrangement is large in the absence of lithium perchlorate, and since a much smaller but definite amount still occurs at relatively high lithium perchlorate concentration, it follows that the special salt effect is distinguishing between kinds of ion pair return.[3a,c,d,4a,7,8] Again, the best working hypothesis is that the special salt effect eliminates external ion-pair return from a solvent-separated ion pair III, but still permits internal return from an intimate ion pair II. On this basis, acetolysis of both IP and IS must yield a common, symmetrical intimate O-methyl-2-methyltetrahydrofuranium ion pair II (solvolysis Scheme II). This interpretation agrees completely with the exchange and special salt effect observations that common intermediates are involved in the solvolysis of IP and IS.

Intimate ion-pair formation in acetolysis of IP or IS bromobenzenesulfonate requires additional comment. The first changing of the C–OBs bond from covalent to ionic character does not form a species capable of directly giving the rearranged isomer. This requires an ionic realignment to a symmetrical species which can return to either isomer. Since most of the positive charge is on the methoxyl oxygen, it is to be expected that the more stable arrangement is with the anion near oxygen, as shown by cyclic oxonium ion II. Return to covalent bromobenzenesulfonate from II

necessitates reversion to unsymmetrical states IIP or IIS.

The present results are of interest in connection with the general question whether the intimate ion pair II represents a molecular species at an energy minimum.[15] In the case of the IP–IS system, it is difficult to explain the rearrangement unaffected by lithium perchlorate in any way other than by the existence of a discrete

is sufficiently large to cause external ion return but not large enough to cause much return in the absence of added bromobenzenesulfonate anion. The fact that rate depression just barely is detectable (only *ca.* 8%), even with added lithium *p*-bromobenzenesulfonate, indicates that dissociated cyclic oxonium ion IV is relatively unimportant in the course of the reaction. In other words, while some product does come by way of

$$k_t = k_1 \Big/ 1 + \frac{k_{-1}/k_2}{k_s^{II}/k_2 + \left[k_s^{III} + k_3 \dfrac{k_s^{IV}}{k_{-3}(X^-) + k_s^{IV}}\right] \Big/ \left[k_{-2} + k_s^{III} + k_3 \dfrac{k_s^{IV}}{k_{-3}(X^-) + k_s^{IV}}\right]} \qquad (9)$$

intimate ion pair type of intermediate at an energy minimum. An examination of a molecular model of the O-methyl-2-methyltetrahydrofuranium ion indicates some steric hindrance at the primary and secondary C–O carbons due to the hydrogen atoms and the methyl group. Thus, definite energy barriers can be visualized in the interconversion of symmetrical cyclic oxonium ion pair II and the unsymmetrical arrangements of IIP and IIS. Considering another solvolysis case, evidence has recently been reported[13,16] for two varieties of ion pair in the solvolysis of *p*-chlorobenzhydryl *p*-nitrobenzoate in aqueous acetone. Racemization and O^{18}-equilibration experiments with azide ion as an ion pair interceptor showed that azide ion eliminates racemization but not carbonyl oxygen equilibration.

Recognition of two types of ion pairs and a dissociated ion for the IP–IS system in acetolysis means that three varieties of O-methyl-2-methyltetrahydrofuranium ion need to be included in interpreting the kinetic results. This is shown in acetolysis Scheme II. While the unsymmetrical arrangements IIP and IIS in this scheme are not required to satisfy the kinetics, the above considerations of the geometry of the transition states imply their presence.

The Question of Product from Intimate Ion Pairs. As indicated in the general solvolysis Scheme I, product ROS may in theory arise from any of the cation species II, III, and IV. In this regard, systems showing MeO-5 participation differ substantially from previously scrutinized systems involving bridged carbonium ions.[3c,4a,5] For the latter cases, solvolysis product was omitted from the k_s^{II} path on the basis of the supposition that the anion portion of the intimate ion pair II effectively shields the bridged cation from attack by solvent.[3c] However, for the case of the IP–IS system it is obvious that the symmetrical O-methyl-2-methyltetrahydrofuranium ion pair II has both the primary and secondary C–O carbon atoms unprotected and potentially open to solvent attack. Therefore, it is necessary to inquire to what extent product arises from intimate cyclic tertiary oxonium ion pairs, as well as from the solvent-separated ion pair and the dissociated ion. This matter may be discussed with the aid of eq 9 which is based on a conventional steady-state treatment of general solvolysis Scheme I.

In eq 9, the term $k_{-3}(X^-)$ accounts for return of dissociated ion R^+ and the depression of k_t by common ion X^-. Since both IP and IS do show depression of rate by added common ion, it is clear that $k_{-3}(X^-)/k_s^{IV}$

IV, most arises from one or both of the ion-pair species II and III.

When common ion X^- returns R^+ to an ion pair or ion pairs, which also give solvolysis product ROS, there is an upper limit to the amount of rate depression by the common ion.[3b] Under conditions of maximum rate depression, all of R^+ is being returned to ion-pair species and $k_{-3}(X^-) \gg k_s^{IV}$. In such a case eq 9 degenerates to eq 10 which defines the fully depressed rate constant k_t^d.

The question of the relative amounts of product coming from the solvent-separated and symmetrical intimate O-methyl-2-methyltetrahydrofuranium ion pairs may be expressed analytically by eq 11 with the aid of the steady-state concentration of $(R^+||X^-)$ and (R^+X^-) given in the Kinetics Appendix. In (11) the term $k_s^{III}/(k_{-2} + k_s^{III})$ is a measure of the fraction of

$$k_t^d = k_1 \Big/ 1 + \frac{k_{-1}/k_2}{k_s^{II}/k_2 + k_s^{III}/(k_{-2} + k_s^{III})} \qquad (10)$$

$$k_s^{III}(R^+||X^-)/k_s^{II}(R^+X^-) = (k_2/k_s^{II})/[k_s^{III}/(k_{-2} + k_s^{III})] \qquad (11)$$

$$k_{ext} = k_1/[1 + k_{-1}/(k_s^{II} + k_2)] \qquad (12)$$

$$k_{-1}/k_2 = [(k_1/k_{ext}) - 1][(k_s^{II}/k_2) + 1] \qquad (13)$$

$$\frac{k_s^{III}}{k_{-2} + k_s^{III}} = \frac{[(k_1/k_{ext}) - 1][(k_s^{II}/k_2) + 1]}{[(k_1/k_t^d) - 1]} - (k_s^{II}/k_2) \qquad (14)$$

$$k_s^{III}/(k_{-2} + k_s^{III}) = 0.047 - 0.953(k_s^{II}/k_2) \qquad (15)$$

$$k_s^{III}(R^+||X^-)/k_s^{II}(R^+X^-) = 0.047(k_2/k_s^{II}) - 0.953 \qquad (16)$$

solvent-separated ion pair III returning to intimate ion pair II. This may be evaluated in the following manner from eq 10. The k_{ext} values for rate constants on the k^0_{ext}, k_t line, which includes the full special salt effect, are rate constants for the formation of solvent-separated ion pair III. Thus, for the special case of k_{ext} where k_{-2} is zero, eq 9 becomes eq 12. The latter relation may be rearranged to give eq 13. Replacing k_{-1}/k_2 in eq 10 with the equivalent from eq 13 allows one to solve for $k_s^{III}/(k_{-2} + k_3^{III})$ as shown in eq 14. Table VII shows that in acetolysis both IP and IS have the same values of k_1^0, k_t^d, and k^0_{ext} within experimental error. Substituting the average of these into eq 14 gives eq 15. Equation 11 then may be evaluated more explicitly for the IP–IS system by replacing the $k_s^{III}/(k_{-2} + k_s^{III})$ term with the equivalent from eq 15 to give eq 16. In 16 the ratio k_2/k_s^{II} can have a minimum value of 20.3, or, in other words, k_2 must be at least 20 times faster than k_s^{II}. If k_2/k_s^{II} is 20.3 all of the ROS product will

(15) P. D. Bartlett and B. T. Storey, *J. Am. Chem. Soc.*, **80**, 4954 (1958).
(16) H. L. Goering, R. G. Broiody, and J. F. Levy, *ibid.*, **85**, 3059 (1963).

Table VII. Summary of Acetolysis Rate Constants for
4-Methoxy-1-pentyl (IP) and 5-Methoxy-2-pentyl (IS)
p-Bromobenzenesulfonates at 25.20°

	IP	IS
$10^5 k_1$, sec^{-1}	5.69	5.64
$10^5 k^0_{ext}$, sec^{-1}	5.09	5.13
$10^5 k_t^0$, sec^{-1}	1.85	1.86
$10^5 k_t^d$, sec^{-1}	1.71[a]	1.72[a]

[a] The rate constant value for 0.001 M lithium p-bromobenzene-sulfonate.

arise *via* the k_s^{II} path; if, on the other hand, k_2/k_s^{II} is even a few times larger than 20.3 most of the product will come from the cyclic oxonium ion pair III. Since the exact value of k_2/k_s^{II} is unknown at present, a more definitive statement concerning the amount of product coming by way of k_s^{II} cannot be made.[17]

While it is not possible to say quantitatively just how much solvolysis product comes from the symmetrical O-methyl-2-methyltetrahydrofuranium ion pair II, other available evidence suggests that the k_s^{II} route is relatively unimportant. As discussed previously,[2a] it is reasonable to rule out product coming by way of the unsymmetrical intimate ion pairs IIP and IIS on the basis of the failure to observe a crossing over of isomeric solvolysis products from the total solvolysis of IP and IS. Even the much more nucleophilic ethanol gave the same ratio of products from both isomers.[2a] This implies that the unsymmetrical intimate ion pairs must lose their identity much more rapidly than they yield solvolysis product. If IIP and IIS do not give solvolysis product, there is no apparent reason to expect the symmetrical intimate ion pair II to be favored much more in this respect. In fact, since k_2/k_s^{II} is a large number (certainly greater than 20.3), it seems likely that II also loses its distinction before giving much product ROS.

Dissection of Ion-Pair Return and Comparison with Other Systems. The fraction of the intimate cyclic oxonium ion pair II returning to covalent bromobenzenesulfonate is evaluated readily from eq 12. From the latter, $k_{-1}/(k_s^{II} + k_2)$ is calculated as 0.107 and $k_{-1}/(k_s^{II} + k_2 + k_{-1})$ as 0.096. In other words, 9.6% of the intimate cyclic oxonium ion pair II undergoes internal return while 90.4% proceeds either to solvent-separated ion pair III or partially to III and partially to product through k_s^{II}.[18]

Equation 15 may be used to estimate the fraction of solvent-separated cyclic oxonium ion pair III which undergoes external ion pair return. In this equation the term $k_s^{III}/(k_{-2} + k_s^{III})$ has a value between zero and 0.047.[19] If $k_s^{III}/(k_{-2} + k_s^{III})$ is 0.047, k_s^{II} will

(17) A similar kinetic analysis for the relative amounts of products arising from solvent-separated ion pair III and dissociated cation IV for the IP–IS system likewise leads to a ratio involving k_s^{II} and k_2, the final equation being

$$k_s^{III}(R^+||X^-)/k_s^{IV}(R^+) = 8.48 - 172.5(k_s^{II}/k_2)$$

This equation also requires that k_2/k_s^{III} be at least 20.3. If k_2/k_s^{II} is 20.3, then k_s^{III} is zero. If k_s^{II} is zero, almost 90% of the product comes from the k_s^{III} route.

(18) Identically the same numerical values are calculated if k_s^{II} is zero.

(19) For the general eq 14, $k_s^{III}/(k_{-2} + k_s^{III})$ can have a value between zero and 1.0 depending on the relative magnitudes of k^0_{ext} and k_t^d. In systems like 3-phenyl-2-butyl arenesulfonate where $k^0_{ext} = k_t^d = k_t^0$ in acetolysis, $k_s^{III}/(k_{-2} + k_s^{III})$ is 1.0.[3c,4a] If k_s^{II} is zero, then eq 14

be zero and the minimum amount of return from solvent-separated ion pair III will be 95.3%. On the other hand, if $k_s^{III}/(k_{-2} + k_s^{IV})$ is zero, all of the product will go through the k_s^{II} path and external ion-pair return will be complete (100%).

It is worth while to compare the IP–IS system with the spectrum of compounds previously scrutinized as to ion-pair return behavior.[3c,4a,5] The comparisons are summarized in Table VIII. For the IP and IS bromobenzenesulfonates, the values listed for per cent return from III are the minimum values allowed by eq 15. As has been brought out before,[5] the total ion pair return does not vary much for the several systems. The major difference is the distribution of the fraction of intimate (II) and solvent-separated (III) ion pairs undergoing ion-pair return. It appears that internal return decreases and external ion-pair return increases as the cation species become more stable. The dominance of external ion pair return over internal return is even greater in the 2-(2,4-dimethoxyphenyl)ethyl system[10] (Table VI). In this case the special salt effect of lithium perchlorate eliminates ion pair return essentially completely.[3g]

Table VIII. Comparison of Ion Pair Return in Acetolysis of Several Systems

Compound	Temp, °C	—Ion pair return, %—		
		Total[b]	From II[c]	From III[d]
threo-3-Phenyl-2-butyl OTs[a]	50	78	78	*Ca.* 0
threo-3-*p*-Anisyl-2-butyl OBs[a]	25	75	37	81
2-*p*-Anisyl-1-propyl OTs[a]	50	74	35	81
2-*p*-Anisyl-1-ethyl OTs[a]	75	73[e]	8	97
4-Methoxy-1-pentyl OBs (IP)	25	70[f]	10[g]	95[h]
5-Methoxy-2-pentyl OBs (IS)	25	70[f]	9[g]	95[h]

[a] Reference 5. [b] Calculated from $100[1 - (k_t^0/k_1^0)]$. [c] $100 \cdot [k_{-1}/(k_{-1} + k_2)]$. [d] $100[k_{-2}/(k_s^{II} + k_{-2})]$. [e] k_t^d is employed for k_t^0. [f] The rate constant value at 0.001 M LiOBs is employed for k_t^d. [g] Identically the same values are obtained for $100[k_{-1}/(k_2 + k_s^{II} + k_{-1})]$. [h] The minimum value allowed by eq 15.

Concerning the Mechanism of the Special Salt Effect. Kinetic analysis of the special salt effect in acetolysis of the 1-anisyl-2-propyl, *threo*-3-anisyl-2-butyl, and *exo*-norbornyl arenesulfonate systems provided strong support for a mechanism involving a metathetical diversion of solvent-separated ion pair III by salt ion pair M^+Y^-.[3d] This is formulated by eq 17. Since cyclic tertiary oxonium ion intermediates represent

$$R^+||X^- + M^+Y^- \longrightarrow R^+||Y^- + M^+X^- \qquad (17)$$
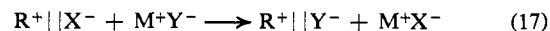
rather an extreme among cation structures in solvolysis, the special salt effect observed in acetolysis of IP and IS bromobenzenesulfonates is an especially interesting example.

The general solvolysis Scheme III incorporates the exchange feature of eq 17 for a system showing a special salt effect, as well as common ion rate depression. In this formulation subscript x refers to the anion from RX, y is the added anion such as perchlorate ion, and subscript e designates the exchange reaction. Ap-
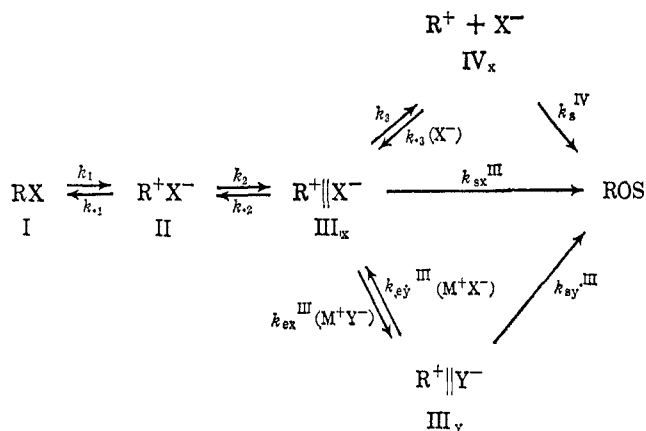
degenerates to

$$k_s^{III}/(k_{-2} + k_s^{III}) = [(k_1/k_{ext}) - 1]/[(k_1/k_t^d) - 1]$$

This is the same relationship derived previously.[3c,4a]

Allred, Winstein / *MeO-5 Participation in Acetolysis*

plication of the usual steady-state approximation to Scheme III leads to eq 18 for k_t, the first-order titrimetric

Scheme III

$$R^+ + X^-$$
$$IV_x$$

RX $\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$ R$^+$X$^-$ $\underset{k_{-2}}{\overset{k_2}{\rightleftarrows}}$ R$^+$||X$^-$ $\xrightarrow{k_{sx}^{III}}$ ROS
I $\qquad$ II $\qquad$ III$_x$

$$R^+||Y^-$$
$$III_y$$

acetolysis rate constant. Definitions for the various quantities k_{ext}, a, b_s, c, g, and h, which are used to make this equation more manageable, are given just below eq 18. A more useful form of eq 18 is eq 19. The

$$\frac{1}{k_t} = \frac{1}{k_{ext}}\left[1 + \cfrac{1}{a + \cfrac{g}{1 + h(X^-)} + \cfrac{b_s(M^+Y^-)}{1 + c(M^+X^-)}}\right]$$

$$(18)$$

$$k_{ext} \equiv k_1 k_2/(k_{-1} + k_2)$$

$$a \equiv (k_{sx}^{III}/k_{-2})[(k_{-1} + k_2)/k_{-1}]$$

$$b_s \equiv (k_{ex}^{III}/k_{-2})[(k_{-1} + k_2)/k_{-1}]$$

$$c \equiv k_{ey}^{III}/k_{sy}^{III}$$

$$g \equiv (k_3/k_{-2})[(k_{-1} + k_2)/k_{-1}]$$

$$h \equiv k_{-3}/k_s^{IV}$$

$$\frac{k_t}{k_{ext} - k_t} = a + \frac{g}{1 + h(X^-)} + \frac{b_s(M^+Y^-)}{1 + c(M^+X^-)} \quad (19)$$

$$k_t/(k_{ext} - k_t) = (a + g) + b_s(M^+Y^-) \quad (20)$$

special salt effect is accounted for by the term involving $b_s(M^+Y^-)$, common ion rate depression is related to $h(X^-)$, and $[1 + c(M^+Y^-)]$ pertains to induced common ion depression. In the absence of added common ion salt eq 19 reduces to eq 20 which is the predicted kinetic form of the special salt effect if ion pair exchange occurs as indicated in eq 17.

It is evident that eq 20 is the equation of a straight line with an intercept at $(a + g)$ and a slope of b_s. The applicability of eq 20 to the special salt effect of lithium perchlorate in acetolysis of IP and IS was tested by plotting $[k_t/(k_{ext} - k_t)]$ vs. (LiClO$_4$).[20] The k_{ext} values, corresponding to points on the k^0_{ext}, k_t straight lines of Figures 2 and its counterpart for IP, are given by eq 21. Very satisfactory straight lines were ob-

$$k_{ext} = k^0_{ext}[1 + b_t(\text{salt})] \quad (21)$$

tained for both IS and IP. Using $(a + g)$ of 0.51 and b_s of 18,000 and 18,500 for IP and IS, respectively, as determined from these straight line plots, eq 20 repro-

(20) If the exchange reaction involved only the perchlorate anion, a plot of $[k_t/(k_{ext} - k_t)]$ vs. (LiClO$_4$)$^{1/2}$ would define a straight line. For both IP and IS, and in other cases thus far investigated,[3d] such plots were extensively curved.

Table IX. Special Salt Effect of Lithium Perchlorate in Acetolysis of 4-Methoxy-1-pentyl (IP) and 5-Methoxy-2-pentyl (IS) p-Bromobenzenesulfonates at 25.20°

(LiClO$_4$) 10^3 M	$10^5 k_t$, sec^{-1} IP Obsd	$10^5 k_t$, sec^{-1} IP Calcd[a]	$10^5 k_t$, sec^{-1} IS Obsd	$10^5 k_t$, sec^{-1} IS Calcd[b]
0.00	1.71	1.72	1.72	1.73
0.02	2.40	2.37	2.46	2.40
0.06	3.04	3.12	3.09	3.17
0.10	3.53	3.55	3.53	3.62
0.25	4.28	4.25	4.34	4.32
0.50	4.68	4.63	4.77	4.68
1.00	4.76	4.87	4.85	4.93
5.00	5.11	5.27	5.30	5.39
	Av fit = ±1.5%		Av fit = ±1.7%	

[a] Calculated from $k_t/(k_{ext} - k_t) = 0.51 + 18,000(\text{LiClO}_4)$. [b] Calculated from $k_t/(k_{ext} - k_t) = 0.51 + 18,500(\text{LiClO}_4)$.

duces the data with a mean deviation of ca. 1.6%. This is shown explicitly in Table IX.

The observations for the IP–IS system are entirely analogous to the results for the 1-anisyl-2-propyl and threo-3-anisyl-2-butyl systems which were treated on the basis of an acetolysis scheme where dissociated carbonium ions were not involved.[3d]

The exchange mechanism in eq 17 and a solvolysis scheme such as Scheme III also explain "induced common ion rate depression."[3d] For the 1-anisyl-2-propyl system, the kinetic data on induced common ion rate depression could be reproduced with a mean deviation of less than 1%. Although a quantitative study has not been made for either IP or IS, it is certain that both show substantially more induced common ion depression than can be accounted for by direct common ion depression. This is in qualitative accord with the description in solvolysis Scheme III.

Experimental Section

Bromobenzenesulfonates. 4-Methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) p-bromobenzenesulfonates were specimens employed previously.[2a]

The following procedure was employed to ensure the absence of common ion salts. A solution of 8.0 g of bromobenzenesulfonate in 45 ml of a 40:60 ether-pentane solvent was washed with five different 100-ml portions of distilled water. Each washing consisted of vigorous shaking for 2 min. After drying over anhydrous magnesium sulfate, the bromobenzenesulfonate was carefully recrystallized from ether and pentane at ca. −15°. A rate measurement was then made in acetic acid from about 2 to 90% reaction giving the acetolysis rate constant shown in Table I. The remaining sample was dissolved in a similar proportion of ether-pentane solvent, and then subjected to ten more washes with 100-ml portions of distilled water. Again the bromobenzenesulfonate sample was recrystallized and another rate measurement completed (Table I).

Salts. Lithium bromobenzenesulfonate and lithium perchlorate were prepared and handled in anhydrous acetic acid as described previously.[3b,9,11] Solutions containing lithium p-toluenesulfonate in anhydrous acetic acid were prepared as described previously.[9,11]

Titrimetric Kinetic Procedure. Anhydrous acetic acid designed to contain 0.01 M acetic anhydride was prepared in the usual way.[3d] All rate measurements were performed in glass-stoppered 50- or 100-ml volumetric flasks as described previously.[2a,21] The acetic acid–salt solutions were equilibrated at 25.20° for at least 1 hr before making up the bromobenzenesulfonate solution. The titration methods have been described adequately.[9,11,21]

Mixing Rate Measurements. A standard lithium aluminum hydride solution was prepared by filtering a solution made from 100 g of lithium aluminum hydride and 1200 ml of anhydrous ether. This clear solution was standardized by measuring the volume of

(21) S. Winstein, E. Grunwald, and L. L. Ingraham, J. Am. Chem. Soc., 70, 821 (1948).

hydrogen gas evolved when an aliquot was slowly added to cold 10% sulfuric acid. The solution was about 2.3 M in lithium aluminum hydride.

The reproducibility of the lithium aluminum hydride reduction of both IP and IS was carefully checked by doing three separate reductions of each ester using the following standard procedure. A 2.11-g (0.006 mole) sample of bromobenzenesulfonate in 30 ml of anhydrous ether was reduced under refluxing conditions with 25 ml of 0.5 M lithium aluminum hydride in ether (prepared from the 2.3 M stock solution). After standing overnight, the excess hydride was decomposed by careful addition of 1 ml of water and 0.7 ml of 10% aqueous sodium hydroxide. The white precipitate was removed by filtration and, after drying with anhydrous magnesium sulfate, the filtrate was concentrated by carefully controlled distillation on a 15-cm Vigreux column. The ether concentrates were quantitatively analyzed by gas chromatography using a 2 m $\times$ 0.6 cm column packed with 30% by weight Carbowax 1500 on 40–60 mesh C-22 Firebrick. Three major components, methyl 1-pentyl ether, methyl 2-pentyl ether, and 2-methyltetrahydrofuran, were identified by comparison of retention times with authentic samples of each. The average ratio of products from each bromobenzenesulfonate is listed in Table III. The average deviation was ca. ±0.15% for both IP and IS.

The same procedure was used in making all mixing rate measurements. Acetic acid solutions (0.1 M ROBs) were solvolyzed in glass-stoppered volumetric flasks at 25.20°. The amount of bromobenzenesulfonate solution used for a given experiment was calculated so that ca. 2.1 g (0.006 mole) of unsolvolyzed material was recovered. The acetic acid solution was prepared from solvent which had been equilibrated at 25.20°. The unsolvolyzed bromobenzenesulfonate was recovered by pouring the acetolysis solution onto 1 kg of crushed ice and then extracting with six 150-ml portions of 50 : 50 ether–pentane solvent. (The time from the moment of mixing to pouring the sample on ice was employed in calculating the mixing rate constant.) Each extract was shaken immediately with cold 5% sodium bicarbonate to remove any extracted acetic acid. The combined extract was thoroughly washed with aqueous sodium bicarbonate and dried with anhydrous magnesium sulfate. Removal of the solvent under vacuum below 25° gave a recovered yield of 90–95% of theory. The whole residue (ca. 2–2.5 g) was dissolved in 30 ml of anhydrous ether and reduced with 25 ml of an ether solution of 0.5 M lithium aluminum hydride, as described above.

A sample of IP was dissolved in acetic acid at 25° and recovered immediately by pouring the solution on crushed ice. As shown in Table IV, less than 2% rearrangement occurred. It is clear that little rearrangement accompanies the recovery work-up procedure. The analysis results by gas chromatography are summarized in Tables IV and V.

2-Pentanol. The Grignard reagent of 1-bromopropane and freshly distilled acetaldehyde were reacted in ether. The magnesium alcoholate was decomposed with saturated ammonium chloride solution. Fractionation gave 2-pentanol, bp 118.5°, n^{20}D 1.4063 (lit.[22] bp 118.8°, n^{20}D 1.4068).

Methyl 2-Pentyl Ether. The sodium salt of 2-pentanol was prepared by adding 4.6 g (0.20 g-atom) of freshly cut sodium to a stirring solution of 43.3 g (0.49 mole) of the alcohol in 50 ml of p-xylene at 110°. After the sodium had reacted, the mixture was cooled to 50° and 30.0 g (0.21 mole) of methyl iodide was added. The reaction mixture was heated to 70–80° and stirred at this temperature for 1 hr. Following this, it was cooled to room temperature and allowed to stand overnight. Direct fractionation through an 8.0 mm $\times$ 80 cm concentric tube column gave 11.4 g (56%) of methyl 2-pentyl ether, bp 88.5°, n^{20}D 1.3827.

Anal. Calcd for $C_6H_{14}O$: C, 70.53; H, 13.81. Found: C, 70.41; H, 13.45.

Methyl 1-Pentyl Ether. This ether was prepared from the sodium salt of n-amyl alcohol and methyl iodide, bp 98–98.5°, n^{20}D 1.3869 (lit.[23] bp 99°, n^{20}D 1.3878).

2-Methyltetrahydrofuran. A commercial sample (Eastman, White Label) was purified by fractional distillation, bp 78°.

Kinetics Appendix

Derivation of Mixing Rate Constants k_{mp} and k_{ms}. Since both IP and IS rearrange into each other during acetolysis, the kinetics of this system are more complicated than other previously studied cases involving structural rearrangement during solvolysis.[4] However, if one keeps in mind the fact that the two esters react to give the same 69:31 mixture (M) of secondary (IS) to primary (IP) bromobenzenesulfonate (see Figure 4), it is possible to treat the acetolysis of both isomers on the basis of the simplified scheme
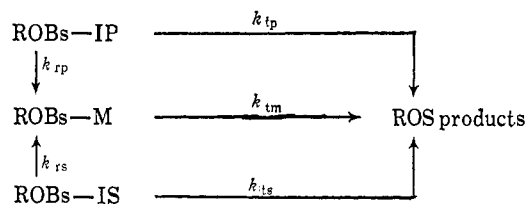
In this scheme, k_{rp} and k_{rs} refer to the first-order rate constants for rearrangement of the primary (IP) and secondary (IS) esters to mixed bromobenzenesulfonate (M). The titrimetric solvolysis rate constants for IP, IS, and M are k_{tp}, k_{ts}, and k_{tM}, respectively.

The method used to derive the kinetic expressions for both k_{rp} and k_{rs} is illustrated for k_{rp}. As derived previously,[4b] the ratio (M:IP) of mixed bromobenzenesulfonate M to primary isomer IP in the residual bromobenzenesulfonate in acetolysis of initially pure IP, at any time t, is given by eq 22. Since $k_{tp} = k_{ts} = k_{tM}$, this equation reduces to eq 23. It is convenient to express the latter relationship in the form of eq 24. It is easily shown that k_{rp} is identical with the mixing rate

$$\frac{M}{IP} = \left[\frac{k_{rp}}{k_{tM} - k_{rp} - k_{tp}}\right][1 - e^{-(k_{tM} - k_{rp} - k_{tp})t}] \quad (22)$$

$$\frac{M}{IP} = [e^{(k_{rp})t} - 1] \quad (23)$$

$$k_{rp}(t) = \ln [(M + IP)/IP] \quad (24)$$

constant, obtained from eq 7. The right-hand sides of eq 7 and 24 are seen to be equal from the following relationships.
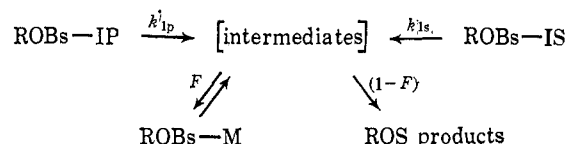
$$IS = 0.69M \quad (25)$$

$$IP = 100 - M = 100 - (IS/0.69) \quad (26)$$

$$\frac{M + IP}{IP} = \frac{100}{100 - \dfrac{IS}{0.69}} = \frac{69}{69 - IS} \quad (27)$$

Analogously, it can be shown that $k_{rs} = k_{ms}$.

Derivation of the Ionization Rate Constants k_{1p} and k_{1s}. In determining the relationship between k_{rp} and k_{rs} (or k_{mp} and k_{ms}) and the ionization rates of IP and IS, k_{1p} and k_{1s}, respectively, the above kinetic scheme is oversimplified and should be expanded to

where the term "intermediates" refers to the intermediate species identified in the Discussion. In this formulation, F denotes the fraction of "intermediates" going to mixed bromobenzenesulfonate M and (1 − F) is the fraction going to solvolysis products.

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Based on this kinetic scheme, the following relationships for IP are apparent.

$$k_{rp} = k_{1p}(F) \quad (28)$$

$$k_{tp} = k_{1p}(1 - F) \quad (29)$$

$$k_{rp} + k_{tp} = k_{mp} + k_{tp} = k_{1p} \quad (30)$$

$$k_{rs} + k_{ts} = k_{ms} + k_{ts} = k_{1s} \quad (31)$$

Similarly, eq 31 can be written for the IS ester.

Steady-State Concentrations for Solvolysis Scheme I. Application of the usual steady-state approximation to solvolysis Scheme I gives relations 32, 33, and 34 for the steady-state concentrations of R^+, $R^+||X^-$, and R^+X^-, respectively.

$$(R^+) = k_3(R^+||X^-)/[k_{-3}(X^-) + k_s^{IV}] \quad (32)$$

$$(R^+||X^-) = \frac{k_2(R^+X^-)}{k_{-2} + k_s^{III} + k_3\dfrac{k_s^{IV}}{k_{-3}(X^-) + k_s^{IV}}} \quad (33)$$

$$(R^+X^-) = $$

$$\frac{k_1(RX)}{k_{-1} + k_s^{II} + k_2\left[1 - \dfrac{k_{-2}}{k_{-2} + k_s^{III} + k_3\dfrac{k_s^{IV}}{k_{-3}(X^-) + k_s^{IV}}}\right]} \quad (34)$$

The Role of Neighboring Groups in Replacement Reactions. XXIX. 5-Methoxyl Participation and Lithium Aluminum Hydride Reduction[1]

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Abstract: Reduction of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) *p*-bromobenzenesulfonates with lithium aluminum hdyride in ether solvent results in formation of rearranged methyl pentyl ether, 2-methyltetrahydrofuran, and unrearranged methyl pentyl ether. The mechanistic implications are discussed; the results are considered to be consistent with salt-promoted anchimerically assisted ionization and fit in the *N* category of the *N-Lim* mechanism spectrum.

Since complex metal hydrides were first introduced as reducing agents,[2,3] several aralkyl and alkyl arenesulfonate and halide systems have been observed to yield appreciable amounts of rearranged hydrocarbons as a consequence of reduction.[4-9] These reductions are clearly the result of neighboring group participation, and in most cases appear to follow anchimerically assisted ionization. However, to date, little attention has been given to the mechanistic details for such product formation. In this regard, the reductions of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) *p*-bromobenzenesulfonates are informative. It has been observed that both IP and IS give rearranged methyl pentyl ether and 2-methyltetrahydrofuran as well as unrearranged methyl pentyl ether when reduced with lithium aluminum hydride in ether.[10] Thus with the same molecular species reduction involves reaction at methyl, primary, and secondary carbon atoms. Reduction also can be compared directly with the related extensively studied solvolytic displacement reactions of IP and IS.[10,11]

The present paper further describes the experimental results of the lithium aluminum hydride reduction of the IP and IS system in ether,[10] and discusses the mechanistic implications.

Results

The samples of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) *p*-bromobenzenesulfonates[11] used for the investigation were recrystallized three times at low temperature from 40:60 ether–pentane solvent. Three separate standardized reduction experiments were performed for each bromobenzenesulfonate using the same clear, homogeneous lithium aluminum hydride stock solution for all reductions. The standard conditions consisted of adding the bromobenzenesulfonate dissolved in anhydrous ether to an excess of 0.5 *M* lithium aluminum hydride in ether. After reflux overnight, the reduced mixture was worked up by addition of water and 10% aqueous sodium hydroxide. Following filtration to remove the aluminum salts, most of the ether was removed by careful distillation, and the concentrate was analyzed by gas chromatography.

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