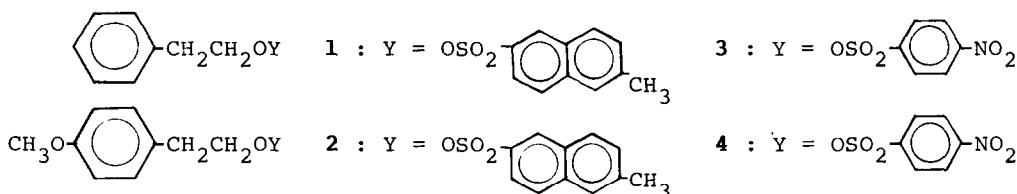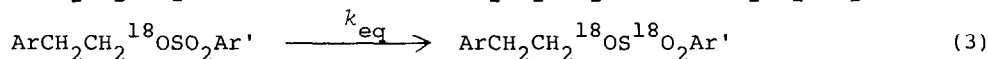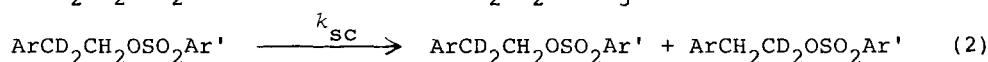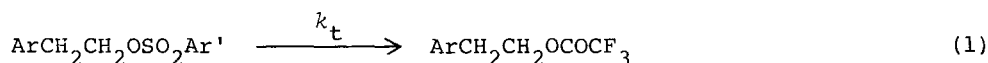ION PAIRS IN TRIFLUOROACETOLYSIS OF 2-ARYLETHYL ARENESULFONATES[1]

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Abstract: The behavior of ion pairs in the trifluoroacetolysis of 2-arylethyl arenesulfonates was studied by means of tracer techniques with deuterium and oxygen-18.

Quite recently, Paradisi and Bunnett[3] reported a simple procedure to determine the rate of oxygen-18 scrambling in alkyl arenesulfonates during solvolysis reactions. They used GC/MS in order to analyze the oxygen-18 contents of both the alcohols and sulfone derived from the recovered arenesulfonates.[3] Tedious conversion of the alcohols to carbon dioxide with subsequent purification of the carbon dioxide was unnecessary.[4-7] Fast scrambling of oxygen-18 accompanying the solvolysis of secondary arenesulfonates was thus observed and discussed by Paradisi and Bunnett.[3] The disclosure of these results prompts us to report a similar study of oxygen-18 scrambling in the trifluoroacetolysis of 2-arylethyl arenesulfonates by a simple procedure to determine the oxygen-18 content in the alkoxyl moiety.[8]

In order to investigate the behavior of ion pairs appearing in the course of the trifluoroacetolysis of 2-arylethyl esters, rate constants of the scrambling of deuterium (eq 2, k_{sc}) and oxygen-18 (eq 3, k_{eq}) as well as those of the solvolysis (eq 1, k_t) were determined for 6-methyl-2-naphthalenesulfonates (menasylates, 1 and 2)[9] and p-nitrobenzenesulfonates (nosylates, 3 and 4).

$$ArCH_2CH_2OSO_2Ar' \xrightarrow{k_t} ArCH_2CH_2OCOCF_3 \qquad (1)$$

$$ArCD_2CH_2OSO_2Ar' \xrightarrow{k_{sc}} ArCD_2CH_2OSO_2Ar' + ArCH_2CD_2OSO_2Ar' \qquad (2)$$

$$ArCH_2CH_2{}^{18}OSO_2Ar' \xrightarrow{k_{eq}} ArCH_2CH_2{}^{18}OS^{18}O_2Ar' \qquad (3)$$

Solvolysis rate constants (k_t) were determined spectrophotometrically by means of an extraction technique.[10,11] Rate constants for the rearrangement of the aralkyl moiety (k_{sc}) were determined by ^{1}H NMR spectroscopy.[11b,12]

Scrambling of oxygen-18 was studied with arenesulfonates 1-4 labeled with ca. 4% of [18]O at the alkyl oxygen. Starting arenesulfoantes (ca. 100 mg per sample) were recovered from the reaction solution six to seven times at various stages (0 to 60% completion) of scrambling, purified by recrystallization, and cleaved with sodium in liquid ammonia. The resulting alcohols were purified by preparative gas chromatography and analyzed directly by mass spectrometry.[13] Thus, rate constants of [18]O scrambling, k_{eq}, were determined without a tedious oxidation step,[8] although the determination from the oxygen-18 content of the sulfonate moiety was impossible.[3] Rate constant data are summarized in Table 1.

Table 1. Trifluoroacetolysis and Deuterium and Oxygen-18 Scrambling Data for 2-Arylethyl Arenesulfonates[a]

Substrate[b]	Temp/°C[c]	$10^5 k_t/s^{-1}$[d]	$10^5 k_{sc}/s^{-1}$[e]	$10^5 k_{eq}/s^{-1}$[f]	F[g]	k_{eq}/k_{sc}
1 (H-OMns)	50	2.93 ± 0.02	7.86 ± 0.20	5.89 ± 0.07	0.27	0.75
2 (CH$_3$O-OMns)	25	2.00 ± 0.01	6.54 ± 0.07	4.35 ± 0.10	0.23	0.67
3 (H-ONs)	30	3.36 ± 0.07[h]	4.81 ± 0.25	3.46 ± 0.02	0.41	0.72
4 (CH$_3$O-ONs)	8	3.08 ± 0.07[h]	8.85 ± 0.01	6.89 ± 0.05	0.26	0.78

[a] No salt was added to trifluoroacetolysis media. See reference 9. [b] OMns: menasylate, 0.025 M; ONs: nosylate, 0.040 M. [c] ±0.02 °C. [d] Average of two or three runs with correlation coefficients (r) better than 0.999. [e] Average of two or three runs with $r > 0.992$. [f] Average of two or three runs with $r > 0.99$. [g] $F = k_t(k_t + k_{sc})$. k_s process was neglected. [h] 0.02 M in substrate.

Errors inherent in MS and NMR measurements as well as the troublesome nature of trifluoroacetic acid[14] may restrict discussions based on these data to rather qualitative ones. Nevertheless, the following conclusions can be drawn safely: (1) in trifluoroacetic acid, a solvent of low nucleophilicity and high ionizing power, ion-pair return is extensive for this primary alkyl system reacting with rearrangement, and (2) most of the rearrangement of the aralkyl moiety is accompanied by the scrambling of oxygen-18 in the sulfonate group, but the rate of the latter does not overtake that of the former. The fact that the scrambling of deuterium is always faster than that of oxygen-18 indicates that any type of ion pairs with an unsymmetrical alkyl structure, e. g., 5 or 6,[11a,15] were unable to be detected experimentally under these reaction conditions. Rather, it is likely that 2-phenylethyl ester, once ionized, gives rise to an ion pair with a symmetrical alkyl structure as a first intermediate, in which the three oxygens of the sulfonate group are

not completely equivalent. It is worth noting that all the values of k_{eq}/k_{sc} are close to 0.75; the return from ion pair **7**, although its presence has been disproved in a secondary system,[6] would give k_{eq}/k_{sc} of 0.75.
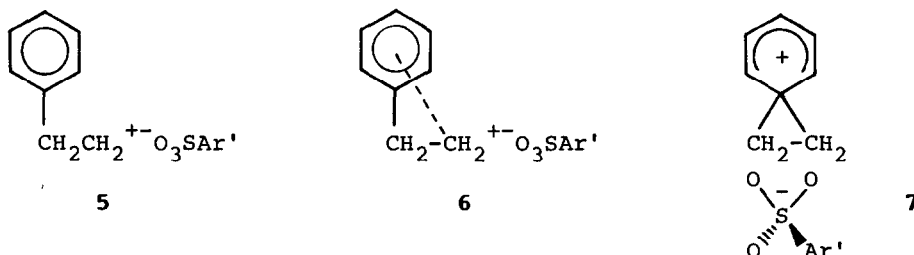
$$CH_2CH_2\overset{+}{}\overset{-}{}O_3SAr'$$

5

$$CH_2\text{-}CH_2\overset{+}{}\overset{-}{}O_3SAr'$$

6

7

References and Notes

(1) Neighboring group participation in solvolysis. 14. For Part 13, see Y. Yukawa, T. Ando, K. Token, M. Kawada, K. Matsuda, S.-G. Kim, and H. Yamataka, *Bull. Chem. Soc. Jpn.*, in press.

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(10) Arenesulfonate anions generated in the course of the reaction were extracted with sodium bicarbonate solutions and determined at 277 nm for menasylates and at 264 nm for nosylates.

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(12) Deuterated arenesulfonates (> 97% D, 30-100 mg per sample) were recovered

from the reaction solution five to seven times at various stages of the scrambling reaction, ranging from 0 to 80% completion, purified by recrystallization, and analyzed by ^{1}H NMR spectroscopy with a Hitachi R-20 instrument at 60 MHz and a Hitachi A-1600A signal averaging analyzer. Rate constants were claculated by the linear regression method using eq 4, in which x is per cent rearrangement of deuterium from the β- to α-position determined from the NMR peak ratios as above.

$$k_{sc} = \frac{1}{t} \ln \frac{50}{50 - x} \qquad (4)$$

Secondary β-deuterium isotope effects for the reaction are close to unity and can reasonably be neglected in these calculations.[11b,15b]

(13) Mass spectra were obtained with a Hitachi RMU-6M mass spectrometer at an electron energy of 80 eV. The relative heights of the parent peak and the peak two mass units higher were measured five to seven times for each sample. This ratio, R, after correction for ^{2}H and ^{13}C of natural abundance,[16] was used for calculation of the fraction of [18]O atoms, P (eq 5).

$$P = \frac{R_c}{R_c + 1} \qquad (5)$$

Rate constants of [18]O scrambling were calculated by the linear regression method using eq 6.

$$k_{eq} = \frac{1}{t} \ln \frac{P_0 - P_\infty}{P_t - P_\infty} \qquad (6)$$

where P_0 and P_∞ are the [18]O fractions at the initial and the final stages of the reaction; the former was determined experimentally and the latter calculated by eq 7.

$$P_\infty = \frac{1}{3} (P_0 + 2 \times 0.204) \qquad (7)$$

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(16) For 2-(p-methoxyphenyl)ethyl alcohol, the ratio was also corrected for natural abundance of one more [18]O.