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Scrambling of Oxygen-18 during the "Borderline" Solvolysis of 1-(3-Nitrophenyl)ethyl Tosylate

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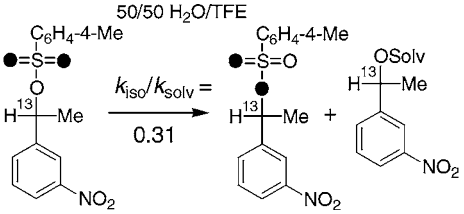
ABSTRACT



There is substantial isomerization ($k_{iso} = 0.32 \times 10^{-3}\ s^{-1}$) of $3\text{-}NO_2C_6H_4{}^{13}CH(Me)OS(^{18}O)_2Tos$ during solvolysis ($k_{solv} = 1.04 \times 10^{-3}\ s^{-1}$) in 50/50 trifluoroethanol/water, even though the estimated lifetime of the putative 1-(3-nitrophenyl)ethyl carbocation intermediate of solvolysis (ca. $10^{-13}\ s^{-1}$) is too short to allow rearrangement that exchanges the positions of ^{16}O and ^{18}O at the sulfonate leaving group. This suggests that isomerization proceeds by a mechanism that avoids formation of the carbocation–anion pair intermediate.

We are interested in characterizing the "borderline" region for solvolysis reactions, where the existence of the putative carbocation reaction intermediate is uncertain.[1] The solvolysis of ring-substituted 1-phenylethyl derivatives in 50/50 water/trifluoroethanol proceeds by a stepwise $D_N + A_N$ reaction mechanism[2] when the ring substituent is electron-donating.[3] The rate constants for addition of this largely aqueous solvent to the carbocation intermediates of these solvolysis reactions increase from $50\ s^{-1}$[4] to $5 \times 10^9\ s^{-1}$[3] as the ring substituent is changed from 4-NMe$_2$ ($\sigma^+ = -1.67$) to 4-Me ($\sigma^+ = -0.32$).[5a] The good linear correlation between log k_s and Hammett ring-substituent constants allows an estimate of $k_s \approx 10^{13}\ s^{-1}$ ($\sigma_{3-NO_2} = 0.71$) for addition of TFE/H$_2$O (TFE = trifluoroethanol) to the 1-(4-nitrophenyl)ethyl carbocation (Scheme 1).[3] This rate constant is near the bond-vibration limit for a "barrierless" reaction, so that it is not certain that this species forms as an intermediate of solvolysis.

Isomerization, which exchanges the position of oxygen isotopes at a substituted benzoate or sulfonate leaving group, during solvolysis may provide a *signature* for a reaction through a carbocation−anion pair intermediate.[6] The addition of solvent to the putative 1-(3-nitrophenyl)ethyl carbocation

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(1) (a) Amyes, T. L.; Toteva, M. M.; Richard, J. P. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; John Wiley & Sons: Hoboken, NJ, 2004, pp 41−68. (b) Richard, J. P.; Toteva, M. M.; Amyes, T. L. *Org. Lett.* **2001**, *3*, 2225−2228. (c) Toteva, M. M.; Richard, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 11434−11445.

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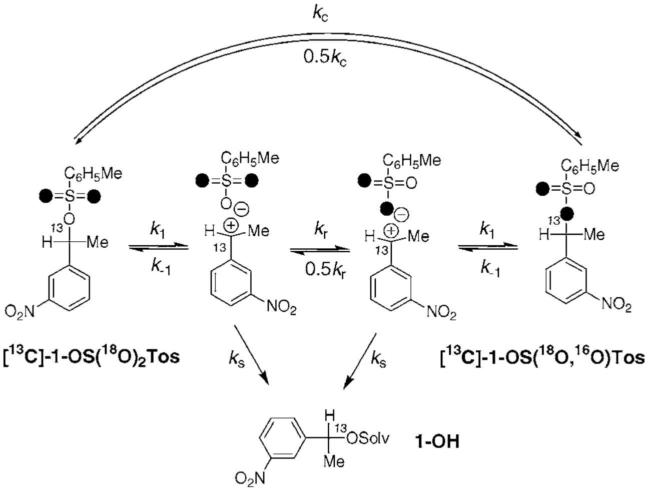
Scheme 1



intermediate of solvolysis of 1-(3-nitrophenyl)ethyl derivatives is apparently too fast to allow for "reorganization" of an ion-pair reaction intermediate ($k_r \approx 10^{11}$ s^{-1}, Scheme 1),[7] which is a step in the isomerization reaction of an ^{18}O-labeled sulfonate substrate. Stepwise isomerization of ^{18}O-labeled substrate **[^{13}C]-1-OS(^{18}O)$_2$Tos** (Scheme 1) may not occur competitively with the stepwise solvolysis reaction, if substrate ionization occurs at a preassociation "complex" where solvent is positioned to react directly, without the requirement for rotation into a reactive position.[5b]

1-(3-Nitrophenyl)ethyl tosylate[8] labeled with ^{13}C at the benzylic carbon and ^{18}O at the nonbridging sulfonate oxygens was prepared by the following series of reactions: (a) the Grignard reaction of C_6H_5MgBr with $^{13}CO_2$ (95% enrichment),[9,10a] (b) addition of MeLi to give $C_6H_5{}^{13}COMe$,[10b] (c) nitration to give $3\text{-}NO_2C_6H_4{}^{13}COMe$, (d) reduction with $NaBH_4$ to give $3\text{-}NO_2C_6H_4{}^{13}CH(OH)Me$, (e) synthesis of $4\text{-}MeC_6H_4S(^{18}O)_2Cl$ by oxidation of *p*-thiocresole with Cl_2 in $H_2{}^{18}O$,[11,12] (f) esterification of $3\text{-}NO_2C_6H_4{}^{13}CH(OH)Me$ with $4\text{-}MeC_6H_4S(^{18}O)_2Cl$ to give **[^{13}C]-1-OS(^{18}O)$_2$Tos**.[13] The proton-decoupled ^{13}C NMR spectrum of **[^{13}C]-1-OS(^{18}O)$_2$Tos** showed a single major peak (Figure S1 in Supporting Information).[14]

(*S*)-1-OH was prepared by reduction of 3-nitroacetophenone with (−)-*B*-chlorodiisopinocampheyl-borane [(−)-DIP-chloride].[15] The ^{1}H NMR spectrum determined for the product of this reaction in the presence of a chiral shift reagent showed that the optical purity of the chiral alcohol was essentially 100%.[16,17] This alcohol was converted to **(S)-1-OSO$_2$Tos** by esterification with tosyl chloride.

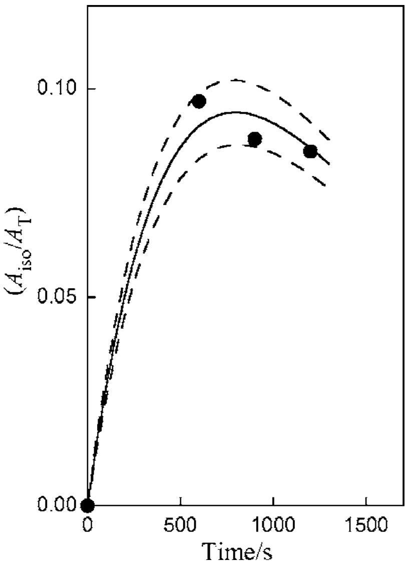


Figure 1. Time course for the formation of isomerization reaction product during solvolysis of **[^{13}C]-1-OS(^{18}O)$_2$Tos** in 50/50 (v/v) TFE/H$_2$O at 25 °C. The solid line shows the nonlinear least-squares fit of the data to eq 1 derived for Scheme 2 using $k_{solv} = 1.04 \times 10^{-3}$ s^{-1} and $k_{iso} = 0.32 \times 10^{-3}$ s^{-1}. The upper and lower dashed lines show the fits obtained using values of k_{iso} that are 10% higher and 10% lower, respectively, than the value from least-squares analysis.

A value of $k_{solv} = 1.04 \times 10^{-3}$ s^{-1} ($t_{1/2}$ = 11 min) for solvolysis of **1-OS(O)$_2$Tos** in 50/50 (v/v) TFE/H$_2$O (80 mol % water) at 25 °C ($I = 0.50$, NaClO$_4$) was determined by monitoring the reaction by UV spectroscopy.[18] The isomerization of **[^{13}C]-1-OS(^{18}O)$_2$Tos** to **[^{13}C]-1-^{18}OS(^{18}O,^{16}O)Tos** under the same reaction conditions was monitored by ^{13}C NMR spectroscopy. Figures S2−S4 in Supporting Information show carbon-13 spectra in the region of the benzylic carbon of **[^{13}C]-1-OS(^{18}O)$_2$Tos** for the remaining substrate determined after reaction times of 10, 15, and 20 min.[19] These spectra show that the disappearance of the peak at 78.92 ppm for the benzylic carbon of the reactant is accompanied by the appearance of a peak at 78.88 for the isomerization reaction product **[^{13}C]-1-^{18}OS(^{18}O,^{16}O)Tos**.

Figure 1 shows the fractional conversion of **[^{13}C]-1-OS(^{18}O)$_2$Tos** to **[^{13}C]-1-^{18}OS(^{18}O,^{16}O)Tos** [A_{iso}/A_T] at different

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(10) (a) The general procedure described in footnote 4 of ref 9 was followed in this synthesis. (b) The general procedure described in footnote 6 of ref 9 was followed.

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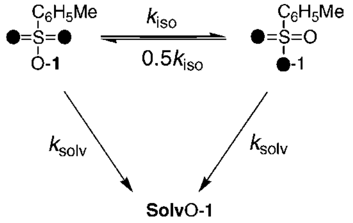
(12) Cl$_2$ gas was bubbled through a solution of *p*-thiocresole (80 mmol) and 5 mL of ^{18}O-water (0.28 mol, 99 atom % escess, ISOTEC, Inc.) for 2 h. The reaction product was extracted into ether, purified by silica gel column chromatography, and recrystallized from benzene/hexane: yield 27%, mp 66.0−67.5 °C.

(13) $3\text{-}NO_2C_6H_4{}^{13}CH(OH)Me$ (5.9 mmol) was dissolved in 2.5 mL of 1,4-dioxane. $4\text{-}MeC_6H_4S(^{18}O)_2Cl$ (1.0 molar equiv) was added at 0 °C, followed by dropwise addition of 5 N NaOH (1.9 mL). The mixture was stirred for 4 h at 0 °C and then poured into water at 0 °C. The crystalline tosylate was collected and recrystallized from ether/hexane: yield 42%, mp 82−85 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (1H, d, $J = 8$ Hz, Ar), 7.93 (1H, dd, $J_{HCCCH} = 2$ Hz, $J_{HCC^{13}C} = 2$ Hz, Ar), 7.63 (2H, A$_2$B$_2$, $J = 8$ Hz, C$_6$H$_4$), 7.57 (1H, m, Ar), 7.44 (1H, t, $J = 8$ Hz, Ar), 7.20 (2H, A$_2$B$_2$, $J = 8$ Hz, C$_6$H$_4$), 5.63 (1H, dq, $J_{HCCH} = 7$ Hz, $J_{H^{13}C} = 150$ Hz, CH(Me)), 2.36 (3H, s, ArCH$_3$), 1.62 (3H, dd, $J_{HC^{13}C} = 4$ Hz, $J_{HCCH} = 7$ Hz, CH(CH$_3$)).

Scheme 2



reaction times t, where A_{iso} is the area of the ^{13}C NMR peak for the benzylic carbon of **[^{13}C]-1-^{18}OS(^{18}O,^{16}O)Tos** and A_T is the total area of the peak for **[^{13}C]-1-OS(^{18}O)$_2$Tos** at $t = 0$. This was calculated as $A_T = (A_S + A_{iso})/\exp(-k_{solv}t)$, where A_S and A_{iso} are the peak areas for the benzylic carbons of **[^{13}C]-1-OS(^{18}O)$_2$Tos** and **[^{13}C]-1-^{18}OS(^{18}O,^{16}O)Tos**, respectively, and $k_{solv} = 1.04 \times 10^{-3}$ s^{-1}.

The solid line in Figure 1 shows the nonlinear least-squares fit of the experimental data to eq 1 derived for Scheme 2

$$\frac{A_{iso}}{A_T} = \left[\frac{2}{3}\right] e^{-k_{solv}t} - \left[\frac{2}{3}\right] e^{-(1.5k_{iso}+k_{solv})t} \qquad (1)$$

using $k_{solv} = 1.04 \times 10^{-3}$ s^{-1} determined by monitoring solvolysis by UV spectroscopy and $k_{iso} = 0.32 \times 10^{-3}$ s^{-1}, which is treated as a variable parameter. The upper and lower dashed lines in Figure 1 show that the experimental data is accommodated by values of k_{iso} that lie within ±10% of the rate constant determined by least-squares analysis. The value of $k_{iso}/k_{solv} = 0.31$ determined for solvolysis of **[^{13}C]-1-OS(^{18}O)$_2$Tos** in TFE/H$_2$O is larger than $k_{iso}/k_{solv} = 0.092$ determined for the reactions of 2-butyl 4-bromobenzensulfonate, labeled with ^{18}O in the nonbridging sulfonate oxygens, in the weakly nucleophilic solvent trifluoroethanol at 30 °C.[20] The existence of the simple secondary 2-butyl carbocation in nucleophilic solvents has been questioned in earlier work.[21] However, the lack of quantitative data for the lifetime of this carbocation in the weakly nucleophilic solvent trifluoroethanol complicates the interpretation of the results from this earlier study of the isomerization of ^{18}O-labeled 4-bromobenzensulfonate.[20]

The enantiomeric composition of **1-OH** formed from solvolysis of (**S**)-**1-OSO$_2$Tos** in 50/50 (v/v) TFE/H$_2$O at 25 °C ($I = 0.50$, NaClO$_4$) was determined by ^{1}H NMR using the chiral shift reagent (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)-ethanol.[16,22] The ratio of the yields of (***R***)-**1-OH** and (***S***)-**1-OH** was determined from the ratio of the peak areas of the benzylic protons for the (*R*)- and (*S*)-enantiomers (Figure S9). Identical product ratios [(***R***)-**1-OH**]/[(***S***)-**1-OH**] = 83/17 were determined for the reactions after 10 and 20 halftimes. This shows that the solvolysis of (**S**)-**1-OSO$_2$Tos** proceeds largely with inversion of configuration at carbon. The rate constant ratio of $k_{MeOH}/k_{TFE} = 2.4$ determined from the ratio of the yields of **1-OMe** and **1-OTFE** from the reaction of **1-OSO$_2$Tos** in 45/5/50 (v/v/v) TFE/MeOH/H$_2$O shows that there is little stabilization of the product-determining step by nucleophilic participation of methanol.[23,24]

There are two possible explanations for our observation of competing solvolysis and isomerization reactions of [**^{13}C**]-**1-OS(^{18}O)$_2$Tos**:

(1) These reactions proceed through a common carbocation−anion pair intermediate, whose lifetime in 50/50 TFE/H$_2$O is long enough to allow for reorganization of the sulfonate oxygens with an estimated rate constant of $k_r \approx 10^{11}$ s^{-1} (Scheme 1).[7] This would require that the rate constant for the addition of solvent to the putative 1-(3-nitrophenyl)ethyl carbocation intermediate be 100-fold smaller than the estimate of $k_s \approx 10^{13}$ s^{-1} from earlier work.[3] The systematic changes from stepwise to concerted mechanisms observed for bimolecular nucleophilic substitution reactions of azide anion, acetate anion, and methanol at ring-substituted 1-phenylethyl chlorides, as the ring substituent is changed from 4-Me to 4-NO$_2$, are consistent with the notion that these changes cause a steady increase in carbocation reactivity.[25]

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(14) Proton-decoupled ^{13}C NMR spectra were recorded at 100.4 MHz. Spectra (ca 1500 transients) at 30 °C used to determine the relative concentrations of the tosylate ester with oxygen-18 bridging and nonbridging were centered at 78.9 ppm and acquired with a 250 Hz sweep width, 8000 data points (0.031 Hz/pt), a 45° pulse angle, and an 8 s relaxation delay time. Chemical shifts are reported relative to ^{13}CDCl$_3$ at $\delta = 77$ ppm.

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(17) (*S*)-(+)-2,2,2-Trifluoro-1-(9-anthryl)ethanol (10−30 mg in 0.6 mL of C$_6$H$_6$) was used as a chemical shift reagent to resolve the benzylic protons of enantiomers of **1-OH** (Figures S5 and S6). The procedure for ^{1}H NMR analysis was as described in ref 16, with decoupling of the benzylic protons of **1-OH** from the methyl protons using an inverse gated coupling procedure. The ^{1}H NMR spectrum for (***S***)-**1-OH** determined in the presence of the shift reagent showed a single peak at 4.08 ppm (Figure S7). A second peak at 4.04 ppm was observed for a mixture of racemic **1-OH** and (***S***)-**1-OH** (Figure S8).

(18) The solvolysis of 1-(3-nitrophenyl)ethyl tosylate was monitored by following the increase in absorbance at 282 nm.

(19) **[^{13}C]-1-OS(^{18}O)$_2$Tos** (30 mg) was dissolved in 1 mL of acetonitrile, and this solution was diluted to 200 mL with 50/50 (v/v) TFE/H$_2$O ($I = 0.5$, NaClO$_4$) to give a final substrate concentration of 0.4 mM. The reaction was incubated at 25 °C for between 10 and 20 min.. The substrate and products were then extracted into 500 mL of diethyl ether and this extract was washed with water and dried over MgSO$_4$. The ether was removed by evaporation, 300 mL of toluene was added to the residue and the toluene was removed by evaporation. The final residue was dissolved in 0.6 mL of CDCl$_3$ and analyzed by ^{13}C NMR.[14]

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(22) (**S**)-**1-OSO$_2$Tos** (30 mg) was dissolved in 1 mL of acetonitrile, and this solution was diluted to 200 mL with 50/50 (v/v) TFE/H$_2$O ($I = 0.5$, NaClO$_4$) to give a final substrate concentration of 0.4 mM. After 2 h (ca. 10 half-lives) and 4 h (ca. 20 half-lives, in a second experiment) the products were extracted into 500 mL of ether, washed with water, dried over MgSO$_4$ and the ether was removed by evaporation. HPLC analysis showed that this reaction gives an 80% yield of **1-OH** and a 20% yield of **1-OTFE**. **1-OH** was purified by HPLC and then dissolved in 0.6 mL of C$_6$D$_6$, and the chiral shift reagent (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol (20−30 mg) was added for ^{1}H NMR analysis at 400 MHz.

(23) The rate constant ratio was determined from the yields of the methanol and trifluoroethanol adducts to **1-OSO$_2$Tos**, as described in earlier work.[24]

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(2) The reaction proceeds by a pathway that avoids formation of a carbocation−anion pair intermediate (k_c, Scheme 1). In this case there is no energy well for the 1-(3-nitrophenyl)ethyl carbocation-tosylate anion pair, and this species lies instead on a flat plateau. The product yields of the solvolysis of **[^{13}C]-1-OS(^{18}O)$_2$Tos** would then be controlled by the direction of movement across this plateau, which may reflect

(a) The dynamics of movement across this flat energy maximum,[26] where the "rate" of exchange in the position of bridging and nonbridging oxygens that leads to formation of isomerization reaction products is about one-third that for movement to form solvolysis products.

(b) The composition of this reactive complex where (i) the larger yield of **1-OH** with inverted compared with retained configuration at carbon would reflect shielding by the leaving group to frontside addition of solvent, and (ii) the larger yield of the methanol (**1-OMe**) compared with the trifluoroethanol (**1-OCH$_2$CF$_3$)** adduct would reflect weak local charge-dipole interactions between nucleophilic and electrophilic species that orient the nonreactive electron-rich CF$_3$ group and the reactive OH group of the trifluoroethanol and methanol nucleophiles, respectively, toward the developing cationic center.[24]

The pathway described here for isomerization of **[^{13}C]-1-OS(^{18}O)$_2$Tos** that avoids formation of a carbocation reaction intermediate has been named "uncoupled concerted",[27] where (i) "concerted" refers to the absence of a reaction intermediate in contrast with stepwise reactions where an intermediate is formed, and (ii) "uncoupled" indicates that bond cleavage, ionic reorganization, and bond resynthesis occur as essentially independent processes. Our data do not exclude the possibility that there is coupling of bond cleavage and bond formation during a concerted isomerization reaction of **1-OS(^{18}O)$_2$Tos**. This coupling will be weak or negligible, provided there is not a large stabilization of the reaction transition state associated with coupling of the two processes for the concerted reaction.[28]

There are related reactions for which there is no intermediate with a vibrational lifetime, *and* no coupling of individual steps in what seem to be multistep reaction processes. These include stereomutation of *cis* and *trans* disubstituted cyclopropanes,[29,30] thermal deazatization of 2,3-diazabicyclo[2.2.1]-hept-2-ene,[31] and thermal interconversion of bicyclo[3.2.0]-hept-2-ene and bicyclo[2.2.1]hept-2-ene.[32] These reactions proceed through unstable diradical-like species that lie at plateaus on energy landscapes in which substrate bonds undergo rotation to a second diradical-like species that collapses to products. We suggest that the framework developed to model such nonpolar reactions might usefully be applied to polar reactions that lie at the "borderline" between stepwise and concerted reaction mechanisms.

Acknowledgment. We acknowledge the National Institutes of Heath grant GM 39754 for generous support of this work.

Supporting Information Available: ^{13}C NMR spectra of **[^{13}C]-1-OS(^{18}O)$_2$Tos** and of the products of solvolysis of **[^{13}C]-1-OS(^{18}O)$_2$Tos** in 50/50 TFE/HOH determined at 10, 15 and 20 min; ^{1}H NMR spectral data for (a) racemic **1-OH** in the absence and presence of shift reagent, (b) **(S)-1-OH** in the presence of shift reagent, (c) a mixture of racemic **1-OH** and **(S)-1-OH** in the presence of shift reagent, (d) **1-OH** from solvolysis of **(S)-1-OS(^{18}O)$_2$Tos** in 50/50 (v/v) TFE/H$_2$O at 25 °C (I = 0.50, NaClO$_4$) in the presence of shift reagent. This material is available free of charge via the Internet at http://pubs.acs.org.

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