

Oxygen-18 Scrambling in Solvolyses of Simple Unactivated Alkyl Arenesulfonates^{1,2}

Sir:

The important role of carbonium ion pair intermediates in solvolysis and related reactions of RX substrates was first recognized with rearranging allylic^{3a} systems or substrates which give rise to bridged cations.^{3b-e,4a} Later it was recognized in solvolysis of systems which neither rearrange nor lead to bridged cations, but which lead to relatively stable classical cations, for example, *p*-chlorobenzhydryl⁴ or trityl.^{4a}

able ion-pair intermediate by ⁻OTs or N₃⁻ with inversion of configuration, competitive with solvent capture, to give inverted solvolysis product. We have sought other, possibly more direct, evidence for ion-pair return in solvolyses of simple unactivated alkyl arenesulfonates, using ¹⁸O equilibration in the residual ROSO₂Ar as a probe for ion-pair return. Some of the results of this search are here described.

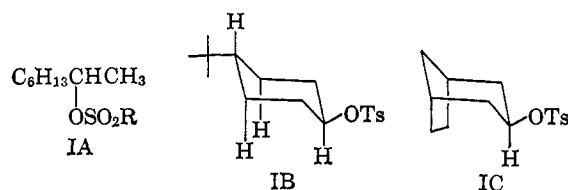
2-Octyl bromobenzenesulfonate (IA-OBs), prepared from ¹⁸O-labeled *p*-bromobenzenesulfonyl chloride, was recovered at various stages of solvolysis and examined for ¹⁸O scrambling.⁶ Summarized in Table I are the

Table I. Summary of Solvolysis and ¹⁸O-Equilibration Data

Solvent	Temp, °C	ROBs, 10 ² M	Other solute	10 ² M	k values, sec ⁻¹		10 ² × F _{eq} ^a
					10 ⁵ k _t	10 ⁵ k _{eq}	
2-Octyl-OBs (IA-OBs)							
MeOH	75.0	2.0			142 ± 1		
MeOH	75.0	6.7				1.52 ± 0.08	1.1
AcOH	75.0	1.1			22.9 ± 0.2	1.52 ± 0.03	6.2
AcOH	75.0	10.5				1.69 ± 0.09	6.9
AcOH	75.0	2.3	NaOAc	2.2	22.5 ± 0.3		
AcOH	75.0	10.7	NaOAc	5.4		2.33 ± 0.03	9.4
AcOH	75.0	1.1	LiClO ₄	5.7	49.3 ± 0.6 ^b		
AcOH	75.0	12.1	LiClO ₄	5.7		3.47 ± 0.02	6.6
AcOH	75.0	1.1	LiClO ₄	13.6	83.1 ± 1.6 ^b		
AcOH	75.0	10.3	LiClO ₄	13.6		6.28 ± 0.04	7.0
AcOH	75.0	0.8	LiOTs	10.1	27.8 ± 0.7		
AcOH	75.0	6.6	LiOTs	10.1		2.2 ± 0.3	7.4
HCOOH	25.0	1-7			12.8 ± 0.4	1.13 ± 0.03	8.1
CF ₃ CO ₂ H	25.0	3.4	CF ₃ CO ₂ Na	2.5	49.2 ± 2.0	12.2 ± 0.06	19.9
<i>trans</i> -4- <i>t</i> -Butylcyclohexyl-OTs (IB-OTs)							
AcOH	75.0	1.1			3.88 ± 0.06	0.159 ± 0.008	3.9
AcOH	75.0	11.0				0.175 ± 0.015	4.3
AcOH	75.0	2.0	NaOAc	2.2	3.86 ± 0.04		
AcOH	75.0	10.3	NaOAc	10.0		0.181 ± 0.009	4.5
AcOH	75.0	2.0	LiClO ₄	10.6	13.5 ± 0.3 ^c		
AcOH	75.0	11.4	LiClO ₄	10.6		0.448 ± 0.030	3.2
HCOOH	25.0	2.0			3.57 ± 0.07		
HCOOH	25.0	1-5				0.107 ± 0.017	2.9
CF ₃ CO ₂ H	25.0	5.0	CF ₃ CO ₂ Na	5.0	24.2 ± 0.9	2.00 ± 0.07	7.6

^a F_{eq} = [k_{eq}/(k_{eq} + k_t)]. ^b b = 19.5 ± 0.4 in the equation k_t = k_t⁰(1 + b[LiClO₄]). ^c b = 23.1.

The present communication concerns itself with the possible role of ion pairs in solvolysis of the very simplest unactivated RX systems. In recent years, Streitwieser^{5a,b} and Sneen^{5c,d} have made observations in solvolyses of 2-octyl arenesulfonates (IA) which they have suggested are best explained by capture of a return-



first-order rate constants, k_{eq}, for the equilibration represented by eq 1, along with titrimetric rate constants, k_t.



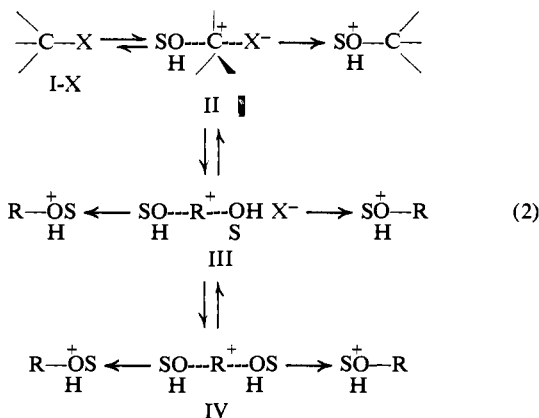
As is obvious from Table I, appreciable ¹⁸O scrambling in the residual ROSO₂Ar does indeed accompany

(6) IA-OBs was recovered by extraction and recrystallized from pentane. This ester was cleaved to alcohol with lithium in liquid ammonia, and the recovered alcohol was purified by vpc. Rates of ¹⁸O equilibration were measured by following the ¹⁸O enrichment in the CO₂ collected from HgCl₂ oxidation of the recovered alcohol. This method gave satisfactory ¹⁸O analyses when the CO₂ was purified by vpc. The k_{eq} values were calculated with the equation k_{eq} = (2.303/t) log [(a_∞ - a₀)/(a_∞ - a_t)], where a_∞ is two-thirds of the ¹⁸O atom % excess in the BsCl used to prepare the ester and a₀ and a_t have the usual meaning. With IB-OTs, recovered ROTs was recrystallized twice and then cleaved to alcohol. The alcohol was purified by chromatography, and the purity was checked by vpc prior to ¹⁸O analysis.

- (1) Research supported by the National Science Foundation.
- (2) Reported in part by S. Winstein in his James Flack Norris Award Address, "Salt, Solvent and Ion Pair Effects in Some Carbonium Ion Chemistry," at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 11, 1967.
- (3) (a) W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951); (b) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (c) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (d) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958); (e) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).
- (4) (a) S. Winstein, B. Appel, R. Baker, and A. Diaz, Special Publication, No. 19, The Chemical Society, London, 1965, p 109, and references included therein; (b) S. Winstein and J. S. Gall, *Tetrahedron Letters*, No. 2, 31 (1960); S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, No. 22, 12 (1960); S. Winstein, A. Ledwith, and M. Hojo, *ibid.*, 341 (1961).
- (5) (a) A. Streitwieser, Jr., and A. C. Waiss, Jr., *J. Org. Chem.*, **27**, 290 (1962); A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **87**, 3682 (1965); (b) A. Streitwieser and T. D. Walsh, *Tetrahedron Letters*, 27 (1963); *J. Am. Chem. Soc.*, **87**, 3686 (1965); (c) H. Weiner and R. A. Sneen, *ibid.*, **84**, 3599 (1962); *Tetrahedron Letters*, 1309 (1963); *J. Am. Chem. Soc.*, **87**, 287 (1965); **87**, 292 (1965); (d) R. A. Sneen and J. W. Larsen, *ibid.*, **88**, 2593 (1966).

solvolytic of IA-OBs in the common solvolysis solvents. Using $F_{\text{eq}} = [k_{\text{eq}}/(k_{\text{eq}} + k_{-1})]$ as a measure of the importance of such ^{18}O scrambling, we see that $100F_{\text{eq}}$ is 1.1, 6.5, 8.1, and 19.9 in MeOH, AcOH, HCOOH, and CF_3COOH , respectively. No very large changes in F_{eq} are introduced on addition of NaOAc, LiClO_4 , or LiOTs in acetolysis. With *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate^{7a} (IB-OTs) as substrate, ^{18}O scrambling is also observed to accompany solvolysis, the results being similar to those with IA-OBs. To check on the intramolecularity of the ^{18}O scrambling as opposed to a process involving exchange with an external arenesulfonate ion, solvolysis of IA-OBs and IB-OTs was followed under various conditions in the presence of ^{14}C -labeled HOTs, residual ROSO_2Ar being counted for ^{14}C content. On the basis of the exchange rate constants observed, intermolecular exchange contributes only slightly to the k_{eq} values in the absence of arenesulfonate salt. For example, in acetolysis of IA-OBs without added salt, intermolecular exchange⁸ accounts for perhaps 3% of k_{eq} . However, it may account for *ca.* 20% in the presence of added NaOAc. In solvolysis of IA-OBs in F_3CCOOH with added NaOCOCF_3 , intermolecular exchange may account for *ca.* 6% of k_{eq} .

Solvolytic of the simple unactivated IA-OBs and IB-OTs systems are best discussed, as in eq 2, in terms of intermediates II ("intimate ion pair"), III ("solvent-separated ion pair"), and IV ("dissociated cation").^{4b,9} Judging by the tremendous preference for inversion of configuration in solvolysis of such systems, *e.g.*, 2-octyl (IA),⁵ *trans*-4-*t*-butylcyclohexyl (IB),^{7a} and *exo*-3-bicyclo[3.2.1]octyl (IC)^b arenesulfonates, formation of solvolysis product occurs essentially exclusively from the "intimate ion pair" II, this species giving inverted product more rapidly than it progresses to III and IV. On this basis, the ^{18}O scrambling accompanying solvolysis of these systems is probably best represented as in eq 3 with ion-pair return (k_{-1}) and equilibration ($k_{\text{eq}}^{\text{II}}$) of sulfonate oxygen atoms in the intimate ion pair II (IIa \rightarrow IIb) competitive with solvolysis (k_s^{II}).



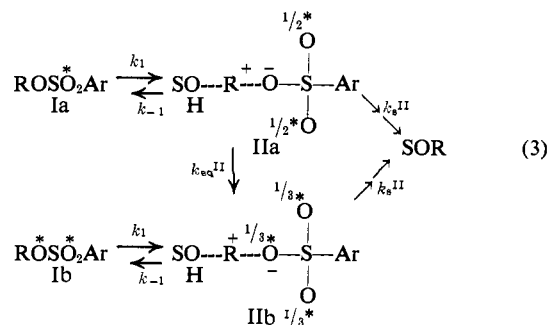
The F_{eq} values in Table I would be an actual measure of ion-pair return $[(k_{-1}/(k_{-1} + k_s^{\text{II}}))]$, provided $k_{\text{eq}}^{\text{II}} \gg k_{-1}$. However, since k_{-1} may be much larger than $k_{\text{eq}}^{\text{II}}$,

(7) (a) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955); M. Whiting, private communication; (b) C. W. Jefford, J. Gunsher, and B. Waegell, *Tetrahedron Letters*, 3405 (1965); C. W. Jefford, D. T. Hill, and J. Gunsher, *J. Am. Chem. Soc.*, **89**, 6881 (1967).

(8) In the case of IA-OBs, exchange with HOBs or NaOBs was assumed comparable to that with HOTs or NaOTs, respectively.

(9) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956); S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **78**, 328 (1956); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

F_{eq} provides only a lower limit to ion-pair return.¹⁰ It is clear from Table I that these F_{eq} values are quite sensitive to the nature of the solvent. The much lower values for F_{eq} observed in MeOH, compared to AcOH, are in line with an expected decrease in the (k_{-1}/k_s^{II}) ratio on going from AcOH to the much more nucleophilic MeOH. It is interesting that the F_{eq} measure of ion-pair return in formolysis of IA-OBs and IB-OTs is comparable to F_{eq} in acetolysis.¹¹ While the $(k_{\text{eq}}^{\text{II}}/k_s^{\text{II}})$ and $(k_{\text{eq}}^{\text{II}}/k_{-1})$ ratios probably both increase on going from AcOH to HCOOH, total ion-pair return may well decrease, *i.e.*, k_{-1}/k_s^{II} decreases.



(10) Even with bridged ion pairs, as in acetolyses of 3-phenyl-2-butyl toluenesulfonate, ion-pair return occurs with incomplete ^{18}O equilibration, k_{eq} being *ca.* half as large as k_{rac} (R. Thies and H. L. Goering, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S38; R. Thies, Ph.D. Thesis, University of Wisconsin, 1967).

(11) Superficially, this appears to contrast with the situation in solvolysis of RX systems leading to bridged ions, where the measured total ion-pair return in HCOOH is very much less important than in AcOH.^{3c-e,4b}

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Received February 7, 1968

Mechanisms of Ozonolysis. Reductive Cleavage of Ozonides

Sir:

In order to test our recent mechanistic proposal¹ for the ozonolysis reaction we have utilized oxygen-labeling techniques in which labeled aldehyde is introduced into the ozonolysis mixture. In the absence of adequate mass spectral fragmentation patterns or infrared spectral assignments for ozonides, we have determined isotopic distribution through ozonide reduction followed by mass spectral analysis of the resulting products. Unequivocal location of the isotopic label in the product ozonide is, of course, critical for a proper interpretation of the mechanisms of ozonide formation.²

We now wish to report the synthesis of a specifically labeled ozonide which, in turn, has permitted an assessment of the mechanisms of reductive cleavage of ozonides. Application of the present findings to the mecha-

(1) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **88**, 3144 (1966).

(2) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, Abstracts of Papers, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 12-16, 1966, Paper S5; P. R. Story, C. E. Bishop, J. R. Burgess, J. B. Olson, R. W. Murray, and R. D. Youssefyeh, Preprints of Papers, Vol. II, International Oxidation Symposium, San Francisco, Calif., Aug 27-Sept 1, 1967, p 327.