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Solvolysis of (*Z*)-5-Trimethylstannyl 2-Adamantyl *p*-Bromobenzenesulfonate: Mechanistic Implications of a Record-Breaking Secondary α-Deuterium Kinetic Isotope Effect for an S_N1 Substrate

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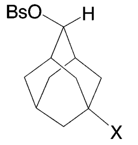
Abstract: The secondary α-deuterium kinetic isotope effect (α-kie) for the solvolysis of (*Z*)-5-trimethylstannyl 2-adamantyl *p*-bromobenzenesulfonate in 97% w/w aqueous 2,2,2-trifluoroethanol (97T) at 25 °C has been measured ($k_H/k_D = 1.33$). The α-kie is abnormally high compared to the value of 1.23 for the corresponding limiting S_N1 solvolysis of 2-adamantyl *p*-bromobenzenesulfonate, which proceeds via an extended ion-pair mechanism. A novel mechanism for the solvolysis of the tin compound is proposed that accommodates not only the high α-kie but also the absence of internal return.

Several years ago, we reported a solvolysis study of (*E*)- and (*Z*)-5-trimethylsilyl (X = $Si(CH_3)_3$) and-trimethylstannyl (X = $Sn(CH_3)_3$)2-adamantyl *p*-bromobenzenesulfonates (**1** and **2**, respectively)[1] in connection with delineating the origin of extended electron-delocalization influences in saturated systems.[2]



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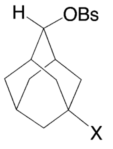

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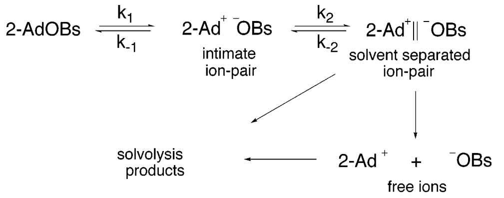
In accordance with expectations of a preferred stereoelectronic requirement for a through-bond transmission mechanism (antiperiplanarity of the participating orbitals, which is met in **1** but not **2**),[3] significantly larger rate accelerations were observed for the σ-electron-donating metalloidal substituents in **1** (factors of 51 and 7000 in 97T for $Si(CH_3)_3$ and $Sn(CH_3)_3$, respectively) versus **2** (factors of 8 and 98 in 97T for $Si(CH_3)_3$ and $Sn(CH_3)_3$, respectively). However, the modest rate accelerations observed for the latter were significantly larger than expected from considerations of the electronic effects of the substituents. We anticipated negligible electrostatic field influences, as the appropriate empirical parameters (σ_F) that characterize this polar effect are effectively *zero* for both $Si(CH_3)_3$ and $Sn(CH_3)_3$.[4] Moreover, significant leakage of extended hyperconjugative effects through the intervening C−C bonds seems to be precluded by the very unfavorable orientation. Thus, since the interpretation of relative rates within a structurally similar series of compounds purely in terms of substituent electronic effects is based on the premise that the mechanism must remain invariant, our suspicions were aroused that a mechanistic change may be responsible.

SCHEME 1



It is now generally agreed that the rate-limiting step in the solvolysis of 2-adamantyl sulfonate esters (**1** or **2**, X = H), long regarded as archetypal S_N1 substrates, is the separation of an initially formed intimate ion pair into a solvent separated ion pair in highly ionizing solvents (Scheme 1).[5] Powerful support for this mechanism comes from oxygen scrambling studies that indicate substantial ion-pair return for 2-adamantyl brosylate.[6] A further important experimental criterion of the mechanism is the particularly large secondary α-deuterium kinetic isotope effect (α-kie; $k_H/k_D \sim 1.23$) observed for the solvolysis of this ester.[7] This is attributed to the fact that in this mechanism, the carbocation is fully formed in the transition state (TS); hence, the α-kie is not significantly suppressed by vestigial bonding between the α-carbon and the oxygen of the departing nucleofuge.[8] For a situation where the latter circumstance is a feature of the TS (e.g., solvolysis of pinacolyl brosylate),[9a] a significantly lower α-kie is observed (ca. 1.16).[9b] Evidence for a change in mechanism in the solvolysis of **2** (X = $Sn(CH_3)_3$) emerged from preliminary findings of a total

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[8] (a) For a summary of references concerning the use of the secondary α-deuterium isotopic effect (α-kie) as a mechanistic probe and, in particular, for characterizing solvolytic reactions of secondary alkyl arenesulfonates, see refs 8b and c. (b) Maskill, H.; Thompson, J. T.; Wilson, A. A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1693 and references therein. (c) Wilgis, F. P.; Neumann, T. E.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4435 and references therein.

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SCHEME 2

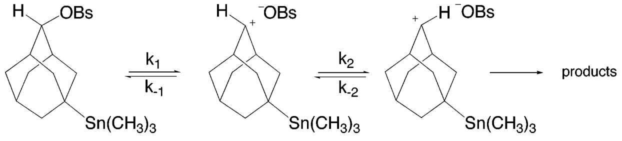
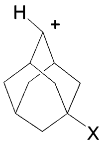


TABLE 1. Solvolysis Rate Constants^{a,b} at 25 °C for 2-Adamantyl Brosylate (1 or 2, X = H), (*Z*)-5-Trimethylstannyl 2-Adamantyl Brosylate (2, X = $Sn(CH_3)_3$), and Their α-Deuterium Isotopomers

compound	k_H	k_D	k_H/k_D
1 or **2**, X = H	0.458	0.375	1.22
2, X = $Sn(CH_3)_3$	44.88	33.81	1.33

[a] First-order rate constants in units of 10^{-5} s^{-1} (experimental error < ±1%). Average values of triplicate measurements. [b] Solvent, 97T.

lack of sulfonyl oxygen scrambling in ^{18}O-labeled **2** (X = $Sn(CH_3)_3$) that was recovered after one half-life of solvolysis.[1,10] This led us to postulate[1] that the acceleration for **2** (X = $Sn(CH_3)_3$) is due to rapid isomerization of the initially formed pyramidal[11] (*Z*)-cation (**3**, (X = $Sn(CH_3)_3$) to the more stable (*E*)-cation (**4** (X = $Sn(CH_3)_3$), thereby reducing internal return[12] (Scheme 2; $k_2 \gg k_{-1}$), i.e., the initial ionization step is now rate-determining.



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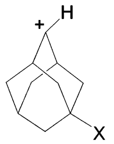

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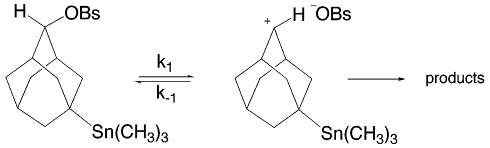
SCHEME 3



We sought confirmation of this proposal by measurement of the α-kie of **2** (X = $Sn(CH_3)_3$) based on reasoning that if ionization is indeed rate-limiting (Scheme 2), then a considerably lower α-kie value should be observed, being similar to that for pinacolyl brosylate[9] rather than that for the parent (**2**, X = H). In Table 1 are listed solvolysis rate constants at 25 °C for 2-adamantyl brosylate (**1** or **2**, X = H), (Z)-5-trimethylstannyl-2-adamantyl brosylate (**2**, X = $Sn(CH_3)_3$), and their α-deuterium isotopomers. The rate constants in 97% aqueous 2,2,2-trifluoroethanol (97T) at 25 °C were determined conductometrically (see Experimental Section). The k_H values are within experimental error of those previously reported.[1] Further, the α-kie (k_H/k_D) for the parent brosylate (**1** or **2**, X = H) is in good agreement with the literature value ($k_H/k_D \sim 1.23$).[7] Most importantly, it can be seen (Table 1) that the α-kie for the (*Z*)-disposed tin-substituted compound is not in accordance with a lower value relative to the parent as expected from the proposed mechanism in Scheme 2. In fact, it is significantly larger than the value for the parent. Moreover, to the best of our knowledge, it is the largest α-kie ever observed for a limiting S_N1 solvolysis reaction of a secondary alkyl arene sulfonate ester. We believe the surprisingly high α-kie is best accommodated by a mechanism whereby an essentially barrierless inversion at the reaction center (C2) occurs concomitantly with ionization in the rate-determining first step (Scheme 3). At the transition state for this pathway, it can be envisaged that the motion of the C−H(D) along the reaction coordinate ensures additional loss of zero-point energy from the out-of-plane C−H(D) bending vibration at the α-carbon. The latter vibration is considered to be largely responsible for the α-kie phenomenon.[8] It is noteworthy that similar to the originally proposed mechanism[1] (Scheme 2), the counterion ion ($^{-}$OBs) associated with the (*E*)-cation in the new mechanism (Scheme 3) is hindered from recombination with the electron-deficient center, hence, marginalizing internal return. However, the lack of internal return in **2** (X = $Sn(CH_3)_3$) is not necessarily the sole explanation for the accelerative effect of the $Sn(CH_3)_3$ group (see above). The new mechanistic proposal (Scheme 3) suggests that at the TS, it is not unreasonable to expect that stabilizing extended hyperconjugative interactions might be sufficiently "switched-on", in a less than optimal orientation, to be largely responsible for the aforementioned kinetic effect.

A notable feature of the mechanism outlined in Scheme 3 is the absence of the Z-cation (**3**, X = $Sn(CH_3)_3$) as a discrete intermediate. This agrees with the products of solvolysis (fragmentation and substitution)[1,4] of **2** (X = $Sn(CH_3)_3$), which appear to be mediated exclusively by the (*E*)-cation (**4**, X = $Sn(CH_3)_3$). To illuminate the picture further, molecular orbital (MO) calculations were carried out in C_1 symmetry on the 5-trimethylstannyl-2-adamantyl cation system, employing the hybrid B3LYP method and a 6-31G* basis set for the light atoms.[13] The valence double ζ pseudopotential basis of Hay and Wadt[14] was used for Sn, supplemented by a single set of d-functions.

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(9) (a) Pinacolyl brosylate is an archetypal S_N1 substrate that reacts with rate-limiting ionization[9b] with no internal return.[6] Recent results[8c] confirm that it ionizes without methyl participation in the rate-determining step and that methyl migration occurs rapidly after formation of the secondary tight ion pair. (b) Shiner, V. J., Jr.; Fisher, R. D.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 7748.

(10) (a) Minimum fraction of return ($k_{eq}/k_{eq}+k_t$) for 2-adamantyl brosylate and the 5-substituted(X) metalloidal derivatives are as follows[10b,c]: 0.54 (**1** or **2**, X = H.; 80E), 0.66 (**1**, X = $Si(CH_3)_3$; 70E), 0.55 (**1**, X = $Sn(CH_3)_3$; 90E), 0.35 (**2**, X = $Si(CH_3)_3$; 70E), 0.00 (**2**, X = $Sn(CH_3)_3$; 70E). (b) Taken from ref 10d. (c) Oxygen-18 scrambling studies were performed according to the procedure outlined in ref 8c. (d) Coope, J. Ph.D. Dissertation, Indiana University, Bloomington, Indiana, 1990.

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TABLE 2. Relative Hydride Affinities (ΔE)[a] of (E)-Cations (4)

structure	ΔE
4 (X = H)	0.00
4 (X = Si(CH$_3$)$_3$)	−9.64
4 (X = Ge(CH$_3$)$_3$)	−10.06
4 (X = Sn(CH$_3$)$_3$)	−14.33

[a] Effects of substituents on the energy (kcal/mol) of the following isodesmic reaction: $\mathrm{HAd^+ + XAdH \rightarrow HAdH + XAd^+}$. See Supporting Information for B3LYP/6-31G* calculated energies and zero-point energies (ZPE) of the various structures. The ΔE values were determined using 0.98ZPE corrected energies.

In previous calculations of a number of 5-substituted(X) 2-adamantyl cations,[15] two minima have generally been located, corresponding to (E)- and (Z)-cation geometries (facially selective C−C hyperconjugation). For **3** and **4** (X = Sn(CH$_3$)$_3$), input geometries were constructed that resembled the (Z)- and (E)- geometries, respectively. However, on optimization, the same structural minimum was found in both cases, having the (E)- configuration. Similar results (only one (E)-cation minimum) have also been found in calculations of the X = Si(CH$_3$)$_3$ and Ge(CH$_3$)$_3$ cations.

The calculated structures of the metalloidal-substituted (E)-cations are quite distorted: the C1−C2−C3 bridge is bent toward the substituent by 17.4° (Si), 16.2° (Ge), and 16.0° (Sn), and the C-2 hydrogen is further bent by 12.7° (Si), 11.6° (Ge), and 13.2° (Sn) in the same direction. These distortions allow for better overlap of the C$^+$ p-orbital with the C1−C9 and C3−C4 bonds and, aided by the metalloidal atom substituent, result in extremely long C−C bonds (1.674 (Si), 1.674 (Ge), and 1.698 Å (Sn)) as well as very long C−X bonds (1.997 (Si), 2.052 (Ge), 2.303 Å (Sn)) compared to normal values. The corresponding opposite face C−C bonds are normal (1.544 (Si), 1.547 (Ge), and 1.545 Å (Sn)) as are the C−X bonds in the corresponding neutral hydrocarbons (1.924 (Si), 1.976 (Ge), and 2.192 Å (Sn)). These geometric parameters are clear manifestations of an extended hyperconjugative interaction as originally proposed.[1] The relative hydride affinities listed in Table 2 clearly exemplify the pronounced stabilizing effects of the metalloidal substituents on the (E)-cation (**4**) in the expected order (X = Sn ≫ Ge ∼ Si).[1,2,16] A notable consequence of the considerable stabilization of the (E)-cation is the significant lowering of the activation barrier ($\Delta E^{\ddagger}$) for the isomerization of the (Z)- to the (E)-cation. The transition-state energy (gas-phase) calculated for the epimerization of the parent ion (**3** or **4**; X = H) is very small (($\Delta E^{\ddagger}$ = 2.02 (MP2/6-31G* + ZPVE 6-31G)[11] and 1.31 kcal/mol (B3LYP/6-31G* + ZPVE 6-31G*)).[17] Thus, it is plausible that the gas-phase (Z)-cation (**3**, X = Si(CH$_3$)$_3$, Ge(CH$_3$)$_3$, or Sn(CH$_3$)$_3$) minimum could vanish, in agreement with the calculated result. Interestingly, application of the SCI-PCM solvation simulation model[18,19] at the B3LYP/6-31G* basis set level to compute the optimized structures of the 5-trimethylsilyl-2-adamantyl cation system, using a dielectric constant of 80, leads to two minima ((E)- and (Z)-) being located on the potential energy surface. The (Z)-cation is 2.96 kcal/mol less stable than the (E)-species. This is in qualitative agreement with the experimental results (product and oxygen-18 scrambling studies),[1,4,10] which suggest a significant lifetime for the (Z)-cation in solution.[20] Due to basis set constraints, the SCI-PCM solvation model could not be applied similarly to the corresponding tin system.

Experimental Section

Preparation of Brosylates (2, X = Sn(CH$_3$)$_3$; 1 or 2, X = H) and Their α-Deuterium Isotopomers. By use of a modified literature procedure,[21] a solution of the appropriate alcohol (ca. 2.5 mmol) in THF (7.0 mL) was added to a suspension of KH (0.03 g) in THF (5.0 mL) containing 18-crown-6 (0.07 g), and the mixture was heated to reflux. After 24 h, p-bromobenzenesulfonyl chloride (0.07 g, 2.8 mmol) was added and heating was then continued for an additional 24 h. The reaction mixture was cooled before the reaction was quenched with ice−water and extracted with CH$_2$Cl$_2$. The extract was dried (MgSO$_4$) and evaporated in vacuo to afford the crude product, which was purified by column chromatography (silica gel, 10% ethyl acetate−hexane as the eluent). The yields varied (70−80%) but in general were much higher than those obtained (10−15%) by the previously deployed[1] modified procedure of Tipson.[22] The physical properties and NMR spectra of the known brosylates were in accordance with those previously reported.[1,23] Those for the α-isotopomer of **2** (X = Sn(CH$_3$)$_3$) are given below.

(Z)-2-Deuterio-5-trimethylstannyladamantan-2-ol: mp = 107−108 °C; ^{1}H NMR (CDCl$_3$) δ 2.27−2.23 (2H, m), 1.94−1.62 (12H, m), −0.05 (9H, s; J^{117}Sn, J^{119}Sn = 49.99, 48.07 Hz); ^{13}C NMR (CDCl$_3$) δ 74.1(C2, $J_{\mathrm{C-D}}$ = 22.0 Hz), 42.0 (C6, J^{117}Sn, ^{119}Sn = 11.0 Hz), 36.6 (C8,10), 35.2 (C4,9), 35.2 (C1,3; J^{117}Sn, ^{119}Sn = 48.5 Hz), 27.8 (C7, J^{117}Sn, ^{119}Sn = 50.1 Hz), 27.0 (C5), −13.1 (CH$_3$, q; J^{117}Sn, ^{119}Sn = 294.8, 281.4 Hz).

(Z)-2-Deuterio-5-trimethylstannyladamantyl *p*-Bromobenzenesulfonate: mp = 113−114°C; ^{1}H NMR (CDCl$_3$) δ 7.77-(2H, d), 7.68 (2H, d), 2.16 (2H, d), 1.95−1.60 (11H, m), −0.05 (9H, s, J^{117}Sn, J^{119}Sn = 50.45, 48.42 Hz); ^{13}C NMR (CDCl$_3$) δ 137.1, 132.5, 129.0, 128.4, 87.1 (C2), 41.5 (C6, J^{117}Sn, ^{119}Sn = 10.2 Hz), 36.5 (C8,10), 35.4 (C4,9), 33.2 (C1,3; J^{117}Sn, ^{119}Sn = 47.9 Hz), 27.2 (C7, J ^{117}Sn, ^{119}Sn = 49.5 Hz), 25.9 (C5), −13.0 (CH$_3$, q; J^{117}Sn, ^{119}Sn = 300.6, 287.2 Hz).

Kinetic Measurements. The rate constants were determined conductometrically at 25 °C in 97T using a bipolar pulsed-conductance (BIPCON) instrument.[24] The solutions were un-

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[17] This study. All the structures were fully optimized, and analytical frequency calculations were performed on the minima and transition state to ensure N_{imag} = 0 and 1, respectively.

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[20] Fact that the (Z)-silyl compound (**2**, X = Si(CH$_3$)$_3$) undergoes oxygen scrambling[10] supports the existence of the barrier to inversion as revealed by the calculations. However, the extent of equilibration is less than that in the parent compound (**1** or **2**, X = H). Presumably, the mechanism of solvolysis of **2** (X = Si(CH$_3$)$_3$) involves the formation of the (Z)- tight ion pair, which may undergo internal return or competitively invert to the (E)- ion pair.

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buffered at concentrations of 1.0−2.0 mM L^{-1}. To ensure reproducibility of the experimental conditions, k_H and k_D were measured at the same time using identical conditions. Temperature control was within ±0.01 °C.

Acknowledgment. We are grateful to the Australian Research Council for partial financial support of this work. Further, we wish to thank Dr. Ian R. Milne for assistance with the BIPCON equipment and Carolyn Diane Dzierba (Indiana University) for some preliminary experimentation.

Supporting Information Available: General experimental information, including syntheses of the alcohols; ^{1}H and ^{13}C NMR spectra for (*Z*)-2-deuterio-5-trimethylstannyladamantan-2-ol and (*Z*)-2-deuterio-5-trimethylstannyl-2-adamantyl *p*-bromobenzenesulfonate; and (Table S1) electronic energies and zero-point vibrational energies (ZPVE) obtained from DFT calculations (B3LYP/6-31G*) for (*E*)-5-substituted(X) 2-adamantanyl cations and their corresponding neutral hydrocarbons. This material is available free of charge via the Internet at http://pubs.acs.org.

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