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Salt Effects and Ion Pairs in Solvolysis and Related Reactions. IX. The *threo*-3-*p*-Anisyl-2-butyl System[1-3]

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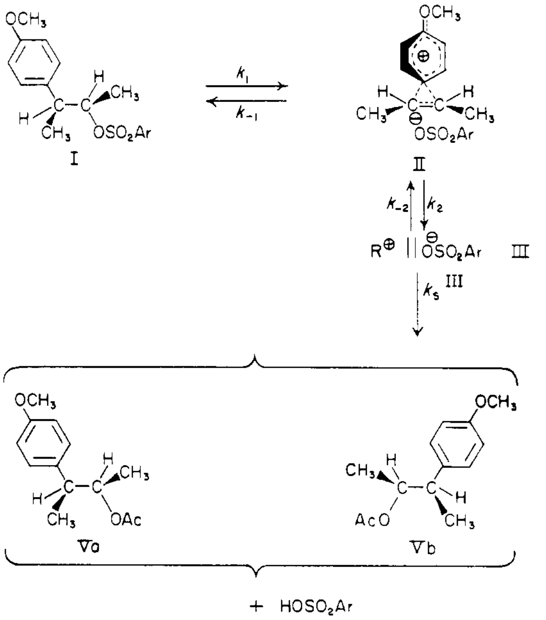
The rates and stereochemical results of solvolysis of *threo*-3-*p*-anisyl-2-butyl arenesulfonates show that ionization is essentially exclusively anchimerically assisted. Such ionization gives rise to the internally compensated *cis*-anisyl-bridged cation, from which racemic *threo*-acetate results in acetolysis. Polarimetric rate constants (k_α) represent ionization rate constants (k_1), while titrimetric solvolysis rate constants (k_t) can be considerably smaller because of ion pair return accompanying solvolysis. With the *threo*-3-anisyl-2-butyl bromobenzenesulfonate, (k_α/k_t) is 4.1 in acetic acid and *ca.* 16 in 10% HCOOH–dioxane. Lithium perchlorate salt effects on k_α in acetolysis of *threo*-3-anisyl-2-butyl bromobenzenesulfonate show only the normal linear pattern. On the other hand, salt effects on k_t show the combination of the steep special and the more shallow normal linear pattern. It is very clear that special salt effects are not concerned with ionization, but with reduction of ion pair return. The most striking aspect of the present results is that the special salt effect only partly closes the gap betwen polarimetric and titrimetric rate constants for acetolysis. On re-examination of the question of identity of polarimetric and ionization rate constants, it is concluded that these are identical for systems such as the present one in the common solvolyzing solvents. Therefore, ion pair return is only partially eliminated by the special salt effect. Regarding the mode of action of the salt in the special salt effect, the indications are strong that it is not by way of a sort of ion atmosphere effect on the relative rate constants determining the importance of ion pair return. The best working hypothesis is that two kinds of carbonium ion pairs, intimate (II) and solvent-separated (III) are distinguishable as discrete intermediates in solvolysis, and that these respond differently to the special salt. The solvent-separated ion pair III is presumed to be much more reactive than the intimate ion pair II toward added lithium perchlorate. The latter is presumed to trap III while still permitting internal return from II. On this basis, it is possible to dissect ion pair return accompanying acetolysis of *threo*-3-anisyl-2-butyl arenesulfonates into internal return from II and return from solvent-separated ion pair III. Comparison of the 3-anisyl-2-butyl and 3-phenyl-2-butyl systems shows that the substitution of the *p*-methoxyl group into the 3-phenyl-2-butyl system has a negligible effect on the over-all importance of ion pair return accompanying acetolysis. On the other hand, it has a major effect on the distribution of ion pair return between internal return from II and return from the solvent-separated ion pair III. The former is decreased, while the latter is introduced strongly. The structure of the two varieties of ion pair is discussed somewhat, and the question of merging of intimate ion pair and cyclic rearrangement mechanisms is touched on. The use of isotopic criteria for the occurrence of ion pairs as intermediates in rearrangements is discussed.

In acetolysis a number of systems[3] have displayed special salt effects[4] clearly to be ascribed to the elimination of a definite and substantial fraction of ion pair return by salts such as lithium perchlorate. With none of the systems displaying special salt effects so far discussed in papers V,[4] VI[5] and VIII[6] of this series, was total ionization rate easily measured. Therefore, it was not clear in those cases whether all or only part of ion pair return was eliminated by the special salt effect.

It was anticipated that the *threo*-3-*p*-anisyl-2-butyl arenesulfonate system I would be useful in this connection, since it was already clear that the *erythro* isomer displayed special salt effects.[5] With *threo*-3-anisyl-2-butyl arenesulfonate I, ionization could be expected to be very predominantly anchimerically assisted, the internally compensated bridged cation II being the intermediate. The rate constant for ionization, k_1, is given by the polarimetric[7] rate constant, k_α, for the change in optical rotation. The fraction of ion pair return eliminated in the special salt effect would be disclosed by the effect of lithium perchlorate on the gap between polarimetric and titrimetric rate constants, k_α and k_t, respectively. The preparation and solvolysis of active *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate and *p*-toluenesulfonate I are described in the present paper. The implications of the present results for the nature and behavior of carbonium ion pairs are discussed.



Results

3-Anisyl-2-butanols and their Derivatives.—The 3-anisyl-2-butanol[8,9] was derived from treatment of 2-anisylpropanal with the methyl Grignard re-

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(1) Sponsored by the Office of Ordnance Research, U. S. Army.

(2) (a) Presented at Kansas City Meeting of the American Chemical Society, March, 1954, page 21-N of Abstracts; (b) presented in summary at VIth Reaction Mechanism Conference, Swarthmore, Pa., Sept. 12, 1956.

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

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

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

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

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

(8) A. Sosa, *Ann. chim.*, [11] **14**, 5 (1940).

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

TABLE I

SUMMARY OF PROPERTIES OF 3-*p*-ANISYL-2-BUTYL DERIVATIVES

Derivative	*Erythro*		*Threo*	
	dl	Active	*dl*	Active
Alcohol, m.p., °C.	60[a]	80–81.5	1.5161[b]	
Acid phthalate m.p., °C.	137–138[c]	109–112	123–124.5	121–122[d]
$[\alpha]_D$ (CHCl$_3$), °		−29.0		
p-Toluenesulfonate m.p., °C.		70–72	49–50[10]	69–70
$[\alpha]_D$ (CHCl$_3$), °		−8.25		−11.3
p-Bromobenzenesulfonate m.p., °C.	67–69[5]		97.5–98.5[10]	84–86
$[\alpha]_D$ (CHCl$_3$), °				+11.3
p-Nitrobenzoate, m.p., °C.	102.5–103.5		84–85	

[a] M.p. of 60° previously reported by Sosa[8] for the solid racemate. [b] n^{25}D. [c] Previously reported[9] 136.5°. [d] Brucine salt.

agent as in previous work.[9] From the crude mixture, roughly 3:1, of solid and liquid diastereomeric 3-anisyl-2-butanols, respectively, considerable solid diastereomer crystallized directly on standing. The residual mixture was separated by repeated crystallization of the acid phthalate[9] into the acid phthalates of the solid and liquid carbinols. By use of a large excess of *p*-nitrobenzoyl chloride the solid and liquid carbinols could be converted essentially quantitatively to *p*-nitrobenzoates, these derivatives being especially useful for characterization of the carbinols.

As indicated in Table I, which summarizes the physical properties of the 3-*p*-anisyl-2-butanols and their derivatives, the *erythro* designation is assigned to the solid racemate and the *threo* designation to the liquid. Such an assignment is suggested by analogy with the diastereomeric 3-phenyl-2-butanols,[11] and it is borne out by the behavior of the arenesulfonates of the optically active 3-anisyl-2-butanols described below.

Optically active specimens of both the *erythro*- and *threo*-3-anisyl-2-butanols were obtained by crystallization from 2-butanone of a 1:1 mixture of brucine and acid phthalate of mainly *threo*-carbinol. The solution first deposited the brucine salt of active *erythro*-acid phthalate. Dilution with petroleum ether and cooling deposited the brucine salt of active *threo*-acid phthalate. The physical properties of the various derivatives of the optically active *erythro*- and *threo*-carbinols are summarized in Table I.

Anisyl Participation.—The pronounced tendency for neighboring anisyl participation in the rate-determining ionization of 3-anisyl-2-butyl arenesulfonate I was indicated in our earlier kinetic work by the substantial rate factor between 3-anisyl-2-butyl and 3-phenyl-2-butyl-*p*-toluenesulfonates.[9] The present work supplies stereochemical evidence for essentially complete control of the solvolysis of 3-anisyl-2-butyl derivatives by neighboring anisyl.

Acetolysis of *dl-threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate (I) and subsequent treatment of the solvolysis product with lithium aluminum hydride gave rise to carbinol containing a small proportion of olefin. The carbinol product was completely *threo* as indicated by formation of very pure *threo-p*-nitrobenzoate. Furthermore, when active *threo*-3-anisyl-2-butyl bromobenzenesulfonate (I) was solvolyzed, the solvolysis product was completely racemic *threo*. These stereochemical results obviously are due to the formation of the *cis*, and therefore internally compensated, bridged cation II, which gives rise to *dl-threo*-acetate V.[9,11]

The above interpretation is confirmed by the behavior in acetolysis of the active *erythro*-3-anisyl-2-butyl *p*-toluenesulfonate. With this diastereomer, optical activity does not disappear during acetolysis. Instead, optical rotation rises as acetolysis proceeds. Optically active *erythro*-acetate results from *erythro*-arenesulfonate which solvolyzes by way of a *trans*, and therefore optically active, intermediate bridged cation.

Polarimetric–Titrimetric Rate Comparisons.—As noted previously,[10] acetolysis of *threo*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate and *p*-toluenesulfonate I, followed titrimetrically, obeyed good first order kinetics. Satisfactory first-order behavior also was observed for the *p*-bromobenzenesulfonate in a series of other solvents, namely, ethanol, 25% formic acid–acetic acid, and 10% formic acid–dioxane. The observed rate constants, k_t, at 25° are summarized in Table II.

Polarimetric rate constants, k_α, were measured for comparison with the corresponding titrimetric values. Decrease of optical activity associated with solvolysis of the active *threo*-3-anisyl-2-butyl arenesulfonates obeyed good first-order kinetics, this being illustrated graphically in Fig. 1 in the case of acetolysis of the *p*-bromobenzenesulfonate. The observed polarimetric rate constants also are summarized in Table II.

As the summary in Table III shows, the polarimetric rate constants exceeded the titrimetric values. The k_α/k_t ratio in acetolysis at 25° was 4.07 for *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate and 4.65 for the corresponding toluenesulfonate. The latter value is analogous to the figure 4.59 observed in acetolysis of *threo*-3-phenyl-2-butyl *p*-toluenesulfonate[7] at 50°. The change of solvent from acetic acid to 10% formic acid–dioxane as a solvent in the case of *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate has the effect of increasing substantially the k_α/k_t ratio to a value of *ca.* 16. On the other hand, the k_α/k_t values are very small in 25% formic–acetic acid (1.08) and ethanol (1.27) as solvents.

Salt Effects on k_α.—In the presence of 0.01, 0.03, 0.06 and 0.10 *M* lithium perchlorate, the active *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate (I) displayed good first-order polarimetric rate constants in acetolysis. These are summarized in

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

(11) D. J. Cram, *ibid.*, **71**, 3863, 3883 (1949).

TABLE II

SUMMARY OF RATE CONSTANTS FOR TITRIMETRIC AND POLARIMETRIC SOLVOLYSIS OF *threo*-3-*p*-ANISYL-2-BUTYL BENZENESULFONATES AT 25.00°

Compound	Solvent	[RX], *M*	Other solute, *M* $LiClO_4$	Method	Initial α, °	10^6k, sec.$^{-1}$
ROBs	AcOH	0.0100		Tit.		19.6 ± 0.3
ROBs	AcOH	.0300		Tit.		19.5 ± 0.4
ROBs	AcOH	.0262		Pol.	+0.57	80.6 ± 8.4[a]
ROBs	AcOH	.0248		Pol.	+ .76	79.0
ROBs	AcOH	.0100	0.00100	Tit.		26.8 ± 0.8
ROBs	AcOH	.0100	.00500	Tit.		46.9 ± 1.6
ROBs	AcOH	.00992	.0100	Tit.		57.0 ± 0.7
ROBs	AcOH	.0270	.0100	Pol.	+ .85	87.3 ± 3.4
ROBs	AcOH	.00995	.0300	Tit.		84.0 ± 2.4
ROBs	AcOH	.0242	.0300	Pol.	+ .63	111[b]
ROBs	AcOH	.00997	.0600	Tit.		115 ± 4
ROBs	AcOH	.0259	.0600	Pol.	+ .65	156 ± 12[c]
ROBs	AcOH	.00994	.100	Tit.		161 ± 10
ROBs	AcOH	.0321	.100	Pol.	+ .98	198 ± 7
ROBs	12.5% AcOH–dioxane	.0271		Pol.	+ .83	*ca.* 0.34
ROBs	10% AcOH–C_6H_6	.0266		Pol.	+ .91	*ca.* 0.55
ROBs	10% HCOOH–dioxane	.0100		Tit.[d]		2.84 ± 0.09
ROBs	10% HCOOH–dioxane	.0100		Tit.		*ca.* 0.15
ROBs	10% HCOOH–dioxane	.0289		Pol.	+ .91	2.45 ± 0.09
ROBs	EtOH	.00884		Tit.		21.3 ± 0.6
ROBs	EtOH	.0278		Pol.	+ .74	27.1 ± 1.4[e]
ROBs	25% HCOOH–AcOH			Tit.		608 ± 20
ROBs	25% HCOOH–AcOH	.0270		Pol.	+ .65	656 ± 42[f]
ROTs	AcOH	.0105		Tit.		5.77 ± 0.10
ROTs	AcOH	.0287		Pol.	− .86	27.0 ± 1.2
ROTs	AcOH	.0102	.0300	Tit.		30.8 ± 0.6
ROTs	AcOH	.0101	.0600	Tit.		45.6 ± 1.8
ROTs	AcOH	.0102	.0800	Tit.		54.5 ± 1.4
ROTs	AcOH	.0287	.0500	Pol.	− .89	52.4 ± 2.4
ROTs	AcOH	.0266	.100	Pol.	− .82	69.9 ± 3.7

[a] 81.0 graphically. [b] Graphically. [c] 150 graphically. [d] 50.0°. [e] 27.0 graphically. [f] 670 graphically.

TABLE III

SUMMARY OF POLARIMETRIC–TITRIMETRIC COMPARISONS IN VARIOUS SOLVENTS

Solvent	*threo*-3-An-2-BuOBs, 25° Rel. k_α°		*threo*-3-Ph-2-Bu OTs, k_α°/k_t°, 50°
		k_α°/k_t°	
HCOOH	44,000[a]		1.18[c]
25% HCOOH–AcOH	1930	1.08	
AcOH	235	4.07, 4.65[b]	4.59
EtOH	80	1.27	2.05[d]
10% HCOOH–dioxane	7.2	*ca.* 16	
10% AcOH–C_6H_6	1.6		
12.5% AcOH–dioxane	1.0		

[a] Based on a k_α of 1.49×10^{-2} sec.$^{-1}$ in formic acid estimated from the values in acetic acid and 25% HCOOH–AcOH with the aid of the *m*Y correlation of solvolysis rates.[14] The *m*-value given by the AcOH and 25% HCOOH–AcOH points is 0.609. [b] *p*-Toluenesulfonate. [c] At 25°. [d] At 75°.

Table II and shown graphically in Fig. 2. Within essentially the experimental error of the polarimetric kinetic measurements, the polarimetric rate constants vary linearly with lithium perchlorate concentration. In other words, the salt effects follow the normal,[4,12] rather than the special[4] pattern. The data may be expressed in the form of equation 1, in the fashion employed previously[3,4–6,12,13] for linear salt effects, the subscript α being used to designate polarimetric data. The value of b_α, 16.2, recorded in Table IV is similar in magnitude to other *b*-values observed previously for linear salt effects.[12]

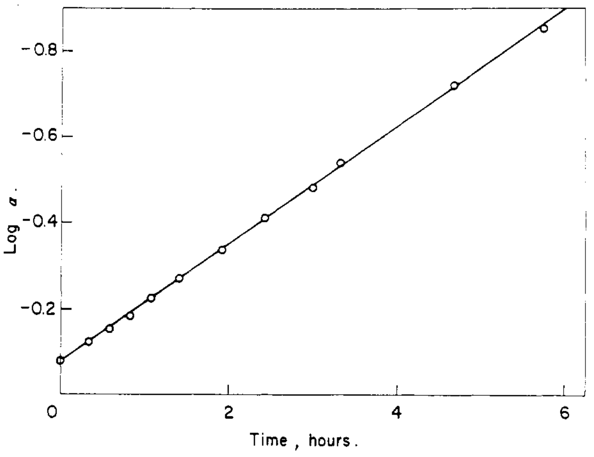

Fig. 1.—Polarimetric rate of solvolysis at 25.0° of (+)-*threo*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate in AcOH, 0.0100 *M* $LiClO_4$.

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

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

[14] (a) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) A. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

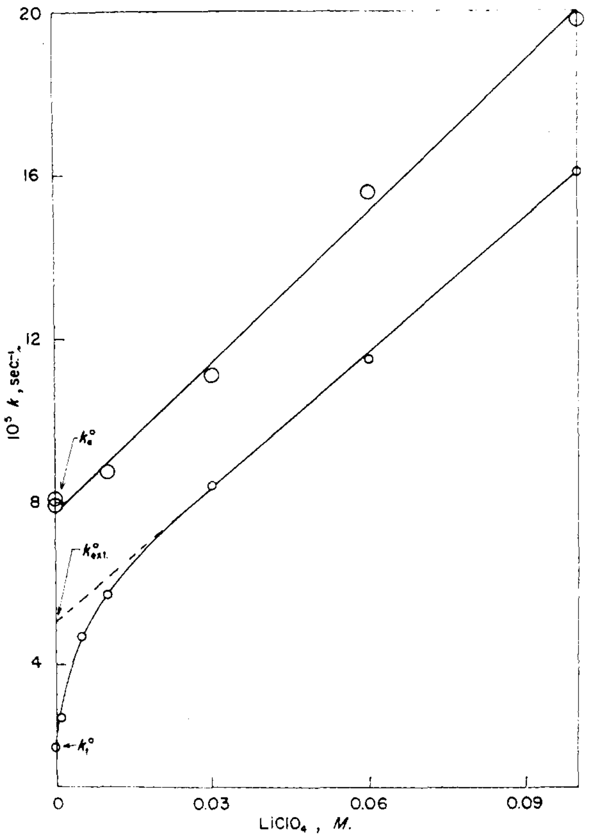

Fig. 2.—Effect of lithium perchlorate on acetolysis of *threo*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate at 25.0°.

$$k_\alpha = k_\alpha^\circ\,[1 + b_\alpha(\mathrm{LiClO_4})] \qquad (1)$$

$$k_t = k_{ext}^\circ\,[1 + b_t(\mathrm{LiClO_4})] \qquad (2)$$

With the active *threo*-3-anisyl-2-butyl toluenesulfonate (I), the effect of only two concentrations of lithium perchlorate on polarimetric acetolysis rate was studied. These data lead to a b_α value, listed in Table IV, similar to the one for the bromobenzenesulfonate.

Table IV

Summary of Lithium Perchlorate Salt Effects in Acetolysis at 25°

	threo-ROBs	*threo*-ROTs	*erythro*-ROBs[5]
$10^5\ k_{ext}^\circ$, sec.$^{-1}$	5.05	1.67	10.6[a]
k_{ext}°/k_t°	2.58	2.88	3.14
$(\mathrm{LiClO_4})_{1/2}$, M	0.0022		0.0040
b_α	16.2	17.4	
b_t	21.6	28.4	18.5

[a] Previously[5] listed erroneously as 1.06 due to typographical error.

Special Salt Effects on k_t.—Titrimetric rate constants were nicely first order for acetolysis of the *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate (I) in the presence of added lithium perchlorate. These rate constants at six concentrations of lithium perchlorate up to 0.1 M are summarized in Table II and plotted *vs.* lithium perchlorate concentration in Fig. 2. From the plot, it is evident that the salt effect has the steep special[4–6] pattern at lower concentrations and develops the normal[4,12] linear pattern at the higher concentrations of salt.

While the special and normal salt effects are not as sharply differentiated as in the cholesteryl,[6] 2,4-dimethoxyphenylethyl[6] or 2-anisyl-1-ethyl[4] cases, the separation is not difficult. In Fig. 2 is shown the extrapolation[4] of the linear k_t *vs.* (LiClO$_4$) plot to the intercept, k_{ext}°, the rate constant which includes the special but excludes the normal salt effect. The fit of the normal part of the salt effect to the linear relation 2 is summarized in Table IV, b_t being 21.6, larger than the b_α. The magnitude of the special salt effect, measured by the k_{ext}°/k_t° ratio of 2.58, turns out to be comparable to that displayed by the *erythro*-3-anisyl-2-butyl *p*-bromobenzenesulfonate,[5] for which the k_{ext}°/k_t ratio is 3.14. Also, the value of $(\mathrm{LiClO_4})_{1/2}$, 2.2×10^{-3} M, for the *threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate is similar to the value observed with the *erythro* diastereomer.[5]

For the *threo*-3-anisyl-2-butyl *p*-toluenesulfonate (I), the effects of 0.03, 0.06 and 0.08 M lithium perchlorate were examined, the behavior here being analogous to that observed with the *p*-bromobenzenesulfonate. Table IV summarizes the values of k_{ext}°/k_t° and b_t, these being slightly larger for the toluenesulfonate than for the bromobenzenesulfonate.

Discussion

Special Salt Effects and Ion Pair Return.—For the other compounds whose behavior in acetolysis was reported in detail in previous papers of this series, it was reasoned that the special salt effects on titrimetric acetolysis rates must be concerned, not with effects on ionization rate, but with reduction of ion pair return.[4–6] The argument was based on the failure to observe special salt effects on ionization rate of closely similar substances. For example, special salt effects were observed on the acetolysis rate of *p*-anisylethyl[4] but not the *p*-methoxyneophyl[12] derivative. For the *threo*-3-anisyl-2-butyl derivatives in the present paper, salt effects are now available for both polarimetric and titrimetric acetolysis rates on the same substances. Thus, it is even clearer that special salt effects are concerned with reduction of ion pair return.

The most striking aspect of the present results is that the special salt effect only partly closes the gap between the polarimetric and titrimetric rates. The value of k_{ext}° is well below k_α° and the k_t points on the normal salt effect line are well below the k_α line, as is clear from Fig. 2. Before we conclude that the special salt effect only partly eliminates ion pair return, we should re-examine our assumption that k_α should be identified with k_1, the ionization rate constant.[7] If k_α were to include an important contribution from an independent cyclic rearrangement reaction[7,15,16] not involving ionization, this might explain simply the failure of the special salt effect to close the gap between k_α and k_t. In discussing the present results with the 3-anisyl-2-butyl system, it will nevertheless be helpful to keep in mind the behavior of other systems in acetolysis, both those displaying and those not displaying special salt effects.

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(15) W. G. Young, S. Winstein and H. L. Goering, This Journal, **73**, 1958 (1951).

(16) C. A. Grob and S. Winstein, *Helv. Chim. Acta*, **35**, 782 (1952).

Identity of Polarimetric and Ionization Rate Constants.—If k_α receives a contribution from an independent cyclic rearrangement reaction,[7,15,16] we can express k_α analytically, as in equation 3, as the sum of k_r, the rate constant for racemization by such a cyclic rearrangement process, and k_1, the rate constant for ionization. As regards salt effects, one would expect k_r to be relatively insensitive to salt and k_1 to show a linear salt effect. The right-hand side of equation 3 is expressed on this basis. Actually, equation 3 for k_α has the observed form of equation 1 as can be seen by rewriting 3 in the form of equation 4. The term $(k_r + k_1^\circ)$ would be the k_α°, and the term $\left(\frac{k_1^\circ b_1}{k_r + k_1^\circ}\right)$ would be the b_α of equation 1.

$$k_\alpha = k_r + k_1 = k_r + k_1^\circ[1 + b_1(\mathrm{LiClO_4})] \qquad (3)$$

$$k_\alpha = (k_r + k_1^\circ)\left[1 + \left(\frac{k_1^\circ b_1}{k_r + k_1^\circ}\right)(\mathrm{LiClO_4})\right] \qquad (4)$$

$$k_t = Fk_1 = Fk_1^\circ[1 + b_1(\mathrm{LiClO_4})] \qquad (5)$$

$$k_r = k_\alpha - k_{\mathrm{ext}} = k_{\mathrm{ext}}^\circ\left[\frac{k_\alpha^\circ}{k_{\mathrm{ext}}^\circ} - 1 + \left(\frac{k_\alpha^\circ}{k_{\mathrm{ext}}^\circ}\, b_\alpha - b_t\right)(\mathrm{LiClO_4})\right] \qquad (6)$$

$$k_r = k_{\mathrm{ext}}^\circ\,[0.58 + 4.0(\mathrm{LiClO_4})] \qquad (7)$$

If the special salt effect were concerned with complete elimination of ion pair return, k_r for a system displaying the special salt effect would be $k_\alpha - k_{\mathrm{ext}}$, where k_{ext} refers to points on the k_{ext}°, k_t normal salt effect line. For a system displaying only the normal salt effect pattern, such as 3-phenyl-2-butyl[2b,7,14] or norbornyl,[2b,7,17] the simplest assumption would be that k_r is equal to $k_\alpha - k_t$. The major objection to an appreciable contribution of an independent cyclic rearrangement process to the solvolyses we are dealing with is based on the behavior of the derived k_r-values toward variation of solvent and the structure of the substrate.

Of the solvent properties, the most relevant in discriminating between ionization and an independent cyclic rearrangement is ionizing power. Thus it already has been emphasized[7] that the derived k_r-values for solvolysis of 3-phenyl-2-butyl *p*-toluenesulfonate[7] are essentially as sensitive to solvent ionizing power as is solvolysis rate. This is also true in the case of norbornyl bromobenzenesulfonate[2b,7,17,18] and norbornyl bromide.[2b,17] To quote fragments of the data available in the case of the latter two substances, solvolysis rate of norbornyl bromobenzenesulfonate varies by some 4 powers of ten in carboxylic acid–dioxane mixtures while k_α/k_t varies by a factor of *ca.* 4. Similarly, for norbornyl bromide in propionic, acetic and formic acid solvents, solvolysis rate varies by nearly 5 powers of ten while k_α/k_t varies from 28 to 4. Nearly equal sensitivity to ionizing power for both the alleged k_r and the solvolysis rate may be seen also in the solvolysis of *cis*- and *trans*-5-methyl-2-cyclohexenyl[19] and *trans*-α,γ-dimethylallyl[20] acid phthalates and α,α-di-methylallyl chloride[21] and *p*-nitrobenzoate[21] in water–acetone mixtures.

The similarity of solvent requirements for the supposedly independent cyclic rearrangement and solvolysis process may be treated more quantitatively with the aid of *m***Y** correlations.[14] For example, in the case of solvolysis of *cis*-5-methyl-2-cyclohexenyl[14c,19] and *trans*-α,γ-dimethylallyl[20] acid phthalates and α,α-dimethylallyl chloride[21] and *p*-nitrobenzoate[21] in water–acetone mixtures, both solvolysis rate and total rate of solvolysis plus rearrangement are well correlated by the *m***Y** rate correlation[14] with similar *m*-values. The fact that both solvolysis rate and total rate of solvolysis plus rearrangement are correlated with the same **Y** values suggests that the rate of the extra rearrangement is sensitive to essentially the same blend of specific and general solvent functions[22] applicable to solvolysis. As emphasized previously,[7] the dependence of rates on solvent suggests strongly that there is a common rate-determining step for solvolysis and the extra racemization or rearrangement.

Another solvent property useful in discriminating between ionization and an independent cyclic rearrangement is nucleophilicity. For example, in solvolysis of α,α-dimethylallyl chloride,[15] rearrangement accompanies solvolysis in acetic acid but not ethanol. The disappearance of the accompanying rearrangement in the more nucleophilic solvent is not explicable on the basis of an independent cyclic process for the rearrangement. However, it is understandable on the basis of a common ion pair intermediate for both solvolysis and rearrangement, this intermediate being diverted essentially completely into solvolysis in the more nucleophilic solvent.[2b,15]

Further evidence against competing cyclic processes in acetolysis is the dependence of the derived k_r values on substrate structure. For example, k_r turns out to be zero with *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate,[23] in contrast with a number of other systems. Such contrast is not understandable on the basis of cyclic processes.[23] Further, there are many cases where k_r varies with change in R or X of the substrate RX molecule almost exactly as does acetolysis rate. For example, this is true for X = Cl, Br, I and OBs in the norbornyl system.[2b,17] This is true for X = OBs and OTs in the present work on the 3-anisyl-2-butyl system. Comparing the 3-phenyl-2-butyl[7] and 3-anisyl-2-butyl toluenesulfonates, it is clear that the *p*-methoxyl group[9] increases k_r and k_t by nearly the same large factor.[24,25] Such effects of substrate structure suggest a common rate-determining ionization step for both solvolysis and racemization.

The pattern of observed salt effects in acetolysis also does not support an interpretation of the gap between k_α and k_{ext} or k_t in terms of a k_r for a cyclic rearrangement process insensitive to salt effects. Formulating k_t as a fraction[13] F of the ionization rate constant k_1, as in equation 5, F would be equal to 1 for norbornyl *p*-bromobenzenesulfonate and

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(17) E. Clippinger, unpublished work.

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

(19) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 1129 (1955).

(20) H. L. Goering and R. W. Greiner, *ibid.*, **79**, 3464 (1957).

(21) C. Wilcox, Thesis, U.C.L.A., 1957.

(22) (a) A. H. Fainberg and S. Winstein, THIS JOURNAL, **79**, 1597 (1957); (b) **79**, 1602 (1957); (c) **79**, 1608 (1957); (d) S. Winstein, A. H. Fainberg and E. Grunwald, *ibid.*, **79**, 4146 (1957); (e) S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957).

(23) S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952).

(24) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

(25) R. Heck and S. Winstein, *ibid.*, **79**, 3432 (1957).

for the 3-anisyl-2-butyl ester along the k°_{ext}, k_{t} line. On this basis, the k_α *vs.* (LiClO$_4$) line should be parallel to the k_{t} *vs.* (LiClO$_4$) line for a system such as norbornyl and parallel to the k°_{ext}, k_{t} line for 3-anisyl-2-butyl or analogous ones.

For the 3-anisyl-2-butyl *p*-bromobenzenesulfonate system, the gap between the k_α line and the k°_{ext}, k_{t} line is not constant. Instead, it actually widens as (LiClO$_4$) increases. This can be seen in Fig. 2. Also, the variation of the presumed k_{r} with (LiClO$_4$) is shown in equation 6, which is derived from equations 1 and 2. Equation 6 is expressed numerically for the 3-anisyl-2-butyl *p*-bromobenzenesulfonate acetolysis in equation 7.

Whereas the presumed k_{r} in the case of the 3-anisyl-2-butyl system rises as lithium perchlorate is added, the same treatment applied to the 2-anisyl-1-propyl[2b,3,26,27] system leads to a negative salt effect on k_{r}. On the other hand, for norbornyl bromobenzenesulfonate in 60% acetic acid–dioxane, k_{r} rises about twice as steeply as does k_{t} with addition of lithium perchlorate.[2b,28] Similarly, the presumed k_{r} is more sensitive to lithium perchlorate than is k_{t} in acetolysis of *cis*-5-methyl-2-cyclohexenyl chloride.[13,29] Thus, instead of being insensitive to salt effects, k_{r} shows variations even in the sign of the salt effect and often rises even more steeply than k_{t} with increase in salt concentration. Such behavior of k_{r} is not anticipated for a cyclic rearrangement process.

All of the above considerations reconfirm that the polarimetric rate constant k_α in acetolysis of a system such as 3-anisyl-2-butyl *p*-bromobenzenesulfonate (I) should indeed be identified with the ionization rate constant k_1. On this basis, the relative ionization rates for 3-anisyl-2-butyl *p*-bromobenzenesulfonate, based on relative k_α values, in the different solvents employed in the present work are summarized in Table III. From this table, it is clear that ionization rates increase by nearly 5 powers of ten over the range of solvents from 12.5% AcOH–dioxane to formic acid.

Interpretation of Special Salt Effects.—The discussion in the previous section has forced us to the conclusion that ion pair return is only partially eliminated by the special salt effect.

It remains to inquire to what extent the apparent special salt effect receives a contribution from the fact that addition of lithium perchlorate introduces salt-promoted[13] ionization which may give rise to less ion pair return than the ionization in the absence of salt. This matter may be discussed analytically by expressing k_1, as in equations 8 and 9, as the sum of two terms, one for salt-unassisted and the other for salt-promoted ionization. It may be useful to associate the one term with ionization to an ion pair, and the other with formation of an ion quadruplet from the substrate molecule and a salt ion pair.[13] In equation 9, F_0 and F_{salt} are the fractions of each of the ionizations, respectively, which result in solvolysis product. Equation 9 may be rewritten in the form of equation 10, division of which by equation 8 leads to equation 11 for F, the apparent fraction of ionization leading to solvolysis product.

Examination of equation 11 shows that neither the magnitude nor the shape of the special salt effects are accounted for in this manner. Even if F_{salt} were 1.00, salt-promoted ionization is introduced too slowly as lithium perchlorate is added to account for much of the apparent reduction in ion pair return. This is especially true in cases such as cholesteryl,[6] 2,4-dimethoxyphenylethyl[6] and 2-*p*-anisylethyl,[4,30] where the special salt effect is introduced at concentrations of lithium perchlorate where salt-promoted ionization is still negligible.

$$k_1 = k_1{}^\circ + k_1{}^\circ b_1(\text{LiClO}_4) \qquad (8)$$

$$k_{\text{t}} = F_0 k_1{}^\circ + F_{\text{salt}} k_1{}^\circ b_1(\text{LiClO}_4) \qquad (9)$$

$$k_{\text{t}} = F_0 k_1{}^\circ \left[1 + \frac{F_{\text{salt}}}{F_0} b_1(\text{LiClO}_4)\right] \qquad (10)$$

$$F = F_0 \frac{\left[1 + \frac{F_{\text{salt}}}{F_0} b_1(\text{LiClO}_4)\right]}{[1 + b_1(\text{LiClO}_4)]} \qquad (11)$$

We can see that the typical cases of special salt effects in acetolysis do not involve primarily the presence of lithium perchlorate already in the rate-determining ionization step. The action of lithium perchlorate is in some later step. Regarding the mode of action of the salt in the special salt effect, the indications are strong that it is not by way of a sort of ion atmosphere effect, or ion pair or ion clump versions of such an effect, on the relative rate constants determining the importance of ion pair return.

One indication against an ion atmosphere description for the special salt effect is the high specificity with regard to the structure of the substrate system. Thus, (LiClO$_4$)$_{1/2}$ varies widely from system to system,[3-6] being very sensitive to structure. On the other hand, the normal salt effects[3-6,12] vary much less with structure.

The worst difficulty encountered by an ion atmosphere type of explanation of the special salt effect is the unique specificity of the effect as regards the common-ion salt, lithium toluenesulfonate or bromobenzenesulfonate, in the case of an alkyl toluenesulfonate or bromobenzenesulfonate, respectively. The common ion salt is able to exercise a normal salt effect[12,13] on ionization rate, but is peculiarly incapable of exercising a special salt effect. For such reasons we have been led to an explanation of the special salt effect which depends on specific reactions between the added salt and ion pair intermediates in acetolysis of the solvolyzing system.

Any formulation of the special salt effect in acetolysis must account for the absence of such effects in acetolysis of certain systems such as norbornyl[17] and 3-phenyl-2-butyl[7,13] where, nevertheless, ion pair return is important. Also, it must account for the elimination of only a discrete fraction of such ion pair return even when special salt effects are displayed, as in the present case. Our best working hypothesis[3] has been that two kinds of carbonium ion pairs, intimate and solvent-separated ion pairs II and III, respectively, may be

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(26) S. Winstein and K. C. Schreiber, THIS JOURNAL, 2171 (1952).

(27) A. Fainberg, unpublished work.

(28) A. Colter, unpublished work.

(29) H. L. Goering, T. D. Nevitt and E. F. Silversmith, THIS JOURNAL, **77**, 5026 (1955).

(30) P. Klinedinst, unpublished work.

distinguished as discrete intermediates in solvolysis, and that these respond differently to the addition of salt to the acetolysis medium. Of the two varieties of ion pair, discussed more fully later in this manuscript, the solvent-separated ion pair III is presumed to be much more reactive than the intimate ion pair II toward added lithium perchlorate. The latter is presumed to trap III while still permitting return from the intimate ion pair, namely internal return.[7,10,14b,15] Thus the special salt effect in the present case and some similar ones is concerned with elimination of external ion pair return.[10] The present work does not supply any definite evidence on the mechanism of the action of the salt in the special salt effect. However, as mentioned already in summary form,[2b,3] the available evidence points to a major mechanism for the action of lithium perchlorate in acetolysis involving diversion of ion pair III to a carbonium perchlorate ion pair by exchange of III with a lithium perchlorate ion pair.

Solvolysis Scheme in Acetolysis.—Invoking two types of carbonium ion pairs as well as dissociated carbonium ions means that, in general, three varieties of the carbonium ion need to be considered in interpreting acetolysis. This is shown in the following solvolysis scheme, the three varieties of carbonium ion, II, III and IV, representing progressively further stages of ionization–dissociation of RX.

$$\begin{tikzcd}
\text{I} \arrow[r, "\text{ionization}"] & \text{II} & \text{III} \arrow[r, "\text{dissociation}"] & \text{IV} \\
 & \text{intimate ion pair} & \text{solvent-separated ion pair} & \text{dissociated ions} \\
\text{RX} \arrow[r, shift left, "k_1"] & \text{R}^{\oplus}\text{X}^{\ominus} \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] & \text{R}^{\oplus} \,\|\, \text{X}^{\ominus} \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] \arrow[d, "k_s^{III}"] & \text{R}^{\oplus} + \text{X}^{\ominus} \arrow[l, shift left, "k_{-3}"] \arrow[d, "k_s^{IV}"] \\
 & & \text{ROS} & \text{ROS}
\end{tikzcd}$$

Return to covalent RX accompanying acetolysis may be from any one of the ionic stages, II, III or IV, as the furthest stage of ionization–dissociation.[2,3,10] From the absence of common ion rate depression[10] of acetolysis of *threo*-3-anisyl-2-butyl bromobenzenesulfonate or toluenesulfonate, it was concluded previously that return from dissociated carbonium ion IV ("external ion return")[10] did not accompany acetolysis in the case of the 3-anisyl-2-butyl system. In fact, a comparison of the behavior of the 3-anisyl-2-butyl system with that of other systems led to the conclusion[10] that dissociation of ion pairs to dissociated ions IV was unimportant in acetolysis of the 3-anisyl-2-butyl system, rate of dissociation being much slower than the rate of other reactions of the ion pairs.

The above conclusion that the dissociated carbonium ion stage was not attained in acetolysis applied to other systems besides the 3-anisyl-2-butyl arenesulfonates.[10] An example of such a system is norbornyl bromobenzenesulfonate.[10] On the basis of the present explanation of special salt effects in acetolysis, we can go further in defining what return accompanies acetolysis of norbornyl bromobenzenesulfonate. The absence of special salt effects in acetolysis suggests that return from the solvent-separated ion pair III ("external ion pair return")[10] is unimportant. Thus only internal return is important in acetolysis of norbornyl bromobenzenesulfonate, and the same conclusion may be drawn for 2-phenyl-1-propyl[26] and 3-phenyl-2-butyl[7,13] arenesulfonates.

Solvolysis product may arise from more than one of the varieties of carbonium ion. In general, all three varieties of carbonium ion, II, III and IV, may lead to solvolysis product ROS with rate constants k_s^{II}, k_s^{III} and k_s^{IV}, respectively. However, the solvolysis scheme shown is designed for a case where ROS arises from solvent-separated ion pair III and dissociated ion IV.[31] Where dissociation is negligible, as in acetolysis of 3-anisyl-2-butyl, norbornyl and 3-phenyl-2-butyl arenesulfonates, the route to ROS from dissociated ion IV may be omitted.

The solvolysis scheme for acetolysis which includes product formation from solvent-separated ion pair III, but omits it from the intimate ion pair II, is intended for systems leading to bridged carbonium ions such as norbornyl and 3-anisyl-2-butyl. It is quite clear that solvent-separated ion pair III has all it needs to enable it to yield solvolysis product ROS. For 3-anisyl-2-butyl arenesulfonate, k_s^{III}/k_{-2} is not large and external ion pair return is important in acetolysis in the absence of added salt. On the other hand, for a system such as norbornyl bromobenzenesulfonate, k_s^{III}/k_{-2} is presumed to be very large, the inevitable result of attaining the solvent-separated ion pair stage of ionization–dissociation being formation of solvolysis product.

The omission of an ROS-forming reaction of intimate ion pair II (rate constant k_s^{II}) for cases such as norbornyl and 3-anisyl-2-butyl arenesulfonates is based on the supposition that the anion portion of the intimate ion pair II effectively shields the bridged cation from covalent solvent attack until solvent intrudes on the intimate ion pair II to the point that the ion pair may be labeled solvent-separated. In qualitative accord with such a description is the relatively low sensitivity of the polarimetric–titrimetric rate ratio in solvolysis of norbornyl bromobenzenesulfonate to solvent nucleophilicity. For example, the change in k_α/k_t is not drastic from acetic acid to absolute ethanol[7,18] as solvent, contrary to what one might expect if covalent solvent attack took place on intimate ion pair II. Previously,[7] the discussion of formation of solvolysis product in acetolysis of norbornyl bromobenzenesulfonate was in terms of "further separation of the (intimate) ion pair with formation of solvolysis product." While the present description is more definite, it remains to be seen whether it will become necessary to complicate the scheme

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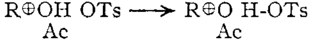
[31] We emphasized previously[10] that this should not be misunderstood[32] as an indication that we believe the intimate ion pair II does not ever give rise to ROS. Also, we mentioned several cases where the intimate ion pair II is believed able to yield solvolysis product.

[32] *E.g.*, B. Bensley and C. Kohnstam, *J. Chem. Soc.*, 3408 (1955).

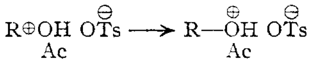
by inclusion of a k_s^{II} path involving attack of solvent on ion pair II.[33,34]

The conversion of solvent-separated ion pair III to solvolysis product may proceed in a number of ways. While one can visualize a carbonium acetate ion pair intermediate along the lines



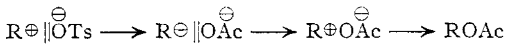
$$\mathrm{R}^{\oplus}\underset{\mathrm{Ac}}{\mathrm{OH}}\ \overset{\ominus}{\mathrm{O}}\mathrm{Ts} \longrightarrow \mathrm{R}^{\oplus}\underset{\mathrm{Ac}}{\overset{\ominus}{\mathrm{O}}}\ \mathrm{H\text{-}OTs}$$

such an intermediate is certainly not necessary. For example, the product formation may be visualized as



$$\mathrm{R}^{\oplus}\underset{\mathrm{Ac}}{\mathrm{OH}}\ \overset{\ominus}{\mathrm{O}}\mathrm{Ts} \longrightarrow \mathrm{R{-}}\underset{\mathrm{Ac}}{\overset{\oplus}{\mathrm{O}}}\mathrm{H}\ \overset{\ominus}{\mathrm{O}}\mathrm{Ts}$$

We have no definitive information in this connection. There is one set of circumstances where it seems relatively certain that acetate formation will involve carbonium acetate ion pairs. This is for acetolysis in the presence of added alkali acetate of a system subject to special salt effects. Under these conditions, carbonium acetate ion pairs, both solvent-separated and intimate, are probably formed.



$$\mathrm{R}^{\oplus}\,\|\overset{\ominus}{\mathrm{O}}\mathrm{Ts} \longrightarrow \mathrm{R}^{\ominus}\,\|\mathrm{O}\overset{\ominus}{\mathrm{A}}\mathrm{c} \longrightarrow \mathrm{R}^{\oplus}\mathrm{O}\overset{\ominus}{\mathrm{A}}\mathrm{c} \longrightarrow \mathrm{ROAc}$$

Dissection of Ion Pair Return.—We can now proceed to perform the arithmetic relating to internal and external ion pair return during acetolysis of the *threo*-3-anisyl-2-butyl arenesulfonates. Since the k_{ext} values for rate constants on the k°_{ext}, k_t line include the full special salt effect, they are rate constants for formation of solvent-separated ion pair III. Thus k_{ext} is given by equation 12 as a function of k_1 (or k_α) and the (k_{-1}/k_2) ratio relating to internal return.

$$k_{\text{ext}} = \frac{k_1}{1 + (k_{-1}/k_2)} = k^{\circ}_{\text{ext}}\,[1 + b_t(\mathrm{LiClO_4})] \quad (12)$$

$$(k_{-1}/k_2) = (k_\alpha/k_{\text{ext}}) - 1 \quad (13)$$

$$k_t = \frac{k_1}{1 + \dfrac{(k_{-1}/k_2)}{k_s^{III}/(k_{-2} + k_s^{III})}} \quad (14)$$

$$\frac{k_s^{III}}{(k_{-2} + k_s^{III})} = \frac{(k_\alpha/k_{\text{ext}}) - 1}{(k_\alpha/k_t) - 1} \quad (15)$$

The latter ratio is given explicitly by equation 13 as a function of k_α and k_{ext}. According to a previous derivation,[3b,10] k_t is given by equation 14 which takes into account both internal and external ion pair return.[35] Substituting for (k_{-1}/k_2) its equivalent from equation 13 allows one to solve for $k_s^{III}/(k_{-2} + k_s^{III})$ as in equation 15.

As summarized in Table V, the k°_α, k°_{ext} and k°_t values lead to values of 0.627 for $k_2/(k_{-1} + k_2)$ and 0.193 for $k_s^{III}/(k_{-2} + k_s^{III})$ in acetolysis of *threo*-3-anisyl-2-butyl bromobenzenesulfonate with no added lithium perchlorate. In other words, 37% of intimate ion pair II formed from covalent bromobenzenesulfonate I returns to the covalent state, while 80.7% of solvent-separated ion pair III formed from II returns to II instead of yielding solvolysis product. As summarized in Table VI, the situation with the toluenesulfonate is quite similar to that for the bromobenzenesulfonate.

TABLE V

ANALYSIS OF EFFECT OF VARIOUS CONCENTRATIONS OF LITHIUM PERCHLORATE

$[\mathrm{LiClO_4}]$, *M*	0	0.003	0.01	0.03
$10^5\,k_{\text{ext}}$	5.05	5.40	6.15	8.32
k_α/k_t	4.07	2.02	1.54	1.35
k_{ext}/k_t	2.58	1.39	1.08	1.00
$k_s^{III}/(k_{-2} + k_s^{III})$	0.193	0.452	0.783	1.00
$k_2/(k_{-1} + k_2)$	0.627	0.679	0.702	0.740
$[(k_{\text{ext}}/k^{\circ}_\alpha) - b_\alpha(\mathrm{LiClO_4})]^a$	0.668	0.666	0.653	0.62

[a] F_0 values from equation 16 assuming $F_{\text{salt}} = 1.00$.

As lithium perchlorate is added in acetolysis of the *threo*-3-anisyl-2-butyl bromobenzenesulfonate, the apparent $k_s^{III}/(k_{-2} + k_s^{III})$ values rise relatively rapidly to 1.00 as external ion pair return is eliminated. This is shown in Table V. On the other hand, the $k_2/(k_{-1} + k_2)$ values show only a small increase, reflecting the relative insensitivity of internal return to the added salt.

The small increase in $k_2/(k_{-1} + k_2)$ values as lithium perchlorate is added does indicate that some change in internal return is included within the normal salt effect pattern.[13] At least some of this effect must be due to the fact that appreciable fractions of ionization of substrate I are salt-assisted as lithium perchlorate is added, and that internal return is less serious for the salt-promoted ionization than for the salt-unassisted ionization.

It is useful here to refer again to equation 10, putting in k_{ext} instead of k_t, k°_α instead of k°_1 and b_α instead of b_1. Rearrangement of the resulting equation leads to equation 16 for F_0, the fraction of

$$F_0 = (k_{\text{ext}}/k^{\circ}_\alpha) - F_{\text{salt}}\,b_\alpha(\mathrm{LiClO_4}) \quad (16)$$

unpromoted ionization escaping internal return. Assuming an extreme value of 1.00 for F_{salt} in equation 16, F_0 values listed in Table V are obtained for comparison with the $k_2/(k_{-1} + k_2)$ values. These actually drift down slightly, showing that the extreme assumption of no internal return in salt-promoted ionization over-corrects for the upward trend in $k_2/(k_{-1} + k_2)$ values.

Comparison of 3-Anisyl-2-butyl and 3-Phenyl-2-butyl Systems.—It is interesting to contrast the behavior of the 3-anisyl-2-butyl system in acetolysis with that of 3-phenyl-2-butyl.[7] In acetolysis of 3-phenyl-2-butyl *p*-toluenesulfonate, previous observations[7] and the previous[7] and present discussion show that internal return is important, but external ion pair return is not, k_s^{III} exceeding k_{-2} by a substantial factor.

The summary in Table VI makes it clear that total ion pair return is of comparable importance in acetolysis of the 3-anisyl-2-butyl and 3-phenyl-2-butyl systems. Where the two systems differ markedly is in the distribution of ion pair return between internal return and external ion pair re-

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(33) See E. Grunwald, A. Heller and F. S. Klein, *J. Chem. Soc.*, 2604 (1957), for a discussion of possible attack of solvent on the α-phenylethyl chloride intimate ion pair from the chloride ion side.

(34) There are many other possible variations of the solvolysis scheme. For example, the first intimate ion pair II could rearrange to a still intimate ion pair, but with the anion near some other portion of the cation, thus leaving the reactive spot on the cation exposed to solvent.

(35) A more convenient form of equation 14 for some purposes is

$$\frac{1}{k_t} = \frac{1}{k_1} + \frac{1}{k_1}\frac{k_{-1}}{k_2} + \frac{1}{k_1}\frac{k_{-1}}{k_2}\frac{k_{-2}}{k_s^{III}}$$

turn. The structural change from 3-phenyl-2-butyl to 3-anisyl-2-butyl which stabilizes the intermediate carbonium ion species does not increase total ion pair return. It decreases k_{-1}/k_2 and thus the efficiency of internal return from II and increases k_{-2}/k_s^{III} and thus the efficiency of return from III.

TABLE VI

COMPARISON OF ION PAIR RETURN IN SOLVOLYSIS OF *threo*-3-PHENYL-2-BUTYL (3-Ph-2-Bu) AND *threo*-3-ANISYL-2-BUTYL (3-An-2-Bu) ARENESULFONATES

Solvent	Compound	Temp., °C.	Ion pair return,[a] % From II[b]	From III[c]	Total[d]
10% HCOOH-dioxane	3-An-2-BuOBs	25			94
AcOH	3-Ph-2-BuOTs[7]	50	78	*ca.* 0	78
	3-An-2-BuOBs	25	37	81	75
	3-An-2-BuOTs	25	38	83	78
EtOH	3-Ph-2-BuOTs[7]	75	51	0	51
	3-An-2-BuOBs	25	21	0	21
25% HCOOH-AcOH	3-An-2-BuOBs	25			7
HCOOH	3-Ph-2-BuOTs[7]	25	15	0	15

[a] At zero $LiClO_4$ concentration. [b] $100k_{-1}/(k_{-1} + k_2)$. [c] $100k_{-2}/(k_{-2} + k_s^{III})$. [d] $100[1 - (k_t^\circ/k_\alpha^\circ)]$.

Other Solvents.—The change from acetic acid to ethanol as solvent causes a very pronounced drop in total ion pair return accompanying solvolysis of 3-anisyl-2-butyl derivatives, the polarimetric-titrimetric rate ratio, k_α/k_t, being only 1.27 in ethanol. For norbornyl bromobenzenesulfonate[7,18] or 3-phenyl-2-butyl toluenesulfonate,[7] the corresponding solvent change produces much less response in the k_α/k_t ratio. Thus, systems whose solvolysis is accompanied by return from solvent-separated ion pair III contrast with those which do not, not only with respect to salt effects, but with respect to behavior toward solvent variation.

A sharp reduction in return from solvent-separated ion pair III accompanying solvolysis as solvent nucleophilicity is increased can be anticipated, since k_s^{III}/k_{-2} should be relatively sensitive to solvent nucleophilicity. It seems likely, therefore, that in ethanol essentially all ion pair return accompanying solvolysis of 3-anisyl-2-butyl bromobenzenesulfonate is the residual internal return from intimate ion pair II. This is the way the data are treated in Table VI.

The contrast between the 3-anisyl-2-butyl and 3-phenyl-2-butyl systems in their response to the AcOH → EtOH solvent change is much reduced if we restrict our attention to internal return alone (Table VI). Also, the contrast between acetic acid and ethanol as solvents for the 3-anisyl-2-butyl system is much less if we consider only internal return, instead of total ion pair return in acetic acid and what is only internal return in ethanol. Thus $(k_{-1} + k_2)/k_2$ is 1.59 in acetic acid and 1.27 in ethanol for 3-anisyl-2-butyl bromobenzenesulfonate.

It is obvious from Tables III and VI that ion pair return accompanying solvolysis of *threo*-3-anisyl-2-butyl bromobenzenesulfonate is increased substantially in 10% HCOOH-dioxane over that occurring in acetic acid. On the other hand, addition of even 25% formic acid to acetic acid nearly completely eliminates ion pair return. The pattern of ion pair return, its possible dissection into internal and external return, and even variation of the solvolysis scheme as solvent varies is being further examined with the 3-anisyl-2-butyl as well as other systems. The results will be reported and discussed elsewhere.

Two Varieties of Ion Pair, Structure and Merging of Ion Pair and Cyclic Mechanisms.—We first visualized two varieties of ion pair in the solvolysis scheme on the basis of *a priori* considerations. In the solvation of ions the inner shell of solvent molecules determines most of the energy of solvation.[36] The first product of ionization of covalent R–X, the intimate ion pair II, is peripherally solvated, but no solvent is yet between the two ions. The solvation shells of the two ions are thus very incomplete and powerful electrostatic, polarization and even other bonding forces are important in stabilizing the intermediate.

Because the medium is not a continuum but composed of discrete molecules of definite size, further separation of the intimate ion pair can be expected to be associated with an energy barrier. In the ascent to the top of the barrier more energy is required to oppose the attractive forces than is compensated for by increased solvation. However, past a certain separation, which permits solvent to enter between the ions, increased solvation more than compensates for energy input required for further separation of the ions. Thus a definite energy barrier is visualized between intimate and solvent-separated ion pairs, these being discrete species. Another way to describe the intimate and solvent-separated ion pairs II and III is as a pair of ions in the same or different solvent cages,[37] respectively.

When only partial elimination of ion pair return by lithium perchlorate was observed in our study of acetolysis of certain arenesulfonates, it was immediately obvious that this was explicable on the basis of two discrete varieties of carbonium ion pairs. Thus, the behavior of arenesulfonates in acetolysis can be taken as support for the idea of discriminating between intimate and solvent-separated ion pairs generally.

At about the same time as intimate and solvent-separated ion pairs were invoked in solvolysis of arenesulfonates,[3] Grunwald[38] furnished an excellent discussion pointing to the probable usefulness of the concept of two distinct chemically different intimate and solvent-separated ion pair species even in the case of ordinary stable ions. Also, Sadek and Fuoss[39] found that, in treating conductivity data on solutions of tetrabutylammonium bromide, a constant interionic distance instead of values dependent on solvent composition was obtained when they assumed a conventional model to describe cation–anion approach up to a separation of one layer of solvent molecules and that the ex-

(36) (a) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933); (b) D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).

(37) S. Winstein, *Experientia*, Suppl., II, 137 (1955).

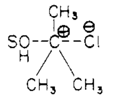
(38) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

(39) H. Sadek and R. M. Fuoss, THIS JOURNAL, **76**, 5905 (1954).

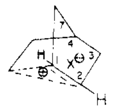
pulsion of the last layer of solvent molecules from between the ions is a discrete stepwise process. Their treatment then involves equilibrium between intimate and solvent-separated ion pairs and dissociated ions corresponding to II, III and IV in our solvolysis scheme.

It seems probable that the fullest understanding of the behavior of various salts in both normal[12] and special[4-6] salt effects will require information on the distribution of the salt ion pairs between intimate and solvent-separated species.

While the cation and anion of the solvent-separated ion pair tend to have little or no definite geometric or structural relationship, the situation can be expected to be different in the intimate ion pair. Here the attraction between the ions is sufficiently strong, that certain structures could well be favored over others. Even on the basis of only electrostatic forces between ions in contact, some structures will correspond to greater stability than others. Further, some covalent character may be visualized for the cation–anion interaction in an intimate ion pair. This is certainly true of ion pairs such as the trimethylcarbonium chloride ion pair VI in solvolysis of *t*-butyl chloride.[14b] Depending on the exact hybridization of orbitals in the $C_7C_1C_2C_3$ framework of a bridged carbonium ion such as norbornyl (VII), there may be some covalent character to the cation–anion interaction in the intimate ion pair even in such cases.[7]



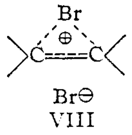
VI



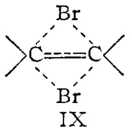
VII

Because of the character of intimate ion pairs, there is no sharp distinction between such an ion pair and a covalently bound intermediate in a so-called cyclic rearrangement. These are not qualitatively distinct, but form extremes in a graded series.[40] Thus, there is no sharp distinction between formation of an intimate ion pair followed by internal return and a cyclic rearrangement, and marginal cases can be anticipated.

Actually, change of solvent may convert one phenomenon to the other and a probable example of this has already been given by Grob and Winstein[16] in the case of mutarotation of Δ^5-cholestene dibromide. Thus the mutarotation–solvolysis could be best described by way of a bromonium bromide ion pair VIII in relatively good ionizing solvents such as acetic acid or ethanol. On the other hand, mutarotation was best described by way of a transition state or intermediate like IX in very poorly ionizing solvents such as heptane.

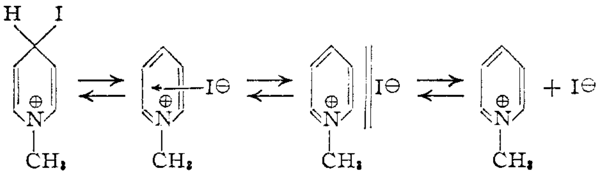


VIII



IX

An analogy has been pointed out recently by Kosower[41] between our solvolysis scheme in acetolysis and the following set of equilibria[42] in ionization–dissociation of N-methylpyridinium iodide



Each of the species in the solvolysis scheme has its counterpart in the N-methylpyridinium case. Specifically, the counterpart of the intimate ion pair II is an intimate ion pair termed a charge-transfer complex[43,44] by Kosower because it displays a charge-transfer absorption band.

The spectral transition energy[45] ΔE^* for the charge-transfer band of the N-methylpyridinium iodide is sensitive to solvent change, and Kosower[41] has observed linear relations between ΔE^* and the solvent **Y** values[14c] which correlate solvolysis rates of alkyl halides, etc., in the Grunwald–Winstein *m***Y** relation.[14] On the basis of the parallelism between ΔE^* and **Y**, as well as the similarity between the ionization–dissociation schemes for RX and for N-methylpyridinium iodide, Kosower[41] has suggested that the intimate ion pair intermediate in solvolysis may derive a portion of its binding energy from charge-transfer forces and that charge transfer may contribute to the stabilization of the transition state for its formation.

The implications of the linear relation between ΔE^* and **Y** may be best understood as follows. The ΔE^* quantity represents the change in energy from the charged ground state pyridinium iodide to the "neutral" excited state in light absorption. Let $\Delta F^{\pm}$ be the free energy change from *t*-butyl chloride to the transition state in solvolysis. Let $\Delta\Delta E^*$ and $\Delta\Delta F^{\pm}$ represent the changes in ΔE^* and $\Delta F^{\pm}$, respectively, associated with a solvent change.[22] From the definition of **Y**, $\Delta\Delta F^{\pm}$ is proportional to Δ**Y**.

As water is added to ethanol, for example, the pyridinium iodide ground state is stabilized and the "neutral" excited state is destabilized; $\Delta\Delta E^*$ is positive. On the other hand, addition of water to ethanol, raises the free energy of the ground state[46] *t*-BuCl molecules and lowers that of the transition state[14,22]; $\Delta\Delta F^{\pm}$ is negative. What the linear relation between ΔE^* and **Y** for a series of solvents means is that relation 17 is obeyed, *c* being a proportionality constant.

$$\Delta\Delta E^* = c\Delta\Delta F^{\pm} \qquad (17)$$

Actually, the response of two phenomena to solvent change can be sufficiently similar for a linear

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[40] Discussion, "Symposium on Molecular Rearrangements," Queen Mary College, Univ. of London, April 6, 1954; see *Chem. Eng. News*, **32**, 1898 (1954); *Nature*, **173**, 898 (1954).

[41] E. Kosower, THIS JOURNAL, **78**, 5700 (1956).

[42] (a) E. M. Kosower, *ibid.*, **77**, 3883 (1955); (b) E. M. Kosower and J. C. Burbach, *ibid.*, **78**, 5838 (1956).

[43] (a) R. S. Mulliken, *ibid.*, **74**, 811 (1952); (b) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[44] Unless charge-transfer forces are shown to account for the major part of the energy of interaction between the two ions, we would prefer the term intimate ion pair. Actually, there are intimate ion pairs of various configurations, many of them presumably unfavorable for the charge-transfer interaction.

[45] The symbol E_T was employed by Kosower,[41] but our discussion is made clearer by the use of ΔE^* to parallel the symbol $\Delta F^{\pm}$ in solvolysis.

[46] **Y** values do not measure the effect of solvent merely on the transition state, as has been stated.[41]

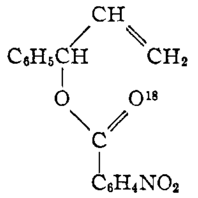
relation such as 17 to be quite successful for each binary solvent set, and yet the structural changes associated with the two phenomena are not strictly analogous. For example, solvolysis rates of substances RX requiring covalent solvent participation give linear log *k vs.* Y plots for aqueous alcohols or aqueous acetones.[14,22] In other words, $\Delta\Delta F^{\ddagger}_{\mathrm{RX}}$ is proportional to $\Delta\Delta F^{\ddagger}_{\mathrm{BuCl}}$ in spite of considerable difference in the structural changes associated with the change from ground state to transition state for RX and *t*-BuCl.

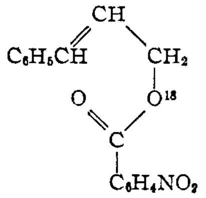
Thus, the proportionality between $\Delta\Delta E^*$ and $\Delta\Delta F^{\ddagger}_{\mathrm{BuCl}}$ does not indicate strict analogy between the structural changes associated with the ΔE^* and the $\Delta F^{\ddagger}_{\mathrm{BuCl}}$. It doesn't indicate sufficient structural analogy between the pyridinium iodide charge-transfer complex and the intimate ion pair II in solvolysis to label the latter a charge-transfer complex because the former is so designated. In spite of the fact that relation 17 should not be offered as support, the suggestion that intimate ion pairs such as VI and II be expressed as charge-transfer complexes is interesting.

For cationic acceptor and anionic donor components like the ions in the intimate ion pair VI there is no big distinction between charge-transfer character and covalent character to the interaction between the ions. Actually, for an interaction to be designated as a charge-transfer interaction between the components of an intimate ion pair II containing a bridged cation such as the one in the present 3-anisyl-2-butyl case, the structure of the first intimate ion pair produced by ionization of I may be unfavorable relative to a structure which has the anion situated near the aromatic ring.

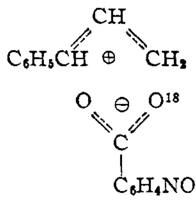
Since intimate ion pairs may well have considerable structure, care needs to be exercised in the use of isotopic criteria for the occurrence of ion pairs as intermediates in rearrangements. For example, for an anionotropic rearrangement and a peroxide rearrangement involving acylate group shifts, it has been stated[47] or implied[48,48a] that the two acylate oxygen atoms must necessarily attain equivalence in an intermediate ion pair. Therefore, O^{18}-scrambling has been employed as a criterion for ion pair formation. Our feeling is that an O^{18}-scrambling result could be support for an ion pair interpretation, but that a unique isotopic result doesn't disprove it. It may merely supply evidence regarding the structure of the intermediate ion pair or ion pairs. In our view, the best criterion for ionization is sensitivity of the reaction to ionizing power of medium.

In the case of thermal isomerization of α-phenylallyl *p*-nitrobenzoate (X) to the γ-phenylallyl isomer XI in chlorobenzene solvent, Braude and Turner[47] have observed that exclusively the acyl oxygen atom of the starting material becomes the alkyl oxygen atom in the rearranged product. A similar result apparently has been obtained by Doering[49] in isomerization of α-phenyl-γ-methylallyl *p*-nitrobenzoate. While Braude and Turner[47] prefer a synchronous cyclic rearrangement mechanism, the facts in the case do not preclude an ion pair intermediate.

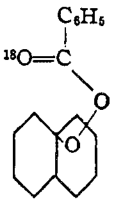

X

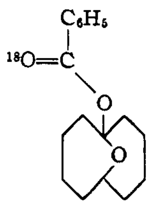

XI

It seems certain that an ion pair intermediate in isomerization of the α-phenylallyl ester X in a solvent like chlorobenzene would tend to remain intimate. Having in mind the distribution of charge in the allylic cation and the acylate anion, it would not be surprising if the intimate ion pair preferred the geometry shown in XII. Thus the O^{18} result constitutes no evidence against an ion pair interpretation.[50] While the rearrangement in question shows considerable sensitivity to salt effects and solvent ionizing power in non-solvolyzing solvents,[51] as well as solvolyzing solvents referred to earlier in this report, it is still not clear whether the rearrangement in chlorobenzene is best described by way of an ion pair intermediate.


XII

In isomerization of 9-decalyl perbenzoate (XIII) to the acylal XIV in both methanol and acetic acid solvents, Denney[48] observed that the O^{18} remained essentially exclusively as carbonyl oxygen. On this basis he regarded the most attractive explanation of the rearrangement to involve a concerted shift of the benzoate group by way of a transition state or short-lived intermediate such as XV. Such a formulation is essentially identical to the one used earlier by Grob and Winstein[16] for the mutarotation of Δ^5-cholestene dibromide in the very poorest ionizing solvents.


XIII


XIV

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(47) E. A. Braude and D. W. Turner, *Chemistry & Industry*, 1223 (1955).

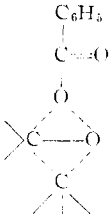
(48) D. B. Denney, THIS JOURNAL, **77**, 1706 (1955).

(48a) NOTE ADDED IN PROOF.—D. B. Denney and D. G. Denney have now employed an ion pair interpretation for the rearrangement of 9-decalyl perbenzoate [*ibid.*, **79**, 4806 (1957)].

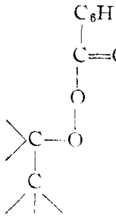
(49) W. E. Doering, quoted by H. L. Goering and R. W. Greiner.[50]

(50) As one of us (S.W.) has already pointed out elsewhere,[40] the same can be said of the isomerization of X in chlorobenzene without isotopic exchange with labeled *p*-nitrobenzoic acid, as reported by E. A. Braude, D. W. Turner and E. S. Waight, *Nature*, **173**, 863 (1954).

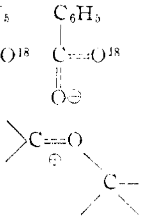
(51) (a) J. Meisenheimer, W. Schmidt and G. Schäfer, *Ann.*, **501**, 131 (1933); (b) A. G. Catchpole and E. D. Hughes, *J. Chem. Soc.*, 1 (1948).



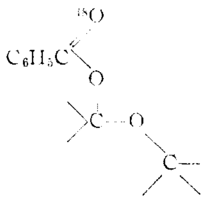
XV



XVI

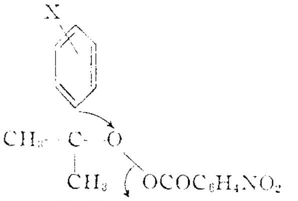


XVII

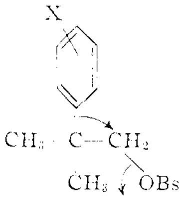


XVIII

There are strong indications that the peroxide rearrangement in question involves ionization[52] and Bartlett[53] and Goering[54] both formulated the rearrangement of 9-decalyl perbenzoate by way of ionization and internal return. The rearrangement reaction is extremely sensitive to solvent ionizing power.[52,55] Also, the addition of water to methanol as solvent raises rate substantially, but it does not affect markedly the proportion of solvolysis and rearrangement.[54] Substituents in the benzoate part of 9-decalyl perbenzoate lead to a Hammett ρ-value of 1.34.[53] Further, substitution in the migrating phenyl group of cumyl per-*p*-nitrobenzoate (XIX) leads to a ρ-value of -5.1 in acetic acid[55] compared to -3.7 for acetolysis of neophyl bromobenzenesulfonates XX.[25]



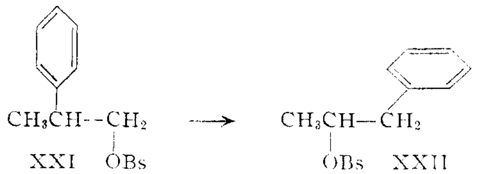
XIX



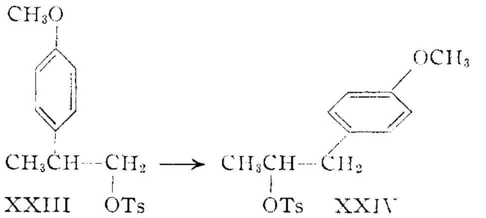
XX

All of the observations support ionization to an ion pair such as XVII as the rate-determining step in rearrangement of 9-decalyl perbenzoate in methanol or acetic acid solvent. Therefore, we regard the O^{18}-result as an indication of preferred structure of the ion pair intermediate or intermediates. Even without covalent character to the cation–anion interaction it seems possible on electrostatic grounds that the greatest stability of intermediates is achieved when only one of the two negative oxygen atoms remains close to both the positive oxygen and positive carbon atoms throughout the sequence of events from starting material XVI to acylal XVIII.

It is interesting that in isomerization of 2-phenyl-1-propyl bromobenzenesulfonate[26] (XXI) and 2-anisyl-1-propyl toluenesulfonate[2b,3,26,27] (XXIII) during acetolysis, Denney[56] has observed quite different O^{18}-results. In the former case, the alkyl oxygen atom in the rearranged ester XXII is 57% the original alkyl oxygen in the 2-phenyl-1-propanol, and 43% one of the other oxygen atoms. With the 2-anisyl-1-propyl ester XXIII, the three oxygen atoms of the toluenesulfonate group have become equivalent in the rearranged ester XXIV.



XXI XXII



XXIII XXIV

The arenesulfonate reactions are no more sensitive than the peroxide reactions to ionizing power of solvent. Therefore, the differences in O^{18}-results in the two kinds of reactions cannot be ascribed to a difference in the ionization character of the rate-determining step in the two cases. Rather, the preferred description in both the peroxide and arenesulfonate cases involves ionization to an ion pair. The differences in O^{18}-results should be discussed on the basis of the nature and behavior of the ion pairs in the several cases.

It is an important feature of the O^{18}-results with the arenesulfonates[56] that essentially complete equivalence of the three oxygen atoms is attained in isomerization of the 2-anisyl-1-propyl ester XXIII, but not in isomerization of the 2-phenyl-1-propyl analog XXI. This difference is in line with our interpretation,[3] based on kinetic evidence, that essentially only internal return occurs with the 2-phenyl-1-propyl ester XXI, but nearly all return with the 2-anisyl-1-propyl analog XXIII involves ion pairs which have attained the degree of interionic separation of the solvent-separated ion pair.

Experimental Part

3-*p*-Anisyl-2-butanols.—2-*p*-Anisylpropanal, b.p. 83–86° (0.4 mm.), was prepared in 67% yield essentially by the method of Sosa.[8] To the Grignard reagent from 64 g. (0.45 mole) of methyl iodide and 10.8 g. (0.45 gram atom) of magnesium, prepared in 400 ml. of ether, was added, as rapidly as possible, a solution of 50.5 g. (0.307 mole) of 2-*p*-anisylpropanal in 200 ml. of ether. The reaction mixture was decomposed with a saturated ammonium chloride solution. On distillation, the crude product yielded 47.0 g. (84%) of a mixture of *erythro*- and *threo*-3-*p*-anisyl-2-butanol, b.p. 85–90 (0.3 mm.). This mixture partially crystallized on standing; 47.0 g. of mixture deposited 21.4 g. of solid *erythro*-alcohol, m.p. 56–60°.

The liquid mother liquors were converted to the acid phthalate in the usual way with phthalic anhydride in pyridine at 90°. The resulting mixture of acid phthalates was subjected to repeated crystallization, first from benzene–Skellysolve F and finally from benzene. The *erythro*-acid phthalate (m.p. 137–138°) was the least soluble component and separated, when pure, as long needles. The *threo*-acid phthalate, when pure, crystallized from benzene as thick prisms, m.p. 123–124.5°. The separation of the last of the *erythro* material from the *threo*-acid phthalate was difficult and was greatly aided by a mechanical separation of the two kinds of crystals. The total recovery of 3-*p*-anisyl-2-butanol in the separation was 67%, and the results indicated that the *erythro*/*threo* ratio in the crude product was *ca.* 3.

Saponification of 1.0 g. (0.00305 mole) of *threo*-3-*p*-anisyl-2-butanol acid phthalate, m.p. 123–124.5°, by refluxing for 2 hours with 2.0 g. of sodium hydroxide in 20 ml. of 50% ethanol, yielded 0.55 g. (quantitative yield) of crude *threo*

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(52) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).

(53) P. D. Bartlett and J. L. Kice, THIS JOURNAL, **75**, 5591 (1953).

(54) H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

(55) K. Nelson, unpublished work.

(56) (a) D. B. Denney, VIth Reaction Mechanism Conference, Swarthmore, Pa., Sept. 12, 1956; (b) D. B. Denney and B. Goldstein, THIS JOURNAL, **79**, 4948 (1957).

3-*p*-anisyl-2-butanol. Micro distillation at 20 mm., with the bath at 155°, gave material, n^{25}D 1.5161.

A solution of 54.6 mg. (0.302 millimole) of *threo*-3-*p*-anisyl-2-butanol and 59.1 mg. (0.318 millimole) of *p*-nitrobenzoyl chloride in 2 ml. of pyridine was heated at 100° for two minutes and diluted with water on cooling. The solid formed was separated by filtration and washed with water, 3 *N* hydrochloric acid, water, 10% potassium carbonate solution and again with water. After drying, there was obtained 72.1 mg. (72%) of crude *p*-nitrobenzoate, m.p. 82–84°, m.p. 84–85°, after one recrystallization from absolute ethanol.

Anal. Calcd. for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.82. Found: C, 65.78; H, 5.75.

erythro-3-*p*-Anisyl-2-butanol was converted to *p*-nitrobenzoate exactly as was the *threo* isomer except that a large excess of *p*-nitrobenzoyl chloride was employed. From 50.6 mg. (0.281 mmole) of *erythro*-3-*p*-anisyl-2-butanol, m.p. 58–60°, 111.0 mg. (0.598 mmole) of *p*-nitrobenzoyl chloride and 2 ml. of pyridine was obtained 90.2 mg. (97%) of crude *p*-nitrobenzoate, m.p. 101–103°, m.p. 102.5–103.5° after one recrystallization from absolute alcohol.

Anal. Calcd. for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.82. Found: C, 65.45; H, 5.85.

Optically Active 3-*p*-Anisyl-2-butyl Derivatives.—A solution of 45 g. (0.137 mole) of acid phthalate, m.p. *ca.* 118°, mostly *threo*, but containing some *erythro* diastereomer, and 61.8 g. (0.132 mole) of brucine in methyl ethyl ketone was prepared. On standing, this solution deposited a very insoluble white powder, m.p. 140° after one recrystallization from methyl ethyl ketone. Regeneration of the acid phthalate from this brucine salt gave rise to active *erythro*-3-*p*-anisyl-2-butyl acid phthalate, m.p. 109–112°, $[\alpha]^{22}$D −29.0° ($CHCl_3$, *c* 2.6).

The filtrate after separation of the insoluble white powder was diluted with a small amount of Skellysolve F and allowed to stand in the ice-box. Fine needle-like crystals slowly separated. Three recrystallizations from methyl ethyl ketone–Skellysolve F yielded 16.1 g. of material, m.p. 121–122°, the brucine salt of the acid phthalate of active *threo*-3-*p*-anisyl-2-butanol.

The saponification of 1.00 g. (0.00305 mole) of the (−)-*erythro*-3-*p*-anisyl-2-butyl acid phthalate, m.p. 109–112°, gave rise to 0.51 g. (93%) of active *erythro*-3-*p*-anisyl-2-butanol, m.p. 74–78° for crude material, m.p. 80–81.5° after one crystallization from Skellysolve F. The crude active *erythro*-alcohol was converted in 55% yield to (−)-*erythro*-3-*p*-anisyl-2-butyl *p*-toluenesulfonate, m.p. 70–72°, $[\alpha]^{25}$D −8.25° ($CHCl_3$, *c* 1.96). In acetolysis of this material, the rotation of the solvolysis solution increases in magnitude.

Regeneration of active *threo*-3-*p*-anisyl-2-butanol acid phthalate from 8.0 g. of the brucine salt, m.p. 121–122°, led to 4.0 g. of crude product which didn't crystallize. This acid phthalate was saponified to yield 1.61 g. (73% over-all) of crude liquid alcohol. This crude alcohol, on conversion to the *p*-bromobenzenesulfonate in the usual way, yielded (after recrystallization from Skellysolve F–benzene) 2.43 g. (66%) of (+)-*threo*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate, m.p. 84–86°, $[\alpha]^{25}$D +11.3° ($CHCl_3$, *c* 2.3). In solvolysis in both acetic acid and ethanol the observed rotation (*ca.* 0.7°) tended to zero.

In another experiment, 2.0 g. of the brucine salt of the *threo*-3-*p*-anisyl-2-butyl acid phthalate gave rise to 0.44 g. (88%) of active *threo*-3-*p*-anisyl-2-butanol. This alcohol gave 0.51 g. (62%) of (−)-*threo*-3-*p*-anisyl-2-butyl *p*-toluenesulfonate, m.p. 69–70°, $[\alpha]^{26}$D −11.3° ($CHCl_3$, *c* 2.0).

Acetolysis of *dl*-*threo*-3-*p*-Anisyl-2-butyl *p*-Bromobenzenesulfonate.—A solution of 0.3968 g. (0.994 mmole) of *p*-bromobenzenesulfonate in 100 ml. of 0.01 *M* lithium acetate was kept at 25.0° for 118 hours (*ca.* 12 half-lives). The solvolysis mixture was then diluted with 1800 ml. of water and extracted twice with 500-ml. portions of ether. The ether extract was washed with 800 ml. of water, dried over potassium carbonate, concentrated to *ca.* 75 ml., and reduced with 1.0 g. of lithium aluminum hydride. The reduction mixture was worked up with water and aqueous sodium hydroxide solution. The ether solution was separated from basic salts by filtration. Subsequent distillation of the ether and micro-distillation of the residual material at 25 mm. with a pot temperature *ca.* 165° gave 0.1194 g. (66% as *threo*-3-*p*-anisyl-2-butanol) of crude product, n^{25}D 1.5198. The *p*-nitrobenzoate, from this material, prepared in 97% yield assuming the crude alcohol was 12% olefin,[57] had a crude m.p. 79–82°, m.p. 83–85° after simple washing with ethanol, undepressed on admixture of pure *threo*-3-*p*-anisyl-2-butyl *p*-nitrobenzoate.

An analogous acetolysis employing acetic acid without added lithium acetate gave 0.27 g. (75% as alcohol) of product, n^{25}D 1.5200, from 0.8017 g. (2.005 mmoles) of *p*-bromobenzenesulfonate in 200 ml. of acetic acid. This product gave rise to a *p*-nitrobenzoate (97% yield assuming 12% olefin in alcohol), crude m.p. 75–82°, m.p. 81–84° after one crystallization from ethanol.

Kinetics.—Anhydrous solvents were prepared and solvolyses were followed by the usual methods.[10]

For the polarimetric rate measurements,[7,16,18] solutions were prepared by dissolving a weighed sample of active material in 5.6 ml. of total solution. The solution was then filtered through a coarse sintered glass funnel into a jacketed 4-dm. side-filling polarimeter tube. The jacket of the polarimeter tube was maintained at 25.0° by circulation of oil from a constant temperature bath. The time required for thermal equilibrium in the polarimeter tube was minimized by keeping the solvents in the 25.0° bath until they were to be used. The initial polarimetric readings were taken from 3–20 minutes after preparation of the final kinetic solution.

With some solvents, the solutions tended to become colored and opaque, so experimental infinity readings could not be obtained. A zero infinity rotation was assumed in these cases, since the infinity polarimeter reading agreed exactly with the instrument zero point reading in solvents, such as 25% HCOOH–AcOH and formic acid, where infinity polarimeter readings were not interfered with.

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[57] Rough estimate based on refractive index, using n^{25}D 1.5478 for the olefin, b.p. 120–135° (25 mm.), obtained by refluxing a mixture of acetic anhydride and the 2-*p*-anisyl-2-butanol from the action of *p*-anisylmagnesium bromide on 2-butanone.