

IDENTIFICATION OF INTERMEDIATES IN SOLVOLYSES OF
2-OCTYL SULFONATES

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Although solvolytic reactions of both primary and tertiary systems have for some time been considered to be fairly well understood in terms of the traditional S_N1-S_N2 picture, an understanding of solvolyses of secondary systems has been more elusive. The earlier literature spoke in terms of "borderline" behavior³ or described the transition state as a resonance hybrid of both S_N1 and S_N2 components.⁴ Although most authors have taken the view that a single mechanism operates in these borderline solvolyses^{3,4} some have continued to think in terms of distinct, competing component mechanisms.⁵

We have undertaken a rather intensive examination, collecting both kinetic and stereochemical data, of the solvolysis reactions of 2-octyl sulfonates with and without added nucleophiles (particularly

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³M. L. Bird, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 634(1954).

⁴S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, 73, 2700(1951).

⁵V. Gold, *J. Chem. Soc.*, 4633(1956).

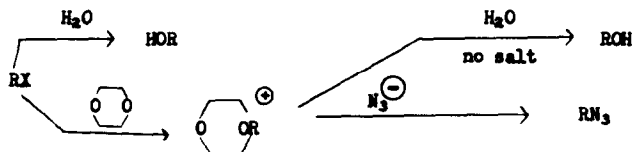
azide ion). Solvent systems varied from pure methanol to pure water and included mixtures of dioxane-water, dioxane-methanol, acetone-water and acetone-methanol. Our results lead us to formulate a rather detailed picture of the various mechanistic happenings. A summary of our results and their mechanistic implications provide the subject matter of this letter.⁶

The results of our experiments, many of which are summarized in the accompanying tables, demand that any picture of the solvolyses conducted in the mixed solvents include two intermediates: 1, an ion formed by the intervention of the "inert" component of the solvent mixture (dioxane or acetone); and 2, an ion-pair. The latter intermediate suffices for an explanation of the observed behavior in pure solvents. Arguments for each of these types of intermediates will be discussed in turn.

Evidence for Solvent Intervention. — In a recent communication⁷ the intervention of dioxane as a nucleophilic agent in competition with water in the hydrolysis of optically active 2-octyl brosylate in aqueous dioxane, with resultant formation of an intermediate oxonium ion, was advanced as an explanation for the observed ability of added sodium azide to increase the optical purity of the inverted alcohol from 77% in the absence of this salt to 100% in its presence. The function of the azide, presumably, is to react preferentially with the ion, thus diverting it to alkyl azide:

⁶A recent paper by A. Streitwieser, Jr. and T. D. Walsh reports experiments dealing with the stereochemistry of acetolysis of 2-octyl *p*-toluenesulfonate. Their conclusions complement, and in many cases, parallel ours. Tetrahedron Letters, No. 1, 1 (1963).

⁷H. Weiner and R. A. Sneed, J. Am. Chem. Soc., 84, 3599 (1962).



With the limited data available to us at that time the intermediate required by our data could not be definitely identified as the oxonium ion; we considered the alternative that it might be a solvated carbonium ion but this latter possibility can now be ruled out.

This conclusion is borne out by the data of Table I. Of particular interest is the observation that, both in pure methanol⁶ as well as in pure water the isolated solvolysis product proved to be essentially completely inverted; thus the optical purity of product in mixed solvents would appear to be an inverse function of the dioxane concentration. Only in the mixed solvents, in dioxane-water and, somewhat less impressively, in dioxane-methanol, is optically impure product formed. Since one would expect carbonium ion formation to be relatively more important in the better ionizing solvents this species can be definitely eliminated as an intermediate, even in pure water.

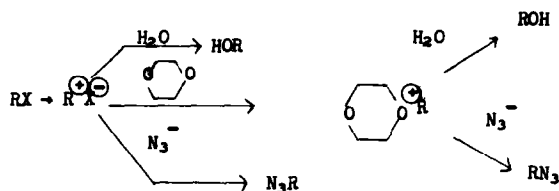
Interpretation of the accumulated data of Table I relating the optical purity of isolated 2-octyl azide as a function of both solvent composition and sodium azide concentration can be shown to be consistent with dioxane intervention, provided a second mechanism, involving, presumably, an ion-pair intermediate, exists for the competitive

⁶It has been reported that ethanolysis of 2-octyl tosylate (0.2 M) takes place with essentially complete inversion of configuration. See A. Streitwieser, Jr. and A. C. Weiss, Jr., *J. Org. Chem.*, **27**, 290 (1962).

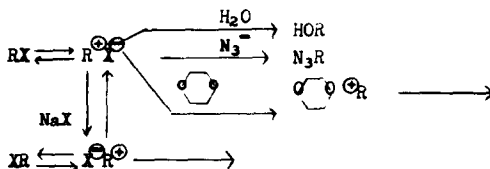
formation of inverted 2-octyl azide. Suffice it here to note that at low concentrations of sodium azide, 0.00637 M, in 75% aqueous dioxane, the alkyl azide is formed, partly inverted, with only 39% optical purity, consistent with the view that some of the alkyl azide is formed by attack of azide ion on the pre-formed oxonium ion; in essence this is a double inversion resulting in overall retention of configuration.⁹

Evidence for Ion-Pair Intervention. —Selected kinetic data are summarized in Table II. Rates were, in some cases, followed both titrimetrically (k_t) and polarimetrically (k_p). It will be apparent that, in 75% aqueous dioxane, azide is influencing the rate of reaction and must therefore be included in the rate-determining step. Such is not the case, however, in the more aqueous 25% dioxane system; here the rate of reaction is unaffected by added sodium azide, even at 0.0463 M, where 31% of the starting ester ends up as alkyl azide. Furthermore, the alkyl azide isolated from this run proved to be essentially completely inverted. (Table I). To accommodate these facts an optically active intermediate must be invoked, an intermediate formed in the rate-determining step, whose subsequent reaction with sodium azide gives overall inversion of configuration. Such an intermediate is most reasonably an ion-pair:

⁹The results of experiments implicating acetone as a nucleophile will be published elsewhere and will thus only briefly be mentioned here: solvolysis of 2-octyl brosylate in 80% methanolic acetone furnished, in addition to the expected 2-octyl methyl ether, 15-5% of 2-octanol. The alcohol forms, presumably, by the acid-catalyzed cleavage of the mixed methyl 2-octyl ketal of acetone which is formed in turn via the 2-octyl acetoxonium ion, $\text{[(CH}_3)_2\text{C=OC}_8\text{H}_{17}]^{\oplus}$



Confirmation of this interpretation of the data is provided by several lines of evidence. First the polarimetric rate constant, k_p , proved always to be somewhat greater than the titrimetric constant, k_t . The ratio, k_p/k_t , varied from 1.05 in the absence of added salt, to 1.15 in the presence of 0.0126 M sodium tosylate. Thus a mechanism must exist for racemization of starting material, competitive with the product-forming reactions. Such a conclusion is equally apparent from the observation that the optical purity of isolated alcohol from the solvolysis of 2-octyl brosylate in 75% aqueous dioxane was decreased from 77% in the absence of salt to 70% in the presence of 0.020 M lithium brosylate (Table I). These data require that the mechanistic scheme be expanded to include this catalyzed racemization:¹⁰



¹⁰ An alternate explanation of the facts, that racemization proceeds by direct attack of anion on covalent starting material, is less attractive in view of the low nucleophilicity of sulfonate anions. In acetic acid solvolyses Streitwieser⁶ has detected similar exchanges and has argued convincingly that the exchange must take place at the ion-pair stage.

TABLE I
Stereochemistry of Solvolyses of 2-Octyl Sulfonates^a

^b Solvent	Salt	[Salt] ^c x 10 ²	Azide, %	ROS ^d % Opt. Purity	RN ₃ ^d % Opt. Purity
75% D:W	—	—	—	77	—
75% D:W	NaN ₃	0.637	8.8	66	39
75% D:W	NaN ₃	1.27	27.0	{76 74}	62
75% D:W	NaN ₃	1.26	—	77	67
75% D:W	NaN ₃	3.07	64.9	107	89
75% D:W	NaN ₃	3.07	—	104	96
75% D:W	NaN ₃	6.18	77.6	100	93
75% D:W	LiOEt	2.02	—	70	—
75% D:W	HOTs	2.85	—	68	—
67.7% D:W	—	—	—	77	—
67.7% D:W	NaN ₃	0.562	—	79	24
50% D:W	—	—	—	88	—
50% D:W	NaN ₃	9.3	51.8	95	—
25% D:W	—	—	—	95	—
25% D:W	NaN ₃	4.43	21.7	97	83
100% W	—	—	—	100	—
100% W	NaN ₃	10.65	—	98	99
90% D:M	—	—	—	92	—
50% D:M	—	—	—	97	—
100% M	—	—	—	100	—
80% A:W	—	—	—	99	—
80% A:W	LiClO ₄	3.07	—	93	—

^a 2-Octyl mesylate was used in all experiments carried out in 50% and in 25% aqueous dioxane as well as in pure water. 2-Octyl brosylate was used in all other runs. All product runs were carried out at 65°. [ROE_s]_i = 0.0174–0.0180 M for all runs in 75% aqueous dioxane, methanolic dioxane, methanol, and aqueous acetone; [ROE_s]_i = 0.0107–0.0177 M for runs in 25%, 50%, and 67.7% aqueous dioxane; [ROE_s]_i = 0.0027–0.00349 M in pure water.

^b Given as volume percentage of first named component. D, dioxane; W, water; M, methanol; A, acetone.

^c Initial concentration.

^d Products were, in all cases, inverted.

TABLE II
Rates of Solvolyses of 2-Octyl Sulfonates ^a

Solvent ^b	Temp., °C	Salt	[Salt] ^c x 10 ²	k _t , sec. ⁻¹ x 10 ⁵	k _g , sec. ⁻¹ x 10 ⁵	k _g /k _t
75% D:W	65.0	— ^d	— ^d	23.5 ⁺ 0.3	24.7 ⁺ 0.6	1.05
75% D:W	65.0	NaOTs ^e	1.26	23.6 [±] 0.6	27.2 ⁻ 0.8	1.15
75% D:W	65.0	NaOTs ^f	0.633 ^e	23.3 [±] 1.0	27.3 ^f	1.17
75% D:W	65.0	NaOTs ^f	1.26	23.7 ⁻ 0.3	25.3	1.08
75% D:W	65.0	NaN ₃	1.25	32.5 ^g		
75% D:W	65.0	NaN ₃	2.52	64 ^g		
75% D:W	65.0	NaN ₃	11.96	182 ⁺ 4	174 ⁻ 5	
25% D:W	38.6	—	—	38.7 ⁻ 0.6		
25% D:W	38.6	NaN ₃	2.90	35.0 ⁺		
25% D:W	38.6	NaN ₃	4.63	37.6 [±] 0.6		
25% D:W	38.6	{ NaN ₃ LiClO ₄ }	{ 6.1 3.0 }	{ 37.2 ⁻ 0.8 }		

^a 2-Octyl mesylate was used in experiments in 25% aqueous dioxane.
2-Octyl brosylate was used in experiments in 75% aqueous dioxane.

^b Given as volume percentage of first named component: D, dioxane;
W, water.

^c Initial concentration unless otherwise noted.

^d Prepared in situ from NaN₃ (0.0126 M) and HOTs (0.0138 M).

^e Prepared in situ from NaN₃ (0.0063 M) and liberated HOTs.
Polarimetric rate constant, k_g, calculated from data after 20%
reaction.

^f Prepared in situ from NaN₃ (0.0126 M) and HOTs (0.00688 M).
Polarimetric rate constant determined from data after 20% reaction.

^g Initial rate.

Final evidence for the ion-pair is provided by an experiment in which 2-octyl brosylate was solvolyzed (75% aqueous dioxane) in the presence of 0.122 M lithium tosylate. Although the rate (titrimetric) appeared to be fairly constant over the measured extent of reaction the amount of acid formed after 8.0 half-lives of reaction (99.6% reaction) of 2-octyl brosylate was only 95.8% of theory. After an additional 2.5 and 4.5 half-lives, 98.4% and 99.0%, respectively, of the theoretical acid had been produced. Thus an exchange reaction is evident, the slower solvolysing 2-octyl tosylate accumulating as reaction progresses.

Only in selected experiments do our data allow us to conclude that nucleophilic attack occurs at the ion-pair stage rather than on covalent starting material. But, for symmetry and simplicity, our mechanistic scheme includes only the former mode of reaction. It is of interest to consider the intriguing possibility that at least some so-called S_N2 reactions may proceed via a rate-determining attack by nucleophile on a reversibly formed ion-pair. We are currently looking into this problem.

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