pK_{high} and pK_{low} are the highest and lowest pK values, in the range of pK values in which catalysis may be observed. For example, for the reaction of MG, $D = 0.55$, $\beta = 0.53$, and $\log (k_W/k_{OH}) = -3.85$. Therefore, $pK_{high} = 13.3$ and $pK_{low} = 7.4$. This pK range is consistent with the fact that buffer catalysis is only barely detectable with 3-quinuclidinone which has a pK of 7.5. Furthermore, these results also explain why the early attempts to find general acid–base catalysis in these reactions with acetate buffer solutions ($pK = 4.75$) proved unsuccessful.[12-14]

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On the Incidence of Internal Ion Pair Return during Solvolysis of *sec*-Alkyl Benzenesulfonates[1]

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Abstract: For solvolyses of four *sec*-alkyl benzenesulfonates, in which the alkyl group is isopropyl (**1**), cyclopentyl (**2**), 2-adamantyl (**3**), and 3,3-dimethyl-2-butyl (**4**), in CF_3COOH and selected other solvents, overall solvolysis rates and rates of equilibration of excess oxygen-18, originally in sulfonyl sites, between alkoxyl and sulfonyl sites in unsolvolyzed ester have been determined. An improved method for oxygen-18 analysis has been developed; it reports the ^{18}O content in both the alkoxyl and sulfonyl moieties and is much simpler to employ than methods previously used. On the assumption that oxygen equilibration occurs via internal return from intimate ion pairs, the results indicate internal return to be extensive (>53%) in the case of **3** in three solvents, significant but of lesser magnitude for **1** and **2**, and undetectable in the case of **4**. These results oblige reinterpretation of solvolysis rate correlations that have been based on the premise that 2-adamantyl *p*-toluenesulfonate solvolyzes with rate-determining ionization. Questions concerning the nature of intimate ion pair intermediates are examined.

The solvolysis of *sec*-alkyl arenesulfonates in protic solvents such as water, alcohols, or carboxylic acids is indicated by many lines of evidence to occur via ionic intermediates with the probable concurrence in some cases of direct nucleophilic participation by the solvent.[3-7]

Ionization of an alkyl arenesulfonate forms a carbocation and an arenesulfonate ion, initially as an intimate (or contact, or tight) ion pair. The two ions may then partially separate to form a loose or solvent-separated ion pair, and the latter may dissociate to free ions.[4,7]

Much attention has been given to how much "internal return", to regenerate the substrate, occurs from the intimate or tight ion pair first formed by heterolysis. Such internal return may conceivably occur whether the carbocation is bare or "nucleophilically solvated".[5] Several kinds of evidence have shown that ion pair solvolysis intermediates may revert to the original substrates,[4] but most of the substrates involved were such as to afford carbocations, such as allylic carbenium ions, with significant stabilizing features, and much of the "return" revealed was from solvent-separated or even dissociated ion pairs.

Solvolyses of plain *sec*-alkyl halides and arenesulfonates have some characteristics suggestive of ionic intermediates, for example, strong kinetic dependence on the polarity of solvents and on polar effects of substituents. Much of what we understand of the mechanism of solvolysis of *sec*-alkyl arenesulfonates has been inferred on the basis of indirect criteria such as kinetic isotope effects[10,11] and reactivity correlations,[5,12-14] but many of the inferences made have failed to win general acceptance.

In these circumstances it is curious that sparse use has been made of what "is probably the single most powerful tool for the detection of ion pairs in solvolysis reactions", namely, oxygen isotope scrambling in the substrate during solvolysis of a sulfonate

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Table I. Solvolysis and Oxygen-18 Scrambling Data for Some Secondary Alkyl Benzenesulfonates

substrate[a]	solvent	other solute[b]	temp, °C	10^5k_t, s^{-1}	10^5k_{eq},[c] s^{-1}	minimal fraction of internal return[d]
1	CF_3CO_2H	CF_3CO_2Na	25.0	3.61 ± 0.15	0.79 ± 0.02	0.18
2	CF_3CO_2H	CF_3CO_2Na	25.0	383 ± 3	84.8 ± 8.3	0.18
2	90% HFIP/10% H_2O	2,6-lutidine	25.0	14.7	0.73 ± 0.09	0.05
3	CF_3CO_2H	CF_3CO_2Na	25.0	147 ± 2	182 ± 6	0.55
3	CH_3CO_2H	CH_3CO_2Na	80.0	2.16 ± 0.03	5.7 ± 0.3	0.73
3	80% EtOH/20% H_2O		80.0	6.60 ± 0.01	7.4 ± 0.4	0.53
4	90% HFIP/10% H_2O	2,6-lutidine	25.0	22.7	*e*	
4	CF_3CO_2H	CF_3CO_2Na	25.0	733	*e*	
4	CF_3CH_2OH	2,6-lutidine	25.0	3.34	*e*	
4	CH_3OH	2,6-lutidine	70.1	10.6 ± 0.6	*e*	

[a] The alkyl benzenesulfonate was 0.04–0.09 M. [b] The acetate and trifluoroacetate salts were 0.1 M. 2,6-Lutidine was 0.05–0.17 M (always in excess relative to the substrate). [c] Calculated by averaging k^A_{eq} and k^S_{eq} data from Table II. [d] $k_{eq}/(k_{eq} + k_t)$. [e] No scrambling could be detected in recovered **4**.

or carboxylate ester. The quote is from Raber, Harris, and Schleyer;[4] 3 years later, however, Bentley and Schleyer[5] expressed uncertainty about this tool, doubting whether the ion pairs that undergo oxygen-18 scrambling are the same as those that undergo solvolysis. The only investigator who has employed this tool extensively is Goering,[15,16] but his attentions have been given mostly to systems in which the intermediate carbocations are rather more stabilized than plain *sec*-alkyl cations. Prior to the present work,[17] the sole application of the oxygen isotope scrambling criterion to plain *sec*-alkyl arenesulfonate solvolyses was by Diaz, Lazdins, and Winstein.[18] Their determinations concerned two esters, 2-octyl *p*-bromobenzenesulfonate and *trans*-4-*tert*-butylcyclohexyl *p*-toluenesulfonate; the minimum fraction of internal return determined was less than 10% except for the former substrate in CF_3COOH, where it was 19.9%.

Perhaps the operose oxygen-18 analysis procedure generally used was a deterrent to other investigators. In our preliminary communication[17] we outlined the sequence of six operations, some quite unusual, that were typically involved, and we repeated the same outline in the original manuscript of this paper. However, a referee thought it "a little too melodramatic" and recommended that we not repeat it, and so we do not.

We have developed an improved method for determination of oxygen-18 in alkyl benzenesulfonates, one which reports not only the alkoxyl but also the sulfonyl oxygen-18 content, which makes use of standard equipment throughout, and which has advantages of convenience. We have applied it to representative solvolyses of four labeled *sec*-alkyl benzenesulfonates in which the alkyl groups are the four that have figured most prominently in recent research in this area.

Method for Determination of Oxygen-18 in the Alkoxyl and Sulfonyl Moieties

The early stages of our determinations were similar to those of previous investigations of oxygen-18 scrambling. An ester having 18–28% oxygen-18 at sulfonyl sites was submitted to solvolysis interrupted at a chosen time, and unsolvolyzed ester was recovered and purified. It was then cleaved with just 2 equiv of sodium in liquid ammonia, an amount appropriate for balanced eq 1. (Earlier workers had used excess alkali metal.) Methylation

$$ROSO_2Ph + 2Na \xrightarrow[NH_3]{} RO^-Na^+ + PhSO_2^-Na^+ \quad (1)$$

with methyl iodide converted the benzenesulfinate ion to methyl phenyl sulfone, obtained in 60% or higher yield, but very little of the alkoxide ion to the corresponding methyl ether. After acidification, the alcohol, sulfone, any alkyl methyl ether that formed, and other minor products were taken into diethyl ether. The diethyl ether solution, after washing, drying, and concentrating, was analyzed by GC/MS.

The reward for employing only 2 equiv of alkali metal to cleave the recovered ester is that one is therefore enabled to recover the sulfonyl moiety, as methyl phenyl sulfone, and to analyze it. Excess alkali metal apparently effects additional cleavage so as to form the parent aromatic hydrocarbon. The formation of toluene when 6 equiv of sodium were used to cleave *p*-toluenesulfonate esters has been reported.[22,23] We observed the formation of small amounts of benzene in our experiments. Also, minor amounts of methyl phenyl sulfide, which assuredly arose from methylation of thiophenoxide ion, were occasionally detected. The latter is apparently a minor byproduct from alkali metal reduction of $PhSO_2^-$. Clearly, despite interesting discoveries that have been made,[23,24] there is more to be learned about the cleavage of sulfonate esters by solvated electrons.[25]

One important feature is, however, clear, namely, that the cleavage and methylation sequence that we employed proceeds without scrambling of oxygen atoms between alkoxyl and sulfonyl moieties. In all cases studied, we found the labeling pattern of the original alkyl benzenesulfonate ester to be maintained unaltered in the alcohol and sulfone resulting from cleavage and methylation.

Solvolysis Experiments and Results

Our studies concerned four alkyl benzenesulfonates, namely the isopropyl (**1**), cyclopentyl (**2**), 2-adamantyl (**3**), and 3,3-dimethyl-2-butyl (or pinacolyl) (**4**) esters. Each was prepared in natural abundance isotopic composition as well as with 18–28% oxygen-18 in the sulfonyl moiety.

Kinetic Studies. These were conducted with esters of natural abundance isotopic composition. Solvolyses in methanol, 80% ethanol, 2,2,2-trifluoroethanol, 90% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)/10% water, and acetic acid were followed by titration techniques, though not for every substrate in every solvent. Solvolyses in trifluoroacetic acid were monitored spectrophotometrically. Our kinetic determinations are presented in Table I.

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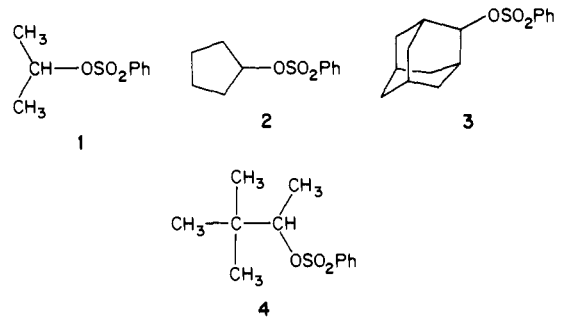


Oxygen-18 Scrambling Experiments: Treatment and Interpretation of Data. The solvolysis kinetic data guided planning of the oxygen scrambling experiments. Each of heavy-oxygen-labeled substrates **1–4**, having 18–28% oxygen-18 in the sulfonyl moiety, was submitted to solvolysis in a chosen solvent for about 2 half-lives. However, experiments with **3** had also to be conducted for shorter times because scrambling is relatively fast with this ester and is nearly complete at 2 solvolysis half-lives. Two to three experiments, normally terminated at different times, were performed with each substrate in any solvent in order to obtain the rate constant for oxygen equilibration.

In the mass spectrometric analysis of the alcohol product of the cleavage of esters, primary attention was given to the parent peak (intensity m) and the peak 2 mass units higher (intensity $m + 2$); the ratio of intensities, $(m + 2)/m$, is symbolized P. For the sulfone product of cleavage and methylation, most analyses were based on the relative intensities $(m + 2)/m$ of the mass 143 and 141 peaks due to phenylsulfonyl cation. This ratio is symbolized R. The relative intensities of the somewhat less prominent mass 158 and 156 peaks due to the molecular ion, when measured, gave results consistent with those based on the mass 143 and 141 peaks.

One can readily derive that, for the alcohol, the fraction of oxygen-18 among the oxygen atoms, symbolized f, is given by eq 2, where P_c is the $(m + 2)/m$ ratio for the alcohol corrected for

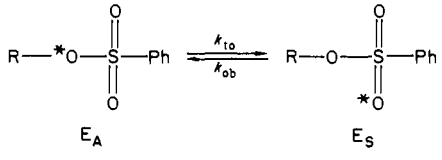
$$f = P_c/(P_c + 1) \tag{2}$$

the contribution of minor isotopes[27] ^2H, ^{13}C, and ^{34}S. Likewise, for the sulfone, the fraction, symbolized g, of oxygen-18 among the oxygen atoms is given by eq 3, where the subscript c again denotes correction for minor isotopes.

$$g = R_c/(R_c + 2) \tag{3}$$

For the reckoning of equilibration rate constants, we let f^0 and g^0 represent fractions of oxygen-18 in the alcohol and the sulfone obtained by sodium cleavage of the unsolvolyzed ester to be used in a scrambling experiment, f^t and g^t the corresponding fractions from ester recovered after time t of solvolysis, and g^∞ (which equals f^∞) the fraction of oxygen-18 in either moiety of the ester after complete equilibration. When the ester originally has excess oxygen-18 in the sulfonyl moiety, as was the case in our experiments, $g^\infty = 2g^0/3$.

In the process of equilibration, the participating molecules have either two ^{18}O and one ^{16}O atoms or two ^{16}O and one ^{18}O atoms. Let us call the isotope singly represented the "unique" isotope, and let E_A and E_S represent molecules with the unique isotope in alkoxyl and sulfonyl sites, respectively. The equilibration reaction and the rate constant symbols assigned to the forward and reverse steps are shown in eq 4. The asterisk labels the "unique" oxygen isotope.



(4)

(27) The contribution of ^{17}O to mass spectral intensities is neglected because it is so small.

For a system of forward and reverse first-order reactions proceeding to a state of equilibrium, the applicable general expression is that of eq 5, where λ^0, λ^t, and λ^e are respectively the

$$\ln \frac{(\lambda^0 - \lambda^e)}{(\lambda^t - \lambda^e)} = k_{eq}t = (k_f + k_r)t \tag{5}$$

magnitudes of some property proportional to extent of reaction at the start, at time t, and at equilibrium, and k_f and k_r are rate constants for the forward and reverse reactions. In terms of our experiments, this generalized equation takes the form of eq 6 or 7.

$$\ln \frac{(f^0 - g^\infty)}{(f^t - g^\infty)} = k^A{}_{eq}t \tag{6}$$

$$\ln \frac{(g^0 - g^\infty)}{(g^t - g^\infty)} = k^S{}_{eq}t \tag{7}$$

For the sulfonate ester equilibration system, eq 8 expresses the equality of forward and reverse rates at equilibrium.[28] Inasmuch

$$k_{to}[E_A] = k_{ab}[E_S] \tag{8}$$

as at equilibrium $[E_S] = 2[E_A]$, it follows that $k_{to} = 2k_{ab}$. Also, with attention to eq 5, $k_{to} = 2k_{eq}/3$ and $k_{ab} = k_{eq}/3$.

In kinetic terms, the reason that k_{ab} is half of k_{to} is that every event of conversion of E_S into E_A, by shift of the alkyl group from nonunique to unique oxygen, is accompanied by an equally rapid shift of the alkyl group from one nonunique oxygen to another. The latter constitutes a degenerate rearrangement of E_S into E_S that is undetectable by our experimental techniques. Thus for E_S only half the alkyl group shifts contribute to equilibration, but for E_A they all contribute.

The above considerations are independent of the mechanism of alkyl group shift from one sort of oxygen to another. When shift occurs by an ionization–recombination mechanism, one must take into account that the oxygen atom from which the alkyl group separated is at least as likely to recoordinate with the carbenium center of the carbocation as is either of the other two. Indeed, there is a higher probability of recoordination with the original alkoxyl oxygen because it is undoubtedly closer to the carbenium center in the ion pair. The rate constant for ionization–recombination starting from E_A is therefore at least $(3/2)k_{to}$ or starting from E_S at least $(3/2)2k_{ab}$, and since $k_{eq} = (3/2)k_{to}$ or $3k_{ab}$, the minimum ionization–recombination rate constant is at least k_{eq}.[29]

Oxygen-18 Scrambling Experiments: Results. Our scrambling experiments are presented in Table II. In this table, it is immediately evident upon comparing R^0 and R^t values that scrambling did occur during most solvolyses. R^0 and R^t are $(m + 2)/m$ ratios from the sulfone at the start and after the extent of solvolysis indicated. When R^t is less than R^0, loss of ^{18}O from the sulfonyl moiety is shown. Gain of ^{18}O in the alkoxyl moiety is evident in the P^t values being larger than P^0 (which is identical with P^u). Cursory inspection suffices to show that scrambling was extensive with **3**, significant with **1** and **2**, and undetectable with **4**.

(28) A consequence of our definition of E_A and E_S with reference to the "unique" oxygen atom is that when the ester is doubly labeled with ^{18}O, k_{to} refers to alkyl group migration from ^{16}O to ^{18}O, whereas when the ester is singly labeled, k_{to} refers to migration from ^{18}O to ^{16}O. The ester may contain also some molecules with only natural abundance ^{18}O. The scrambling reaction thus comprises three components in which the ester molecules contain two, one, or zero (except for natural abundance) oxygen-18 atoms. One can readily show that, providing singly and doubly labeled esters react at the same rate, as they do when kinetic isotope effects are inconsequential, the sum of f or g from the two sorts of esters will show first-order kinetic behavior according to eq 6 or 7 just as well as the dissected f or g for each sort of ester would do separately.

(29) In our preliminary communication,[17] $2k_{eq}$ was taken to be a conservative minimum estimate of the ionization–recombination rate constant. That was incorrect; it amounted to summing the rate constants starting with E_A and E_S, whereas either represents the rate constant of interest. Diaz, Lazdins, and Winstein[18] used k_{eq} to represent the minimum ionization–recombination rate constant. We presume that their choice was based on the type of intellectual analysis that we present here.

Table II. Determinations of Oxygen Isotope Scrambling during Solvolysis[a]

substrate	substrate concn, M	solvent	added substance (concn, M)	temp, °C	reaction time, s	extent of solvolysis, %	R^t	R^u	P^t	P^u	R^0	k^S_{eq}, s^{-1}	k^A_{eq}, s^{-1}
1	0.064	CF_3COOH	CF_3COONa (0.106)	25.0	22455	55.5	0.715 ± 0.008[b]	0.054 ± 0.001[b]	*c*	*c*	0.765 ± 0.005[b]	7.74×10^{-6}[d]	*c*
1	0.064	CF_3COOH	CF_3COONa (0.106)	25.0	43500	79.2	0.672 ± 0.005[b]	0.055 ± 0.001[b]	*c*	*c*	0.762 ± 0.009[b]	7.99×10^{-6}[d]	*c*
2	0.088	CF_3COOH	CF_3COONa (0.100)	25.0	436	81.2	0.473 ± 0.004	0.051 ± 0.001	0.045 ± 0.003	0.0034 ± 0.0012	0.536 ± 0.004	8.90×10^{-4}	8.41×10^{-4}
2	0.048	CF_3COOH	CF_3COONa (0.05)	25.0	405	78.8	0.710 ± 0.008	0.048 ± 0.003	0.041 ± 0.002	0.0048 ± 0.0038	0.790 ± 0.007	6.88×10^{-4}	5.34×10^{-4}
2	0.050	CF_3COOH	CF_3COONa (0.051)	25.0	404	78.7	0.752 ± 0.004	0.052 ± 0.001	0.068 ± 0.002	0.0057 ± 0.0011	0.844 ± 0.007	7.35×10^{-4}	9.25×10^{-4}
2	0.044	90% HFIP/ 10% H_2O	lutidine[e] (0.084)	25.0	10020	77.1	0.529 ± 0.005	0.052 ± 0.004	0.014 ± 0.001	0.0028 ± 0.0015	0.543 ± 0.005	7.05×10^{-6}	8.84×10^{-6}
							0.583 ± 0.010[f]	0.062 ± 0.006[f]	0.012 ± 0.001[f]	0.0032 ± 0.0007[f]	0.594 ± 0.005[f]	4.85×10^{-6}[f]	6.54×10^{-6}[f]
2	0.0885	90% HFIP/ 10% H_2O	lutidine[e] (0.17)	25.0	9660	75.8	0.529 ± 0.006	0.061 ± 0.002	0.014 ± 0.002	0.0031 ± 0.0004	0.601 ± 0.003	4.08×10^{-6}	7.99×10^{-6}
							0.584 ± 0.006[f]	0.062 ± 0.006[f]	0.013 ± 0.001[f]	0.0032 ± 0.0007[f]	0.594 ± 0.005[f]	4.88×10^{-6}[f]	7.78×10^{-6}[f]
3	0.055	CF_3COOH	CF_3COONa (0.106)	25.0	69	9.6	0.756 ± 0.005[f]	0.060 ± 0.006	0.029 ± 0.001	0.0072 ± 0.0007	0.790 ± 0.009	1.54×10^{-3}	1.85×10^{-3}
3	0.049	CF_3COOH	CF_3COONa (0.106)	25.0	150	19.8	0.713 ± 0.001	0.060 ± 0.006	0.053 ± 0.002	0.0072 ± 0.0007	0.790 ± 0.009	1.79×10^{-3}	1.90×10^{-3}
3	0.048	CF_3COOH	CF_3COONa (0.106)	25.0	1065	79.1	0.536 ± 0.004	0.066 ± 0.006	*g*	*g*	0.790 ± 0.010	1.76×10^{-3}	*g*
3	0.055	AcOH	AcONa (0.1)	80.0	4860	10.0	0.687 ± 0.008	0.065 ± 0.006	0.0529 ± 0.0004	0.0087 ± 0.0020	0.756 ± 0.009	5.32×10^{-5}	5.86×10^{-5}
3	0.055	AcOH	AcONa (0.1)	80.0	10304	20.0	0.615 ± 0.004	0.066 ± 0.004	0.104 ± 0.003	0.0125 ± 0.0054	0.748 ± 0.006	5.88×10^{-5}	6.64×10^{-5}
3	0.055	80% EtOH/ 20% H_2O		80.0	1650	10.3	0.723 ± 0.002	0.065 ± 0.006	0.030 ± 0.002	0.0087 ± 0.0020	0.756 ± 0.009	6.87×10^{-5}	7.92×10^{-5}
3	0.055	80% EtOH/ 20% H_2O		80.0	3540	20.8	0.686 ± 0.004	0.065 ± 0.006	0.051 ± 0.002	0.0087 ± 0.0020	0.756 ± 0.009	7.39×10^{-5}	7.69×10^{-5}
3	0.036	80% EtOH/ 20% H_2O		80.0	21550	75.9	0.524 ± 0.004	0.070 ± 0.002	0.174 ± 0.002	0.021 ± 0.005	0.748 ± 0.006	7.55×10^{-5}	7.20×10^{-5}
4	0.020	CH_3OH	lutidine[e] (0.05)	70.1	8160	61.2	0.520 ± 0.005	0.051 ± 0.001	*g*	*g*	0.518 ± 0.005		
4	0.054	CF_3CH_2OH	lutidine[e] (0.09)	25.0	41340	76.6	0.557 ± 0.007		0.003 ± 0.001	0.004 ± 0.001	0.544 ± 0.011		
4		90% HFIP/ 10% H_2O	lutidine[e] (0.084)	25.0	6491	77.4	0.580 ± 0.012		0.0034 ± 0.0004	0.0031 ± 0.0003	0.572 ± 0.007		
4	0.083	CF_3COOH	CF_3COONa (*h*)	25.0	189	75[i]	*j*		*j*		*j*		

[a] R^t is observed $(m + 2)/m$ ratio for $PhSO_2CH_3$ from recovered substrate after solvolysis for stated time. P^t is observed $(m + 2)/m$ ratio for alcohol from same recovered substrate. R^u is observed $(m + 2)/m$ ratio for $PhSO_2CH_3$ from unlabeled substrate. R^0 is observed $(m + 2)/m$ ratio for $PhSO_2CH_3$ from labeled substrate before solvolysis. P^u is observed $(m + 2)/m$ ratio for alcohol from unlabeled substrate and from labeled substrate before solvolysis, averaged since they were identical within experimental error. k^S_{eq} and k^A_{eq} were reckoned as described in Experimental Section. [b] Representative from a set of replicate determinations reported fully in ref 2. [c] Isopropyl alcohol was insufficiently separate from Et_2O and CH_3CN under the GLC conditions used to enable satisfactory determination of P^t and P^u. [d] Average from replicate determinations detailed in ref 2. [e] 2,6-Lutidine. [f] Contrasting results obtained from two sets of determinations are reported. [g] Not determined. [h] Concentrations not recorded. [i] Approximate. [j] Precise determinations not possible because of erratic GC/MS performance; the data obtained did not suggest any decrease from R^0 to R^t.

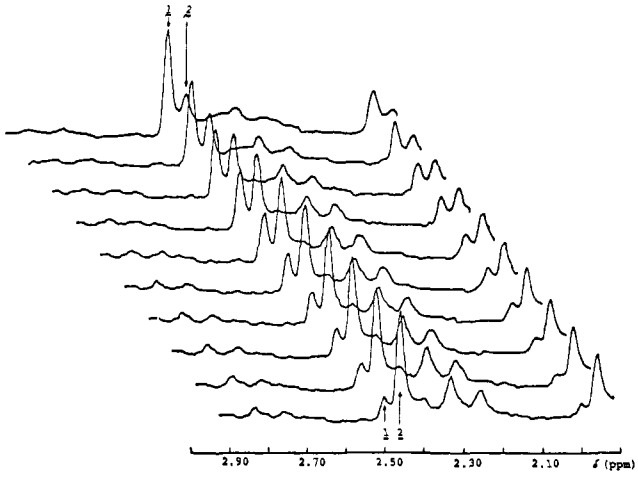


Figure 1. Solvolysis of cyclopentyl *p*-toluenesulfonate (CpOTs), 4.83 × 10^{-2} M, in CF_3COOH containing 5.11 × 10^{-2} M CF_3COONa at 22.7 °C. Expanded NMR spectral region (99.6 MHz) centered around the absorption of the methyl groups of the *p*-toluenesulfonate ion (peak 2, δ 2.47) and of CpOTs (peak 1, δ 2.50). The top spectrum was recorded 121 s after mixing, those lower (offset for clarity) at progressively longer times, until the bottom spectrum was recorded 772 s after mixing. In the "infinity" spectrum (not shown), peak 1 had disappeared. From the times and peak areas, k_ψ for solvolysis is estimated to be 2.55 × 10^{-3} s^{-1}.

Application of our analytical method to sulfonyl-labeled sulfonate esters prior to solvolysis gave results as expected; ^{18}O in excess of natural abundance was found in the sulfonyl moiety but not in the alkoxyl moiety.

We tested for the possibility that scrambling occurred by external return or by direct attack of external ions on the substrate by performing solvolyses of **2** and **3**, of natural abundance isotopic composition, under the conditions of scrambling experiments except that a substantial amount of sodium *p*-toluenesulfonate was also present. Coordination of the carbocations with arenesulfonate ions in the open solution would have formed in each case some of the corresponding alkyl *p*-toluenesulfonate. Evidence for the latter was sought by NMR spectroscopy. There is a small but distinct difference between the chemical shifts of the *p*-CH_3 groups in the *p*-toluenesulfonate ion and in an alkyl *p*-toluenesulfonate. In CF_3COOH, the peaks occur at δ 2.47 and 2.50, respectively, vs. $(CH_3)_4Si$.

Efforts to detect chemical exchange when **2** or **3** was solvolyzed in the presence of sodium *p*-toluenesulfonate were conducted in two ways. In type I experiments, solvolyses of **2** in CF_3COOH buffered with excess CF_3COONa, of **3** in CH_3COOH buffered with excess CH_3COONa, and of **3** in 80% EtOH/20% H_2O were interrupted, and unsolvolyzed ester was recovered by standard extraction techniques, dried, and examined by NMR spectroscopy. No alkyl *p*-toluenesulfonate was found, although control experiments showed that as little as 1% was easily detectable. In type II experiments, solvolyses of **2** and **3** were conducted in CF_3COOH buffered with excess CF_3COONa and containing excess sodium *p*-toluenesulfonate, and the solvolyzing mixture was examined at times by NMR spectroscopy. Again no alkyl *p*-toluenesulfonate could be detected. The possibility that scrambling occurred via external return is thus excluded.[30]

It is, however, noteworthy that solvolysis of **2** in CF_3COOH containing sodium *p*-toluenesulfonate but CF_3COONa in deficiency did furnish some cyclopentyl *p*-toluenesulfonate. This phenomenon and its interpretation are presented in detail below.

It is parenthetically of interest that one can monitor the solvolysis of an alkyl *p*-toluenesulfonate in CF_3COOH by observing the NMR spectrum as a function of time. Figure 1 presents a representative set of spectra concerning the solvolysis of cyclopentyl *p*-toluenesulfonate.

In Table I we list averaged equilibration rate constants for each substrate and solvent. Each k_{eq} in Table I is the average of all k^S_{eq} and k^A_{eq} values for all relevant experiments in Table II.

Solvolyses of Cyclopentyl Arenesulfonates in CF_3COOH with and without CF_3COONa. These experiments are incidental to the main theme of this research, but nevertheless illuminate a significant feature of solvolysis reactions.

Kinetic runs for solvolysis of **2** afford linear first-order plots when CF_3COONa is in excess of the substrate or when it is absent, but the first-order rate constant is much higher in the former case. When the concentration of CF_3COONa is less than that of the substrate, the plots comprise two approximately linear segments, of which the earlier is steeper, corresponding to a higher rate constant. Insofar as investigated, solvolyses of cyclopentyl *p*-toluenesulfonate behave similarly. Our kinetic experiments are summarized in Table III.

Solvolysis of **2** (0.053 M) in CF_3COOH containing sodium *p*-toluenesulfonate (0.048 M) and CF_3COONa (0.017 M) was observed (by NMR monitoring of the reacting solution) to form a small amount of cyclopentyl *p*-toluenesulfonate. A small peak at δ 2.50 due to the latter gradually but definitively developed. This is in contrast to a similarly monitored trifluoroacetolysis experiment (with 0.047 M **2** and 0.054 M sodium *p*-toluenesulfonate) in which CF_3COONa was in excess (0.052 M); in this case there was not even a suggestion of development of a peak at δ 2.50. Incorporation of external arenesulfonate ion thus occurs when the lyate ion is in deficiency but not when it is in excess.

Table III. Kinetics of Solvolysis of Cyclopentyl Arenesulfonates in CF_3COOH at Various Concentrations of CF_3COONa

substrate	[substrate] × 10^2, M	temp, °C	$[CF_3CO_2^-]$ × 10^2, M	k_{obsd} × 10^3,[a] s^{-1}
2	5.04	22.7	0	1.66
2	4.76	22.7	5.29	3.32
2	4.85	22.7	1.62	2.85,[b] 0.97
2	4.94	22.7	1.62	2.84,[b] 0.95
CpOTs[c]	4.99	22.8	1.59	2.06,[b] 0.66
CpOTs[c]	4.94	22.8	5.74	2.52

[a] Slopes of plots of $-\ln |(OD_\infty - OD_t)|$ vs. time. [b] The higher slope early in the run, the lower slope later. [c] CpOTs is cyclopentyl *p*-toluenesulfonate.

Discussion

Our results as summarized in Table I show that the incidence of internal return during solvolysis of four representative *sec*-alkyl benzenesulfonates is strongly dependent on the identity of the alkyl group. Internal return is extensive during solvolysis of **3** in three solvents, moderate during solvolysis of **1** and **2** in CF_3COOH, significantly less during solvolysis of **2** in 90% hexafluoro-2-propanol/10% water, and undetectable during solvolysis of **4** in four solvents.

These results have novelty and significance, as we discuss below. However, the experimental methodology that we have developed is perhaps equally important. By means of it, one can straightforwardly perform oxygen scrambling experiments of the sort that we have carried out in any laboratory with GC/MS equipment. Such equipment is fortunately now widely available. We believe that the more extensive performance of such oxygen scrambling experiments will provide important insight into solvolysis phenomena.

Subsequent to completion of our experiments, Chang and le Noble[32] described the determination of oxygen-17 scrambling during solvolysis of *exo*-2-norbornyl *p*-bromobenzenesulfonate by NMR measurements. Whether theirs or ours is the better method

(30) Streitwieser and Walsh[31] observed substantial conversion of optically active 2-octyl *p*-nitrobenzenesulfonate to inverted 2-octyl *p*-toluenesulfonate to occur during solvolysis in acetic acid saturated with lithium *p*-toluenesulfonate. Their observations are not in conflict with ours because theirs involved different alkyl and nucleofugal groups and a much higher concentration (ca. 0.1 M) of *p*-toluenesulfonate salt. Diaz et al.[18] observed minor amounts of exchange with ^{14}C-labeled *p*-toluenesulfonate ion during acetolysis of two alkyl arenesulfonates but indications of as much as 20% exchange in the presence of added sodium acetate.

(31) Streitwieser, A., Jr.; Walsh, T. D. *J. Am. Chem. Soc.* **1965**, *87*, 3686.

(32) Chang, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 3708.

to employ may depend on the availability of equipment in a particular laboratory.

2-Adamantyl Benzenesulfonate (3). Experimentally, we find (Table I) that the minimum fraction of internal return during solvolysis of **3** ranges from 53% to 73%, depending on the solvent.

Solvolyses of **3** and related esters have received much attention. It is generally agreed that the nucleophile that ultimately replaces the nucleofuge does not participate significantly in the rate-limiting step of solvolysis,[5,33-35] but there has been disagreement as to which step is rate-limiting. Some investigators[12,13] have concluded that heterolysis is rate-determining and that internal return is not significant in acetic acid, formic acid, and ethanol/water solvents. Others hold that the transformation of intimate to solvent-separated ion pair is largely rate-limiting.[11,35]

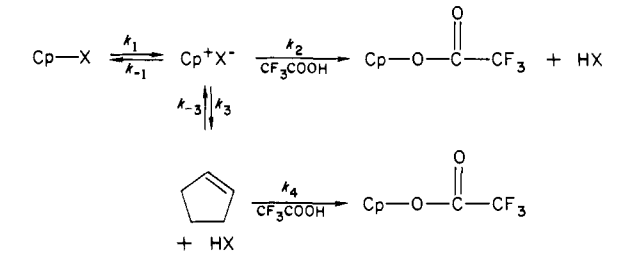
Our demonstration that in three solvents more than half of the ion pairs immediately formed during solvolysis of **3** return to covalent substrate substantially settles this question. However, because our data indicate only the minimum incidence of internal return, it is unclear whether the fraction of internal return is only 53–73%, or whether it may be 90%, or 99%, or even higher. There is also the semantic question as to how large the fraction of internal return must be to be "significant";[12] thus, if internal return were no more than the minimum 53% that we find for solvolysis of **3** in 80% EtOH/20% water, it would cause the overall solvolysis rate to be reduced below the rate of heterolysis by only a little more than twofold. One might argue that the resulting adjustment of a point on a logarithmic plot by slightly more than 0.3 was scarcely significant. However, it seems to us that a partitioning ratio whereby the rate of return exceeds that of formation of solvolysis products can hardly be regarded as insignificant.

Our finding that the minimum fraction of internal return is much the same, varying only from 53% to 73%, in three solvents of differing nucleophilicity constitutes further support for the conclusion that solvent molecules do not participate as nucleophiles in the rate-limiting steps. As to why this fraction varies from one solvent to another, we hesitate to offer an interpretation. Many solvent properties, including dielectric constant, viscosity, and strength of hydrogen bonding to benzenesulfonate ions, may affect partitioning of an intimate ion pair between internal return and separation. Also, the change in temperature between our experiments in CF_3COOH (25 °C) and those in CH_3COOH and 80% EtOH/20% water (80 °C) may have affected differentially relevant solvent properties and the ways in which they affect partitioning.

We call attention to the compatibility of our finding of extensive internal return in the case of **3** with observations of Maskill, Thompson, and Wilson.[35] These workers found that solvolyses of 2-adamantyl azoxy-*p*-toluenesulfonate in chloroform, ethanol, and 90% aqueous ethanol afforded appreciable amounts of 2-adamantyl *p*-toluenesulfonate. They argued convincingly that solvolysis occurs by an ionization–fragmentation mechanism that liberates the 2-adamantyl cation and the *p*-toluenesulfonate anion, probably at some distance from each other, separated by a molecule of nitrous oxide. That ion pair should be less intimate than the one formed by solvolysis, but nevertheless the anion competes significantly with solvent nucleophiles such as ethanol and water for coordination with the cation.

Isopropyl (1) and Cyclopentyl (2) Benzenesulfonates. We find (Table I) the minimum fraction of internal return during trifluoroacetolysis of these esters to be 0.18. However, the minimum fraction is only 0.05 for solvolysis of **2** in 90% HFIP/10% water. The former value closely resembled the minimum fraction of 0.20 observed by Diaz, Lazdins, and Winstein[18] for solvolysis of 2-octyl *p*-bromobenzenesulfonate in CF_3COOH.[36] Diaz et al. did not report any experiments in 90% HFIP/10% water, but they did report for solvolysis of two *sec*-alkyl arenesulfonates in acetic or formic acid, in the presence of various salts, minimum fractions of internal return varying from 0.03 to 0.09. Our value in 90% HFIP/10% water falls within that range and suggests that in its effect on the extent of internal return this solvent resembles acetic and formic acids.

Scheme I



Shiner, Nollen, and Humski[11] have fitted a large body of information about kinetic isotope effects and product yields for solvolysis of cyclopentyl *p*-bromobenzenesulfonate in several solvents to a mechanism involving two ion pair intermediates and have derived therefrom estimates of the magnitudes of numerous mechanistic parameters. Of immediate interest are their estimates of the return ratio, that is, the ratio of the rate of internal return from the intimate ion pair to the sum of the rates of product-forming steps, for solvolysis in 90% HFIP/10% water. Among five fitting procedures that they favor, this return ratio varied from a low of 37.5 to a high of 250. In contrast, our data indicate for the cyclopentylium benzenesulfonate intimate ion pair a minimum return ratio in the same solvent of 0.052; this is k_{eq}/k_t. Though we grant that the benzenesulfonate and *p*-bromobenzenesulfonate ions may behave a little differently in comparable situations and that a minimum estimate of the return ratio is likely to be less than the actual ratio that obtains, we are nevertheless struck by the large differences between their estimates and our data. Their lowest favored estimate of the return ratio implies, with attention to our data, that internal return without change of oxygen site (that is, without scrambling) occurs 720 times more often than return with change of oxygen site.[37-39] (The foregoing implication is based on the approximation that the two arenesulfonate ions behave the same.) Let us say that their scheme is qualitatively consistent with our data but that our determinations offer little support for their quantitative estimates.

The facts that the minimum fraction of internal return is lower for solvolyses of **1** and **2** than for **3** and that for **2** it is sensitive to the solvent but for **3** rather insensitive are no doubt associated with the greater accessibility of the first atoms of the isopropyl and cyclopentyl groups to nucleophilic attack than C-2 of the adamantane system. In solvents of higher nucleophilicity, **1** and **2** can perhaps react in part by direct S_N2 attack on the ester molecules and in part by nucleophilic attack on the carbocations of the intimate ion pairs.[40] Both these modes of reaction, which are evidently unavailable to **3**, would reduce the rate of scrambling (k_{eq}) relative to that of overall solvolysis (k_t). Also, the intimate ion pairs from **1** and **2** can be converted to alkenes by loss of hydrons[41] either to benzenesulfonate gegenions or to solvent molecules, but such pathways are unavailable to **3** because of the high energy of adamantene.

Pinacolyl Benzenesulfonate (4). Our data give zero indication of internal return from an intimate ion pair, in four solvents ranging from methanol to CF_3COOH in characteristics. From

(33) Raber, D. J.; Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 4821.
(34) Shiner, V. J.; Fisher, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2553.
(35) Maskill, H.; Thompson, J. T.; Wilson, A. A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1693.
(36) However, for solvolysis of *trans*-4-*tert*-butylcyclohexyl *p*-toluenesulfonate in CF_3COOH, Diaz et al.[18] observed a minimum fraction of internal return of 0.08.
(37) In another case, somewhat analogous to ours, the oxygen isotope equilibration rate is about 20% of the total rate of return.[38]
(38) Goering, H. L.; Humski, K. *J. Am. Chem. Soc.* **1975**, *40*, 920.
(39) Aspects of the data analysis of Shiner et al.[11] have been criticized by: McLennan, D. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1316.
(40) Diaz et al.[18] observed the extent of scrambling of sulfonyl-^{18}O-labeled 2-octyl *p*-bromobenzenesulfonate during solvolysis to decrease as the solvent became more nucleophilic and similarly interpreted the effect.
(41) "Hydron" is a term for a monohydrogen cation of whatever mass, whether proton, deuteron, or triton.

the data alone, it does not necessarily follow that there is no internal return, for they do not exclude the possibility of internal return without change of oxygen site. Nevertheless the conclusion that internal return to regenerate substrate does not occur is strongly suggested. That conclusion would agree with those of other investigators,[14,42-44] reached on various grounds. Our data do not, however, distinguish whether internal return fails to occur because methyl migration is concerted with heterolysis of the C–O bond[7,45] or because unassisted ionization is followed by methyl migration so quickly that internal return has no chance to occur.[47]

It is noteworthy that there are strong similarities between the solvolytic behavior of pinacolyl and neopentyl arenesulfonates. Neopentyl *p*-toluenesulfonate with excess oxygen-18 in the sulfonyl moiety undergoes no detectable scrambling of oxygen sites in the unsolvolyzed ester during acetolysis.[48] There is a substantial γ-carbon kinetic isotope effect[46] but scarcely any γ-hydrogen (γ-D_9 vs. γ-H_9) kinetic isotope effect,[46,49] and the latter manifestation is understood to represent cancellation of normal and inverse secondary isotope effects.[4,44,46]

Kinetics of Trifluoroacetolysis of Cyclopentyl Arenesulfonates As Affected by Sodium Trifluoroacetate. We address the data of Table III. From the first two experiments, it is evident that solvolysis is faster when CF_3COONa is present in excess of **2**. We interpret this effect with references to Scheme I, in which Cp stands for a cyclopentyl and X for an arenesulfonate group.[50] Scheme I provides for the intimate ion pair to react in three ways: internal return to substrate, reaction with the solvent nucleophile (perhaps via the solvent-separated ion pair) to form cyclopentyl trifluoroacetate, and loss of hydron to form cyclopentene. The cyclopentene may readd arenesulfonic acid, if present, to regenerate the ion pair. One must also consider the possibility of addition of the solvent to cyclopentene, with rate constant k_4, to form cyclopentyl trifluoroacetate.

When excess CF_3COONa, which is the strongest base that may exist in this solvent system, is present, the HX formed as a by-product in steps 2 and 3 is quickly neutralized and thereby rendered impotent to readd to cyclopenene in step 3, reverse. However, when CF_3COONa is not present, readdition of arenesulfonic acid may occur, regenerating the intimate ion pair and thence, by collapse, the substrate. The latter events reduce the rate of consumption of substrate.

This interpretation hinges on the addition of arenesulfonic acid to the olefin to form CpX being faster than the addition of the solvent to form $CpOOCCF_3$. Other workers who investigated the behavior of alkenes in CF_3COOH solution have reported observations to that effect.[51-53] In our own experience, although solutions of cyclopentene in CF_3COOH undergo only slow chemical change,[52] 1 min after mixing approximately equimolar amounts of cyclopentene and *p*-toluenesulfonic acid in CF_3COOH solution, the ^1H NMR spectrum showed the presence of the cyclopentyl esters of *p*-toluenesulfonic and trifluoroacetic acids, with the former in excess of the latter, as well as of cyclopentene.

In terms of these concepts, one can understand why first-order kinetic plots for solvolysis of **2** in the presence of a lesser concentration of CF_3COONa show changes of slope; see Table III. As long as CF_3COONa is present to neutralize the arenesulfonic acid formed, readdition of the latter to cyclopentene is thwarted, but once the base is all used up the readdition can occur with resultant depression of overall solvolysis rate.

Some Major Questions of Interpretation. We have taken the observed scrambling to indicate internal return from the intimate ion pair. We now examine some other conceivable interpretations, some of which have been suggested elsewhere in the literature.

(1) The Possibility of Scrambling without Ionization. There are several arguments against the possibility that the changes of oxygen site shown in eq 4 could occur without the intermediacy of ions. The first takes account of the solvent effect on equilibration rate, k_{eq}; see Table I. k_{eq} for **3** in CF_3COOH at 25 °C is much higher than in CH_3COOH or 80% EtOH/20% water at 80 °C. When the CF_3COOH value is adjusted to 80 °C by applying the rule of thumb that rate doubles for a 10 °C rise in temperature, the rate in CF_3COOH is more than 1000 times greater than in the other two solvents. Thus, there is a strong solvent effect on scrambling rate. However, little solvent effect on rate would be expected if scrambling occurred by a nonionizing mechanism.

One might imagine scrambling without ionization to occur by an intramolecular S_N2 mechanism, in which a sulfonyl oxygen attacked alkyl carbon as the alkoxyl oxygen was displaced. This possibility is disqualified by the fact that S_N2 reactions have a strong requirement for the nucleophile to attack exactly at the back side of carbon with respect to the bond to the nucleofugal group.[54,55] That geometry would be impossible to attain in a four-membered-ring transition state.

Any intramolecular, nonionizing scrambling mechanism would be somewhat hindered by steric bulk about the alkyl carbon. Accordingly, scrambling within our set of four substrates by such a mechanism should be greater for **1** and **2** than for **3** and **4**, with the latter two somewhat comparable. Since the observed rates of equilibration (Table I) bear no relationship to those expectations, nonionizing mechanisms of scrambling are excluded.

(2) The Question of Whether Intimate Ion Pairs Qualify as Intermediates. This question has been raised by Knier and Jencks[56] and by Jencks.[57] The question has two facets, one concerning the definition of an intermediate, the other concerning how fast an intimate ion pair collapses back to covalent substrate.

As a definition, Jencks suggests that an ion pair does not qualify to be considered a reaction intermediate if its lifetime is less than the period of a molecular vibration, which is about 10^{-13} s. This definition serves to recognize a boundary line concerning the lifetimes of species that is important with respect to what one can detect by kinetic and product analysis experiments concerning reactions in solutions. It is, however, an arbitrary definition, and if accepted would create difficulties in the expression of chemical thought. Knier and Jencks themselves encountered one such difficulty in their discussion of transient conditions of shorter lifetimes; they dodged the issue by using quotation marks to designate an "intermediate" whose existence is shorter than 10^{-13} s. Another kind of difficulty would arise in connection with the kind of chemical reaction involved in electron transmission spectroscopy.[58] The product of capture of an electron by a molecule is a radical anion, the lifetime of which is shown by experimental evidence to be sometimes as short as 10^{-15} s. It would seem awkward to allow products to have shorter lifetimes than intermediates.

These semantic questions apart, we address the chemically significant second facet of the question raised by Knier and Jencks.[56,57] Let us represent scrambling via ion pairs as in eq 9,

$$E_A \rightleftarrows I_A \rightleftarrows T \rightleftarrows I_S \rightleftarrows E_S \qquad (9)$$

(42) Shiner, V. J., Jr.; Fisher, R. D.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 7748.
(43) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
(44) Shiner, V. J., Jr.; Tai, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 436.
(45) Ando, T.; Morisaki, H. *Tetrahedron Lett.* **1979**, 121. See also ref 48.
(46) Ando, T.; Yamataka, H.; Morisaki, H.; Yamawaki, J.; Kuramochi, J.; Yukawa, Y. *J. Am. Chem. Soc.* **1981**, *103*, 430.
(47) Shiner, V. J., Jr.; Imhoff, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 2121.
(48) Nordlander, J. E.; Kelly, W. J. *J. Org. Chem.* **1967**, *32*, 4122.
(49) Schubert, W. M.; Henson, W. L. *J. Am. Chem. Soc.* **1971**, *93*, 6299.
(50) Scheme I is the simplest scheme that accommodates our observations. We realize that elaboration of it might be required in order to accommodate certain data from other sources.
(51) Peterson, P. E.; Allen, G. *J. Org. Chem.* **1962**, *27*, 1505.
(52) Shiner, V. J., Jr.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 6528.
(53) Dannenberg, J. J.; Goldberg, B. J.; Barton, J. K.; Dill, K.; Weinwurzel, D. H.; Longas, M. O. *J. Am. Chem. Soc.* **1981**, *103*, 7764.
(54) Tenud, L.; Farooq, S.; Seibl, J.; Eschenmoser, A. *Helv. Chim. Acta* **1970**, *53*, 2059.
(55) King, J. F.; McGarrity, M. J. *J. Chem. Soc., Chem. Commun.* **1979**, 1140.
(56) Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789.
(57) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161; *Chem. Soc. Rev.* **1981**, *10*, 345.
(58) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341.

where E_A and E_S are as shown in eq 4, I_A and I_S are ion pairs with geometries resembling E_A and E_S, respectively, but with longer carbon–oxygen distances, and T is a condition of maximum energy between I_A and I_S. They question whether there is a significant energy barrier between I_A and E_A or between I_S and E_S, that is, one large enough to cause the collapse rate constant to be less than about 10^{13} s^{-1}. They argue that if there is no significant barrier the transformation of E_A to E_S, or vice versa, via ion pairs I_A and I_S cannot be said to occur via ion pair intermediates and must be classified as a single-step process for which T is the transition state.

Several factors contribute toward slowness of collapse of intimate ion pair to substrate. These may be classified as "adjustments", geometrical and of solvation, and "bonding" factors. The bonding factors are of familiar sort. There is an enthalpy requirement to compensate for mesomeric or hyperconjugative stabilization of the cation. Another enthalpy requirement is for geometrical change as a planar trigonal carbenium carbon changes to a tetrahedral carbon in the regenerated substrate, for groups attached to the carbenium center become somewhat compressed.

The geometrical and solvation adjustments are less often discussed. One of them is desolvation of the ions. Solvation, especially of the arenesulfonate ion, greatly assists ionization. Substantial desolvation must occur before or during return of ion pair to substrate, against an enthalpy gradient,[59] somewhat offset by the accompanying gain in entropy. Desolvation takes time. The second is adjustment of conformation in the anion and/or cation in order that bonding by coordination may occur. A third is readjustment of the positions of molecules in the solvent cage surrounding the ion pair. As collapse occurs with the associated desolvation, some solvent molecules are pushed aside and others move in to occupy vacated space. These adjustments also take time. Solvent reorganization as a factor affecting rates of coordination of carbocations with nucleophiles has been discussed by Ritchie.[60]

Precise evaluation of these factors is difficult, but useful indications are provided by several phenomena. Certain measured rate constants,[61-63] which happen to be much lower than 10^{13} s^{-1}, for combination or recombination of anions with rather stabilized carbocations are only remotely relevant to the present case. More useful are molecular rotational relaxation times, measured by depolarized Rayleigh light scattering or by NMR, which are of the order of magnitude of 1×10^{-11} s for substances such as acetic acid, nitrobenzene, and the xylenes.[64] The rotational relaxation times for acetate and trifluoroacetate ions in water are also of this order of magnitude. These relaxation times suggest how long it may take to effect the positional adjustments of solvent molecules that are associated with ion pair collapse.

The extent to which conformational adjustment is significant depends on the differences in conformation that may exist, for both moieties of the ester, between the ester and the ions. For the 2-adamantyl moiety of **3**, conformational change between the ester and the cation is surely minimal, but it may be appreciable in the isopropyl moiety of **1**. Rotational barriers have been reviewed by Wilson,[68] Pethrick and Wyn-Jones,[69] and Lowe;[70] for many molecules they are in the range of 1–3 kcal/mol. For a barrier of 2 kcal/mol and a typical torsional frequency of 3×10^{12} s^{-1}, one reckons a rate constant for conformational change of 1×10^{11} s^{-1}.

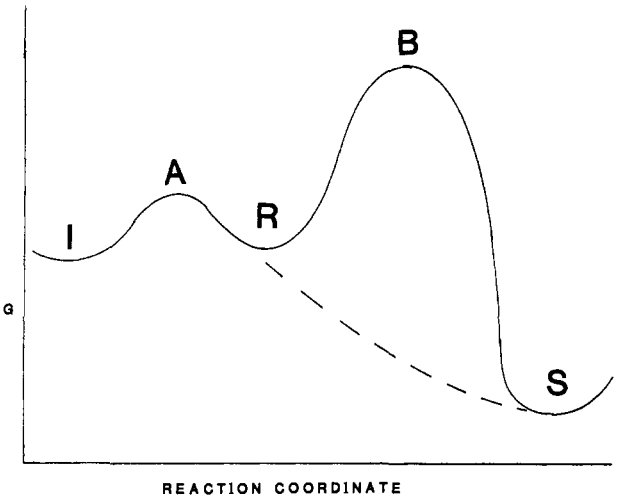


Figure 2. Schematic energy profile for coordination of an arenesulfonate anion with a carbocation to form alkyl arenesulfonate ester. I represents the (intimate) ion pair, A an energy barrier for adjustments (of conformations, conditions of solvation, and arrangement of ions and solvent molecules), R the readjusted condition optimum for coordination to occur, B the barrier to bonding (by coordination), and S the ester product. At B, the solid line represents a case in which there is a substantial barrier to bonding while the dashed line represents the case in which there is no barrier. In the latter case, the adjustments barrier (A) limits the rate of coordination.

Still further guidance comes from the experimentally based estimates of Koenig and Owens[65] of the lifetimes of radical pairs within a solvent cage. The radicals were derived from a chiral precursor. The estimated lifetimes are 1.8×10^{-10} s for all radical pairs that combine and 6.0×10^{-12} s for radical pairs that combine to form a product of retained configuration. These estimates are highly relevant to the present discussion, for the driving force for colligation of one radical with another is comparable to that for coordination of a *sec*-alkyl cation with an arenesulfonate ion; radical colligation lacks the Coulombic factor that furthers ion pair collapse, but it is largely free of the desolvation factor.

These several indications suggest the rate constant for collapse of intimate ion pairs of present interest to be about 10^{11} s^{-1}. Somewhat similar estimates, on different grounds, have been made by Monitz and Whiting.[66a] These estimates are higher than the 10^9–10^{10}-s^{-1} range earlier postulated by Winstein.[66b]

In this connection, let us recall the basis of the judgment of Knier and Jencks[56] that encounter or cage complexes of many carbocations with nucleophiles have no barrier for collapse to covalent substances. It stems from inferences of Young and Jencks[67] that reactions of α-aryl-α-methoxyethyl cations with sulfite ion occur at encounter-controlled rate and from an extrapolation of rate constants thereby inferred for reactions of these cations with water. The rate constants that were the basis of extrapolation range from 7×10^6 to 4×10^8 s^{-1}, and the extrapolated rate constants estimated for reactions of water with other oxocarbenium ions range up to 10^{15} s^{-1} for the hydroxymethyl cation.

It is noteworthy that the rate constants that are the basis of this extrapolation are beneath the encounter-controlled limit. Of the factors recognized above to limit the rate of collapse of a carbocation–nucleophile intimate ion pair, the bonding factors are probably the most important for the α-aryl-α-methoxyethyl cations concerned. The extrapolation essentially predicts the rate behavior that might be anticipated if that were the only significant factor. However, as the bonding barrier becomes very low, the adjustment factors become dominant. That is, what limits the rate of collapse may not be the energetics of formation of the covalent bond but rather the time taken for the concomitant geometric and solvent reorganization.

(59) If the carbocation is nucleophilically solvated, as has been proposed,[5] the enthalpy cost of desolvation would be correspondingly greater.
(60) Ritchie, C. D. *Pure Appl. Chem.* **1979**, *51*, 153.
(61) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348; Ritchie, C. D.; Virtanen, P. O. *J. Am. Chem. Soc.* **1973**, *95*, 1882.
(62) Dorfman, L. M.; Sujdak, R. J.; Bockrath, B. *Acc. Chem. Res.* **1976**, *9*, 352. Sujdak, R. J.; Jones, R. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1976**, *98*, 4875.
(63) Feigel, M.; Kessler, H. *Chem. Ber.* **1978**, *111*, 1659; **1979**, *112*, 3715; *Acc. Chem. Res.* **1982**, *15*, 2.
(64) Alms, G. R.; Bauer, D. R.; Brauman, J. I.; Pecora, R. *J. Chem. Phys.* **1973**, *58*, 5570; **1973**, *59*, 5310, 5321.
(65) Koenig, T.: Owens, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4052.
(66) (a) Monitz, M.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1982**, 613. (b) Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 381.
(67) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238.
(68) Wilson, E. B., Jr. *Adv. Chem. Phys.* **1959**, *2*, 370.
(69) Pethrick, R. A.; Wyn-Jones, E. *Q. Rev., Chem. Soc.* **1969**, *23*, 301.
(70) Lowe, J. P. *Prog. Phys. Org. Chem.* **1968**, *6*, 1.

The switch from bonding to adjustment control of coordination rate may be visualized with respect to the schematic energy profile of Figure 2, in which I represents the ion pair, R the ion pair readjusted with respect to geometry and solvation, S the ester regenerated by ion pair collapse, and A and B the adjustment and bonding barriers. When the bonding barrier is substantially larger than that for adjustment of geometry and solvation, it determines coordination rate, and the magnitude of the adjustment barrier has no effect. But if the bonding barrier vanishes, as represented by the dashed line, the adjustmment barrier becomes rate controlling.

(3) The Question of Whether the Ion Pairs That Undergo Internal Return Are Solvolysis Intermediates. Bentley and Schleyer[5] and Bentley, Bowen, Parker, and Watt[71] have questioned whether the ion pairs that undergo oxygen-18 scrambling in experiments such as we have performed are the same as those that undergo solvolysis. They conjecture that there may be several kinds of contact ion pairs, differing in their solvation, and that perhaps those more strongly solvated are more likely to undergo solvolysis than ^{18}O scrambling.

This question also has two facets, one semantic, the other chemical. The semantic question is what "the same" means. If, within its lifetime, an ion pair can explore the relevant reactive conformations and conditions of solvation, it is effectively "the same", even though the particular conformation or condition of solvation of the ion pair as it engages in one mode of reaction is different from that involved in another.[72] Whether there is time for the ion pair to explore the relevant conformations and conditions of solvation depends on how rapidly their interconversion occurs and on the rate constants for the various reaction pathways available to the ion pair.

Certainly it is conceivable that the transition states for internal return and for separation of intimate to solvent-separated ion pair should have different solvation and therefore that the ion pairs that precede these transition states should differ in solvation. The key question is how rapidly the two kinds of intimate ion pair, differing in solvation, interconvert as compared to how rapidly they separate or reorganize so as to be able to collapse to scrambled substrate. If solvation change is rapid as compared to the other two processes, the ion pairs that form scrambled or solvolysis products are the same, but if solvation change is relatively slow, the ion pairs must be counted as different.

Assigning rate constants to changes of condition can only be done approximately. Some guidance as to rates of change of solvation affiliations is given by the lifetime of H_3O^+ and OH^- ions in water,[73a] with respect to hydron exchange with solvating water molecules, which are about 2×10^{-13} s. Another indication is the fast correlation time for water reorganization about proteins,[73b] which is about 2×10^{-11} s.

For scrambling via ion pairs I_A and I_S (eq 9), the conversion of I_A into I_S may occur either by whole ion rotation, of the anion or cation or both, or by the seemingly less drastic rotation about the C–S bond of the benzenesulfonate ion so as to bring a different oxygen atom into juxtaposition with the carbenium center. A suggestion of the barrier entailed in the latter process is that for rotation about the C–S bond in CH_3SO_2X (X = F, Cl, or CH_3) or $PhSO_2Cl$, estimated from infrared data to fall variously in the range of 2–4 kcal/mol.[74] If $\Delta S^{\ddagger}$ is 0, the rate constant for rotation is about 10^{10}–10^{11} s^{-1}. For conversion of I_A to I_S by whole ion rotation, one estimates rate constants of the same general order of magnitude for considerations mentioned above.

For transformation of intimate to solvent-separated ion pair, again two mechanisms are conceivable. One is whole ion rotation, as just mentioned; if the new orientation of anion to cation is inappropriate for collapse to occur, the interposition of one or more solvent molecules between anion and cation becomes more probable. The other is straight separation of anion from cation. The rate of the latter must approach that for diffusive separation of an encounter complex. Thus again rate constants in the range of 10^{10}–10^{11} s^{-1} are probable.

These estimates are not firm enough for a final answer to the question of Bentley and Schleyer[5] to be given. On the whole, solvation change appears to be faster. More definitive data would be welcome.

(4) Implications with Respect to Solvolysis Rate Correlations Based on 2-Adamantyl *p*-Toluenesulfonate. Recently some useful correlations of solvolysis rates have been developed and used as criteria for the evaluation of solvolysis mechanisms.[5,12,43,75] A premise underlying these correlations was that "internal ion pair return is not significant [in solvolysis of 2-adamantyl *p*-toluenesulfonate] in acetic acid, formic acid, and ethanol/water."[12]

In our preliminary communication,[17] we commented that our oxygen scrambling results (Table I) call for reinterpretation of correlations with the solvent parameter, $Y_{2\text{-AdOTs}}$. Lest that comment be alarming, we elaborate. An analysis of solvolysis mechanisms based on the premise that internal return is not significant clearly requires reinterpretation when it is demonstrated, as we have done, that more than half of the intimate ion pairs undergo internal return.

However, that does not mean that the correlations or the main conclusions drawn from them need to be discarded. Insofar as their validity is concerned, the most important judgment of Bentley, Schadt, and Schleyer[75] regarding the solvolysis of 2-adamantyl *p*-toluenesulfonate is that the solvent does not participate as a nucleophile in the rate-limiting step. That judgment is not challenged by our work. The situation, viewed in grandiose terms, is something like the reinterpretation of Newton's laws of motion that was obliged by quantum mechanics and relativity theory. Newton's laws are as valid today for macro mechanics as they ever were, but we now understand them rather differently.

Experimental Section

Materials and Solvents. Alkyl benzenesulfonates and *p*-toluenesulfonates were prepared by reactions of the respective alcohols and arenesulfonyl chlorides in dry pyridine. Melting points of solid esters were in agreement with literature values. The purity of esters obtained as oils was checked by NMR spectroscopy. 3,3-Dimethyl-2-butyl benzenesulfonate (**4**), previously unreported, was obtained as a crystalline material: mp 39.5–41 °C; NMR ($CDCl_3$) δ 0.84 s (9 H), 1.22 d (J = 6.4 Hz) (3 H), 4.43 q (J = 6.4 Hz) (1 H), 7.49–7.82, m (5 H); major IR (KBr pellet) absorption bands 2970, 2950, 1470, 1440, 1350, 1330, 1185, 1095, 1075, 1045, 1000, 985, 900, 805, 755, 720, 690, 598, 575 cm^{-1}; MS (70 eV), m/e 242 (243), 198, 187, 185, 159, 141, 94, 85, 77, 69, 57 (100%). Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.47; H, 7.49. Found: C, 59.63; H, 7.63.

Benzenesulfonyl Chloride Containing Oxygen-18. A procedure adapted from Oae et al.[76] was used. Water-^{18}O (30% ^{18}O content of Bio-Rad Laboratories or 20% ^{18}O content of Stohler Isotope Chemicals) (3 g) was added to a solution of thiophenol (7.65 mL), freshly distilled under N_2, in 80 mL of CCl_4. Chlorine gas from a Matheson cylinder was dried by passing it through two traps containing concentrated H_2SO_4 and one containing P_2O_5, bubbled into the reaction mixture, and vigorously stirred with a good mechanical stirrer, until no more HCl evolved (ca. 4.5 h) and the color had gone through the change described in the literature.[76] In the first phase, the reaction flask was kept in an ice-water bath. After removal of the solvent at atmospheric pressure, the product was distilled under reduced pressure; yield 11.7 g (80% based on $H_2{}^{18}O$).

Alkyl benzenesulfonates specifically labeled with ^{18}O in the sulfonyl position were prepared by reaction of equimolar amounts of the precursor unlabeled alcohol and of $PhS^{18}O_2Cl$ in dry pyridine, except that a 20% molar excess of $PhS^{18}O_2Cl$ was used in the reaction with 2-adamantanol. Unreacted 2-adamantanol was removed from the crude product by dissolving it at room temperature in the minimum amount of toluene, removing insoluble materials by filtration, and adding pentane to the filtrate; crystallization often occurred spontaneously, or it was induced by cooling.

(71) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244.
(72) See the definition of "chemical species" by IUPAC Commission III.2: Gold, V. *Pure Appl. Chem.* **1979**, *51*, 1725.
(73) (a) Bell, R. P. "The Proton in Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 21. (b) Halle, B.; Andersson, T.; Forsen, S.; Lindman, B. *J. Am. Chem. Soc.* **1981**, *103*, 500.
(74) Hargittai, I. *Lect. Notes Chem.* **1978**, *6*, 39, 42, 45, 84.
(75) Bentley, T. W.; Schadt, F. L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 992.
(76) Oae, S.; Kitao, T.; Kitaoka, Y. *Tetrahedron* **1963**, *19*, 827.

Cyclopentene. The literature procedure[77] was employed, except that 85% H_3PO_4 (60 mL for 10 g of cyclopentanol) was used instead of 89% H_3PO_4. The proton NMR spectrum of the final product matched the reported spectrum (Aldrich Library of NMR Spectra).

***p*-Toluenesulfonic Acid, Anhydrous.** The commercial monohydrate was heated at 110 °C under a pressure of 0.1–0.5 torr until all the material had liquefied. Benzene was then added and the residual water removed by azeotropic distillation at atmospheric pressure. The deep purple solution was concentrated, and crystallization was induced by placing the flask (kept under a nitrogen atmosphere) in an ice-water bath. The product was filtered, dried, and crystallized twice from benzene in a N_2-filled glove bag; mp 35–38 °C (lit.[78] mp 38 °C).

2,6-Lutidine was distilled before use.

Sodium Trifluoroacetate, Anhydrous. Sodium carbonate (9.9 g) was dissolved in water. Distilled CF_3COOH (21.38 g) was added, the water was removed under reduced pressure, and the salt dried at 110 °C under vacuum for 48 h before use.[79] The product was not recrystallized.

Sodium Acetate. A reagent grade commercial product was dried under reduced pressure for 4–6 h before use.

Methanol. Reagent grade methanol (from Mallinckrodt) was first fractionally distilled. The distillate was then dried by the method of Lund and Bjerrum.[80] The final distillation was done under nitrogen atmosphere, with use of a 36-cm-long Vigreux column.

80% v/v Ethanol–Water. Absolute ethanol was heated under reflux with magnesium ethoxide and distilled under nitrogen through a 36-cm-long Vigreux column. Deionized water was distilled in an all-glass apparatus. The purified solvents were mixed by transferring 100 mL of water by pipet into a 500-mL volumetric flask filled halfway with ethanol; the flask was shaken and filled to the mark with ethanol.

Acetic Acid. Glacial acetic acid (J. T. Baker) was purified by freezing most of it and pouring off the remaining liquid.

2,2,2-Trifluoroethanol. The Eastman Kodak product was purified as described by Shiner et al.[81] except that a smaller reflux ratio (7–8:1) and P_2O_5 in excess of the specified amount were used.

90% w/v 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP). The solvent was used as supplied (one batch from Apache Chemicals, one from Eastman Kodak). The alcohol and deionized distilled water were mixed by weighing the two solvents in the correct proportions (90% alcohol, 10% water).

Trifluoroacetic Acid. Commercial material (Mallinckrodt or Aldrich) was fractionally distilled through a 36-cm-long Vigreux column. The distillation apparatus was equipped with a drying tube filled with $CaCl_2$; alternatively the distillation was done under dry nitrogen atmosphere.

Kinetics. Reactions were followed for 4 half-lives and the data fitted to the first-order rate equation by means of linear regression analysis.

Trifluoroacetolysis rates were measured by the spectrophotometric technique described in the literature.[82] Measurements were carried out on a 240 Gilford UV-vis spectrophotometer at a wavelength of 271.0 nm. Kinetics in all other solvents were followed titrimetrically. For reactions in TFE and 90% HFIP 10% H_2O, the solvent, thermostated at 25.00 ± 0.01 °C, was added to the mark in a volumetric flask containing substrate and 2,6-lutidine. Aliquots (5 mL) were removed by pipet at measured times; the time was taken when one-half of the aliquot had been released into 20 mL of ice-cold water. The organic products were then extracted with 20 mL of diethyl ether and the aqueous layer was titrated potentiometrically with standardized NaOH solution.

For reactions at 70 and 80 °C, aliquots of reaction solution[83] were sealed in ampules, after being flushed with N_2 or Ar. For experiments in CH_3OH and 80% EtOH 20% H_2O, the content of an ampule (3 or 5 mL) was poured into ice-cold H_2O (15 or 20 mL) and extracted with ice-cold diethyl ether (15 or 20 mL); the aqueous layer was titrated with standardized NaOH solution to the phenolphthalein end point (ethanolysis) or potentiometrically (methanolysis). For acetolysis runs, 3-mL aliquots were delivered into 25-mL Erlenmeyer flasks containing 5 mL of glacial acetic acid and 8 drops of a saturated solution of bromophenol blue in acetic acid. The aliquots were titrated to the end point (yellow → pale yellow → colorless) with 0.15 M $HClO_4$ in acetic acid.[84]

Oxygen-18 Scrambling Experiments. These experiments consist of four stages: (i) partial solvolysis, (ii) cleavage of recovered benzenesulfonate ester, (iii) GC/MS analysis of the cleavage reaction mixture, and (iv) data treatment.

(i) Enough of an 0.05–0.09 M solution of **1**, **2**, **3**, or **4** having 18–28% oxygen-18 in its sulfonyl moiety was allowed to react in the chosen solvent for the desired time so as to recover 0.2–0.4 g of unsolvolyzed ester. Conditions were kept identical with those employed in kinetic experiments. For experiments run at 70 and 80 °C, the reaction mixture, sealed in an ampule, was chilled in an ice-water bath before the ampule was opened; then the contents of the ampule were poured into a separatory funnel containing ice-cold water. For experiments run at 25 °C, the reaction mixture was quenched by pouring it into a separatory funnel containing ice-cold water. The organic materials were extracted with three portions of diethyl ether (pentane for runs in trifluoroacetic acid). The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed at room temperature under vacuum, and the residual oil, after prolonged high vacuum drying, was purified by methods such as used when the esters were first prepared. The purity of the recovered ester was checked by NMR spectroscopy and, when applicable, by melting point.

(ii) The recovered and purified benzenesulfonate ester (ca. 0.1 g) was dissolved in 15 mL of ammonia distilled from sodium in a 25-mL three-neck flask topped with a cold finger condenser filled with a solid CO_2/2-propanol bath. The apparatus was kept under nitrogen atmosphere. Anhydrous diethyl ether (2–3 mL) was injected into the flask for reactions of **3** in order to obtain an homogeneous solution. Two equivalents of sodium metal was then added. A rapid reaction took place. When all the metal had disappeared (a few minutes), the solvent was allowed to evaporate. Acetonitrile (15 mL), freshly distilled under nitrogen after refluxing over CaH_2, was then added, followed by excess CH_3I (1–1.5 mL). The reaction mixture was maintained at ca. 30 °C under stirring for about 1 h, then poured into 25 mL of water, and extracted with ether (20 mL, twice). After being dried over $MgSO_4$, the ether solution was concentrated by evaporation and analyzed.

(iii) Analyses were done on a Finnigan 4000 GC-MS instrument equipped with a 6-ft-long glass column packed with 3%-OV-17 on 60/80 Chromosorb Q. The mass spectrometer was operated at 70 eV. Three solutions, A, B, and C, were used in each analysis. These were ether extracts of the reductive cleavage–methylation product mixtures derived from three types of arenesulfonate esters: (a) recovered from partial solvolysis, i.e., the scrambling experiment solution (A); (b) specifically labeled in the sulfonyl oxygens, i.e., the starting material for the scrambling experiments (B); and (c) of natural abundance isotopic composition, the unlabeled reference (C). Solutions A and B are samples at times t and 0, respectively, for the oxygen equilibration process. Solution C was used for calibration purposes. The three solutions were injected alternately, with different syringes to avoid possible contamination, under identical instrumental conditions and data acquisition parameters. Mass ranges around peaks of interest were scanned at fractional mass increments (0.1 amu). Peaks of interest were, for $PhSO_2CH_3$, the m/z 141 and 143 (loss of CH_3), redundantly, the m/z 156 and 158 (parent ion), and, for alcohol products, the parent and $m + 2$ ions. For each injection, the intensity ratio $(m + 2)/m$ was measured, both for alcohol and $PhSO_2CH_3$, in 3–5 scans, after background subtraction, taken at the apex of the "GC-peak" on the total ion current (TIC) profile. For a given product in a given solution, all $(m + 2)/m$ data relative to 3–5 injections were averaged; standard deviations were always better than ±0.1 (cf. Table II). This sampling of $m + 2$ and m data at the apex of the TIC trace was more satisfactory than use of the integrated total intensities due to the two ions, probably because of peak tailing.

Calculation of k_{eq} from $(m + 2)/m$ Data. Equations 6 and 7 were used to calculate k_{eq}; the fractions of oxygen-18 in molecules of alcohol (f) and of $PhSO_2CH_3$ (g) are related to the $(m + 2)/m$ ratios through eq 2 and 3, respectively. Equations 2 and 3 were derived as follows.

Analysis of ROH. Let $\mathcal{N}$ be the total number of molecular ions that arrive to the analyzer in a given scan. $\mathcal{N}$ is the sum of ions of mass m, $m + 1$, $m + 2$, etc. which differ only for isotopic composition. The fraction of molecular ions that has mass m represents ions having only light isotopes in the same molecule; this fraction is the product of the fraction of oxygen atoms that are ^{16}O $(1 - f)$,[85] of hydrogen atoms that are protium, and of carbon atoms that are ^{12}C. Letting M^0 represent the product of the latter two fractions, we have eq 10. By analogous reasoning, the fractions of molecular ions that have masses $(m + 1)$, $(m +$

$$\frac{m}{\mathcal{N}} = (1 - f)M^0 \qquad (10)$$

(77) Kögl, F.; Ultee, A. J., Jr. *Recl. Trav. Chim. Pays-Bas* **1950**, *69*, 1576.
(78) *Beilstein, 4th ed. 11*, 44.
(79) Jansen, M. L.; Yeager, H. L. *J. Phys. Chem.* **1974**, *78*, 1380. Harriss, M. G.; Milne, J. B. *Can. J. Chem.* **1971**, *49*, 1888.
(80) Lund, H.; Bjerrum, J. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 210.
(81) Shiner, V. J., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. *J. Am. Chem. Soc.* **1969**, *91*, 4838.
(82) Peterson, P. E.; Kelley, R. E., Jr.; Belloli, R.; Sipp, K. A. *J. Am. Chem. Soc.* **1965**, *87*, 5169.
(83) **3** is sparingly soluble in 80% EtOH–20% water; it took 15–20 min of vigorous shaking to obtain an 0.05 M solution.
(84) Winstein, S.; Grunwald, E.; Ingraham, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 821.
(85) The contribution of ^{17}O is neglected throughout these derivations.

2), etc. are given by eq 11, 12, etc., where M^{I} and M^{II} represent re-

$$\frac{(m+1)}{\mathcal{N}} = (1-f)M^{I} \tag{11}$$

$$\frac{(m+2)}{\mathcal{N}} = (1-f)M^{II} + fM^{0} \tag{12}$$

spectively the probabilities that the molecule contains only one ^2H or only one ^{13}C, and any of the combinations two ^2H, two ^{13}C, or one ^2H plus one ^{13}C. The intensity ratio $(m+2)/m$, P, is then given by

$$P = \frac{m+2}{m} = \frac{f}{1-f} + \frac{M^{II}}{M^{0}} \tag{13}$$

From eq 13, f is derived as in eq 14.

$$f = \frac{\{P - (M^{II}/M^{0})\}}{\{P - (M^{II}/M^{0})\} + 1} \tag{14}$$

If one lets

$$P_c = P - (M^{II}/M^{0}) \tag{15}$$

and substitutes eq 14, one obtains eq 2. The correction term (M^{II}/M^{0}) was determined for each analysis by using the appropriate reference solution C, for which $f = 0.0020$, natural abundance fraction of the isotope ^{18}O. Using a rearranged form of eq 13, one obtains

$$(M^{II}/M^{0}) = P^{u} - \frac{0.0020}{1-0.0020} \tag{16}$$

where P^{u} is the measured $(m+2)/m$ ratio for ROH of natural isotopic composition (solution C). Substituting in eq 15, one finally obtains

$$P_c = P - P^{u} + \frac{0.0020}{1-0.0020} \tag{17}$$

Analysis of $PhSO_2CH_3$. By applying a treatment analogous to the one described for ROH analysis, one obtains eq 18–22, etc., where N^0 rep-

$$\frac{m}{\mathcal{N}} = (1-g)^2N^{0} \tag{18}$$

$$\frac{m+1}{\mathcal{N}} = (1-g)^2N^{I} \tag{19}$$

$$\frac{m+2}{\mathcal{N}} = (2g-2g^2)N^{0} + (1-g)^2N^{II} \tag{20}$$

$$\frac{m+3}{\mathcal{N}} = (2g-2g^2)N^{I} + (1-g)^2N^{III} \tag{21}$$

$$\frac{m+4}{\mathcal{N}} = g^2N^{0} + (2g-2g^2)N^{II} + (1-g)^2N^{IV} \tag{22}$$

resents the fraction of molecules having only ^{12}C carbons, ^1H hydrogens, and ^{32}S sulfur atoms; N^I represents the fraction of molecules having carbon, hydrogen, and sulfur atoms only as light isotopes except for one ^2H, one ^{13}C, or one ^{33}S; and so on. $(1-g)^2$, $(2g-2g^2)$, and g^2 represent the probabilities of having in the same molecule two ^{16}O, one ^{16}O and one ^{18}O, and two ^{18}O, respectively.[85] The intensity ratio $(m+2)/m$, R, is derived as in eq 23,

$$R = \frac{m+2}{m} = \frac{2g}{1-g} + \frac{N^{II}}{N^{0}} \tag{23}$$

from which g is derived as in eq 24.

$$g = \frac{\{R - (N^{II}/N^{0})\}}{[R - (N^{II}/N^{0})] + 2} \tag{24}$$

If one lets

$$R_c = R - (N^{II}/N^{0}) \tag{25}$$

and substitutes eq 24, one obtains eq 3. The correction term N^{II}/N^0 was determined for each analysis by using the reference solution C, for which $g = 0.0020$, natural abundance fraction of the isotope ^{18}O. Using a rearranged form of eq 23, one obtains eq 26, where R^u is the measured

$$\frac{N^{II}}{N^{0}} = R^{u} - \frac{(2)(0.0020)}{1-0.0020} \tag{26}$$

$(m+2)/m$ ratio for $PhSO_2CH_3$ of natural isotopic composition. Substituting eq 25, one finally obtaines eq 27. Equations 17 and 27 were

$$R_c = R - R^{u} + \frac{(2)(0.0020)}{1-0.0020} \tag{27}$$

used to calculate P_c and R_c data that allow one to calculate k_{eq} through eq 2 and 6, and 3 and 7.

Exchange Experiments. Type I. To a solution of sodium *p*-toluenesulfonate (0.030 M) and sodium acetate (0.10 M) in acetic acid was added enough **3** to make its concentration 0.051 M. Three portions, one of 20 mL, one of 35 mL, and one of 45 mL, were sealed in ampules under argon atmosphere. At fixed times the ampules were withdrawn from the temperature bath and quenched in an ice-water bath. The content of each ampule was poured into water and extracted 3 times with Et_2O. The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residual oil was dried under vacuum. The dry solid residue (in $CDCl_3$ solution) was directly examined by NMR spectroscopy.

Sodium metal (0.067 g) was dissolved in 90 mL of 80% ethanol 20% water under nitrogen atmosphere. An equimolar amount of anhydrous *p*-toluenesulfonic acid was added, and the pH of the solution was adjusted to 7.0 by addition of a few drops of 2 M NaOH. **3** (1.1128 g) was added, and the solution was diluted to exactly 100 mL with 80% ethanol 20% water. Thenceforth the same procedure was used as for the experiments in acetic acid.

For experiments involving trifluoroacetolysis of **2**, the procedure described for the above experiments involving **3** was employed, except that the reactions were run at 25 °C and that pentane (four portions) instead of Et_2O was used to extract the water-diluted solvolysis mixtures.

NMR analyses were done on a 60-MHz JEOLCO instrument.

Type II. The experiments were performed in a 100-MHz JEOLCO NMR spectrometer. D_2O in a coaxial capillary tube inserted into the reaction tube (5 mm in diameter) was used as a deuterium-containing external reference. The system was "locked" on the D_2O signal prior to the beginning of the experiment. A 5-mL volumetric flask was filled almost to the mark with a CF_3COOH solution of CF_3CO_2Na and sodium *p*-toluenesulfonate of desired concentrations. At time zero the desired amount of **2** was added to the volumetric flask with a syringe (weighed before and after the addition), the solution was quickly stirred, and 0.35 mL of it was transferred into an NMR tube. The D_2O-containing capillary was introduced into the reaction tube, which was then set into the NMR cavity. Accumulation was started, and the time of the first pulse was recorded (normally 1–1.5 min). Appropriate computer programs were used for automatic acquisition of data at desired times (AUTOSTACKING program) and automatic data reduction and recording (ANALYZ program).

A different procedure for mixing the reactants was used in the experiments involving 2-adamantyl esters or addition of *p*-toluenesulfonic acid to cyclopentene. A weighed amount of the ester or a measured volume of cyclopentene (1–2 μL) was added directly into an NMR tube containing 0.35 mL of the reaction solution of desired composition.

We found that in order to be able to detect the signal due to the *p*-CH_3 of cyclopentyl *p*-toluenesulfonate formed during addition of *p*-toluenesulfonic acid to cyclopentene, sodium *p*-toluenesulfonate had to be present in the system.

The *p*-methyl group of *p*-toluenesulfonic acid has a chemical shift identical with that of the analogous methyl group in its esters. However, in the presence of its anion, the acid and the anion give one single peak at δ 2.48–2.49, for the *p*-methyl groups, which is shifted upfield with respect to the absorption of the *p*-methyl group in the ester, thereby making the analysis feasible. The phenomenon must be due to fast exchange processes between acid and its conjugate base.