

CORRELATION OF THE RATES OF SOLVOLYSIS OF THE  
2-(2-ADAMANTOXYSULFONYL)-N, N, N-TRIMETHYLETHANAMINIUM  
(2-ADAMANTYL [2]BETYLATE) ION

DENNIS N. KEVILL AND RICHARD W. BAHNKE

Department of Chemistry, Northern Illinois University  
DeKalb, Illinois, 60115 USA

(Received in USA 5 April 1988)

**Abstract** - Despite the remote positive charge within the leaving group, the specific rates of solvolysis at 25.0°C of the 2-(2-adamantoxysulfonyl)-N, N, N-trimethylethanaminium ion ( $2\text{AdOSO}_2\text{CH}_2\text{CH}_2\text{NMe}_3^+$ ) in 28 pure and mixed hydroxylic solvents have been found to correlate, in a linear free energy relationship plot, very well with  $\text{YOT}_s$  values (slope of 1.032, correlation coefficient of 0.991). In 50% ethanol, the specific rates of solvolysis are virtually identical for 1 and 2-adamantyl 2,2,2-trifluoroethanesulfonate; for substitution in the methyl of the ethanesulfonate leaving group, one  $\text{NMe}_3^+$  group has the same influence as three fluorine atoms.

Since its introduction<sup>1</sup> in 1948, the Grunwald-Winstein equation (1) has been

$$\log (k/k_0) = \rho Y \quad (1)$$

widely used for the correlation of the specific rates of solvolysis of  $\text{S}_{\text{N}}1$  reactions and, also, the magnitude of  $\rho$  has been used as a mechanistic criterion for unimolecular ( $\rho \sim 1$ ) or bimolecular ( $\rho < 1$ ) reaction. For systems, such as simple secondary alkyl derivatives, considered borderline on the basis of other criteria, intermediate values for  $\rho$  are usually observed.<sup>2</sup> In equation 1,  $k$  represents the specific rate of solvolysis of a substrate in the solvent under consideration,  $k_0$  represents the specific rate of solvolysis of that substrate in 80% ethanol, and  $\rho$  represents the sensitivity of the specific rate of solvolysis to changes in solvent ionizing power  $Y$ .

To correlate the specific rates of  $S_N2$  solvolyses, Grunwald, Winstein, and Jones<sup>3</sup> proposed a two-term linear free energy relationship (eqn. 2), where the

$$\log(k/k_0) = \rho N + \rho' Y \quad (2)$$

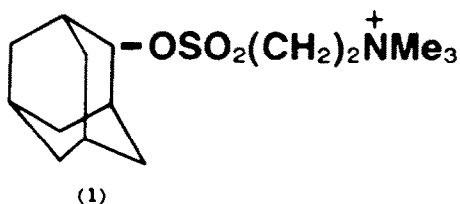
additional term represents the sensitivity  $\rho'$  of the specific rate of solvolysis to changes in solvent nucleophilicity  $N$ . Scales of solvent nucleophilicity based upon the solvolysis of methyl *p*-toluenesulfonate<sup>4</sup> or the triethyloxonium ion<sup>5,6</sup> are available.

The original  $Y$  scale was based upon the solvolysis of *tert*-butyl chloride. While this scale has given excellent service over the last forty years, there are strong indications that a nucleophilic component ( $\rho'$  value of about 0.3) is involved.<sup>6-11</sup> It has been suggested that 1-adamantyl<sup>12</sup> or 2-adamantyl<sup>13,14</sup> derivatives, where backside attack is blocked or severely hindered, constitute excellent substrates for the development of  $Y$  scales. It has been proposed<sup>4,8,15-21</sup> that different anionic leaving groups ( $X^-$ ) each require an individual  $Y_X$  scale, for use in the correlation of the specific rates of solvolysis of a  $RX$  substrate. For relatively poor leaving groups,  $Y_X$  values are more conveniently obtained using the 1-adamantyl derivatives ( $X = Cl^8, Br^8, I^8, OC_6H_2(NO_2)_3^{20}, CO_2CF_3^{21},$  and  $CO_2C_3F_7^{21}$ ) and, for better leaving groups,  $Y_X$  values are conveniently obtained using the about  $10^5$  times slower reacting<sup>22,23</sup> 2-adamantyl derivatives ( $X = OTs^{4,15,16}, OTf^{19,20}, OCIO_3^{17,20},$  and  $OSO_2C_6F_5^{24}$ ). While large deviations do indeed exist (for example, for solvolyses in 95% acetone,<sup>17</sup> the  $Y_{OTs}$  value is -2.95 and the  $Y_{OCIO_3}$  value is -0.23), there are several leaving groups for which, for most mixed-solvent systems, the  $Y_X$  values correlate quite well with the original adamantyl-based scale ( $Y_{OTs}$ ) with a slope not far removed from unity. Among the causes of the deviations are differences in electrostatic and/or electrophilic solvation, in lipophilic effects, and in the solvation of aryl and alkyl groups.<sup>20</sup>

In contrast to scales based upon 1- and/or 2-adamantyl derivatives with initially neutral leaving groups (leaving as an anion), studies of the 1-adamantyldimethylsulfonium ion<sup>6</sup> and the 1-adamantylpyridinium ion<sup>25</sup> (in which an initially positively charged leaving group leaves as a neutral molecule) show extremely modest rate variations with change in solvent composition. For the 1-adamantyldimethylsulfonium ion, a rate variation of less than seven was observed across a range of solvents for which a rate variation of about  $10^6$  was observed for adamantyl derivatives with initially neutral leaving groups. These findings are consistent with the qualitative theory of solvent effects, put forward by Hughes and Ingold,<sup>26</sup> for reactions

producing charges (large effects) and dispersing charges (small effects) in going from the ground state to the transition state.

In the present study we have considered a salt, 2-(2-adamantoxysulfonyl)-N,N,N-trimethylethanaminium trifluoromethanesulfonate (2-adamantyl [2]betylate triflate). Although this salt contains a cation (1) of the R-X<sup>+</sup> type, during solvolysis charge is developed in the same manner as for the adamantyl derivatives containing initially neutral leaving groups; the leaving group is the zwitterion (<sup>+</sup>Me<sub>3</sub>NCH<sub>2</sub>-CH<sub>2</sub>SO<sub>3</sub><sup>-</sup>, 2). One would predict, on the basis of the qualitative Hughes-Ingold theory of solvent effects,<sup>26</sup> large variations in the specific rates of solvolysis upon varying the solvent composition. It will be of interest to see to what extent a "remote" positive charge influences the logarithmic correlation of the specific rates of solvolysis against the X<sub>OTs</sub> scale, a scale based upon an initially neutral sulfonate leaving group.



A series of [2]betylates, with simple alkyl groups have been prepared in the presence of non- or weakly-nucleophilic counterions and they have been found to be good water-soluble alkylating agents.<sup>27,28</sup> The more recent synthetic procedure<sup>28</sup> can be utilized for the preparation of 1 as its trifluoromethanesulfonate salt. Several related amylates [alkyl g-(trimethylammonio)benzenesulfonate ions] have also been prepared<sup>29</sup> and their hydrolyses briefly studied.<sup>30</sup>

## RESULTS

The specific rates of solvolysis of the cation 1, to produce the zwitterion 2, protonated solvent, and ether or alcohol (or a mixture of the two), have been determined at 25.0°C in the following aqueous-organic mixtures: 90-40% ethanol (six compositions), 100-90% methanol (two compositions), 90-40% acetone (six compositions), 100-70% 2,2,2-trifluoroethanol (TFE) (five compositions), 90-70% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (three compositions). The average values, using all of the integrated first-order rate coefficients from duplicate runs, are reported within Table 1, together with X<sub>2Ad[2]B</sub> values (calculated according to equation 3) and X<sub>OTs</sub> values.<sup>4,15,16,17,31</sup>

$$\log(k/k_0)_{2AdOSO_2CH_2CH_2NMe_3^+} = X_{2Ad[2]B} \quad (3)$$

TABLE 1. First-order rate coefficients for the solvolysis of the 2-(2-adamantoxysulfonyl)-N, N, N-trimethylethanaminium ion<sup>a, b</sup> in pure and aqueous organic solvents at 25.0°C and  $X_{2Ad[2]B}$ <sup>c</sup> and  $X_{OTs}$ <sup>d</sup> values.

Solvent <sup>e</sup>	$10^6 k, s^{-1}$	$X_{2Ad[2]B}$	$X_{OTs}$
90% EtOH	0.631 ± 0.008	-0.763	-0.58
80% EtOH	3.66 ± 0.03	0.000	0.00
70% EtOH	13.1 ± 0.1	+0.554	+0.47
60% EtOH	35.9 ± 0.5	+0.992	+0.92
50% EtOH	95.3 ± 2.9	+1.416	+1.29
40% EtOH	262 ± .	+1.855	+2.08 <sup>f</sup>
100% MeOH	0.136 ± 0.005	-1.430	-0.92
90% MeOH	1.01 ± 0.02	-0.559	-0.17 <sup>f</sup>
90% Acetone	0.0687 ± 0.0015	-1.730	-1.708 (-1.99) <sup>h</sup>
80% Acetone	0.728 ± 0.004	-0.701	-0.798 (-0.94) <sup>h</sup>
70% Acetone	3.19 ± 0.04	-0.060	-0.01 <sup>i</sup> (-0.33) <sup>i</sup>
60% Acetone	11.8 ± 0.2	+0.508	+0.66
50% Acetone	38.9 ± 1.4	+1.026	+1.26 <sup>f</sup>
40% Acetone	120 ± 4	+1.516	+1.85 <sup>f</sup>
100% TFE	196 ± 3	+1.729	+1.80
97% TFE	197 ± 4	+1.731	+1.83
90% TFE	198 ± 4	+1.733	+1.87 <sup>i</sup>
80% TFE	207 ± 6	+1.752	+1.95 <sup>i</sup>
70% TFE	227 ± 5	+1.793	+2.00
90% HFIP	4557 ± 3	+3.095	+2.90 <sup>j</sup>
80% HFIP	1746 ± 3	+2.679	+2.57 <sup>i, j</sup>
70% HFIP	1103 ±	+2.479	+2.41 <sup>i, j</sup>

<sup>a</sup>Concentration of SA, 0.004 M. <sup>b</sup>With associated standard deviations.

<sup>c</sup> $\log(k/k_0)$  at 25.0°C, where  $k_0$  refers to the first-order rate coefficient in 80% ethanol. <sup>d</sup>Values from reference 4, unless otherwise indicated. <sup>e</sup>Percentage of organic solvent by volume for aqueous-ethanol, -methanol, and -acetone and percentage of organic solvent by weight for aqueous-2,2,2-trifluoroethanol (TFE) and aqueous-1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). <sup>f</sup>Values from reference 15b.

<sup>g</sup>Calculated from  $X_{OTs} = -0.868 \log(k/k_0)_{1-AdOTs} + 0.027$  (equation from reference 32). <sup>h</sup> $\log(k/k_0)_{1-AdOTs}$  (references 15b and 17). <sup>i</sup>Interpolated value.

<sup>j</sup>Values from reference 16.

The specific rates of solvolysis have also been determined for four TFE-ethanol compositions, and the average values are reported (together with  $X_{2Ad[2]B}$  values) in Table 2;  $X_{OTs}$  values are not available for this mixed solvent system.

## DISCUSSION

It can readily be seen, from the data of Table 1, that the first-order rate coefficients vary enormously with the solvent composition. This behavior is in marked contrast to the very small rate variations observed for the 1-adamantylidimethylsulfonium and 1-adamantylpyridinium<sup>25</sup> ions. A large variation is to be

TABLE 2. First-order rate coefficients for the solvolysis of the 2-(2-adamantoxysulfonyl)-N,N,N-trimethylethanaminium ion<sup>a,b</sup> in ethanol-2,2,2-trifluoroethanol mixtures at 25.0°C and  $\chi_{2Ad[2]B}$ <sup>c</sup> values.

Solvent <sup>d</sup>	$10^6 k, s^{-1}$	$\chi_{2Ad[2]B}$
80% TFE - 20% EtOH	28.8 ± 0.2	+0.896
60% TFE - 40% EtOH	4.65 ± 0.03	+0.104
40% TFE - 60% EtOH	0.731 ± 0.021	-0.700
20% TFE - 80% EtOH	0.135 ± 0.002	-1.433

<sup>a-c</sup>See Table 1. <sup>d</sup>On volume-volume basis.

expected on the basis of the Hughes-Ingold theory<sup>26</sup> for a reaction proceeding with charge development in the slow step (equation 4). Indeed, inspection of Table 1



shows that, for any given solvent composition, the  $\chi_{2Ad[2]B}$  value resembles closely the  $\chi_{OTs}$  value. The two sets of  $\chi$  values presented in Table 1 are plotted in the figure.

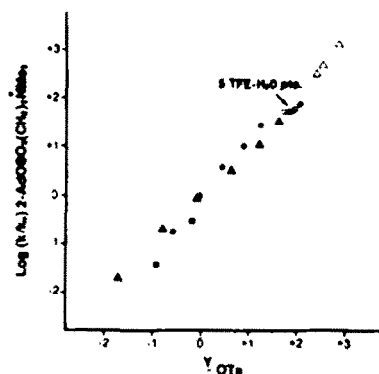


Figure. Plot of  $\log(k/k_0)_{2AdOSO_2CH_2CH_2NMe_3^+}$  ( $\chi_{2Ad[2]B}$ ) against  $\chi_{OTs}$ : closed circles: aqueous ethanol; open circles: aqueous TFE; closed triangles: aqueous acetone; open triangles: aqueous HFIP; closed squares: aqueous methanol.

In the figure,  $\chi_{OTs}$  values for 90 and 80% acetone are based directly upon 1-adamantyl p-toluenesulfonate solvolysis.<sup>17,31</sup> Allard and Casadevall<sup>32</sup> have suggested, however, that, for use in conjunction with  $\chi_{OTs}$  values based on 2-adamantyl p-toluenesulfonate solvolysis,  $\chi_{OTs}$  values of this type are better obtained using equation 5. When all 28 solvents of Table 1 are considered,

$$Y_{OTs} = 0.868 \log(k/k_0)_{1-AdOTs} + 0.027 \quad (5)$$

a slope ( $\rho$  value) of 1.032 is obtained when  $Y_{OTs}$  values for 90, 80, and 70% acetone based on equation 5 are used, and the  $\rho$  value is 0.987 when these values are based directly on the 1-adamantyl tosylate specific solvolysis rates (Table 3).

Individual solvent mixtures also give  $\rho$  values fairly close to unity, ranging from 0.90 for aqueous acetone to 1.26 for aqueous HFIP. For aqueous TFE, the points were closely bunched together and a meaningful slope could not be obtained. It must be concluded that the kinetic solvolytic behavior of sulfonate esters with a remote positive charge mimics closely that of the more familiar uncharged sulfonate esters. The relatively high solubility of betylates<sup>28</sup> or ansylates<sup>30</sup> in highly aqueous media presents a way of conveniently obtaining  $Y$  scales for sulfonate esters over the full range of aqueous-organic solvent composition, without the solubility problems<sup>15,17,20</sup> which often plague studies of neutral sulfonate esters. The very weakly nucleophilic triflate has been found to be a convenient counterion.<sup>33</sup>

TABLE 3. Correlation of  $Y_{2Ad[2]B}$  values with  $Y_{OTs}$  values.<sup>a</sup>

System (n) <sup>b</sup>	Slope ( $\rho$ value)	Intercept	$r^c$
90-40% EtOH (6)	0.999	-0.020	0.988
100-90% MeOH (2)	1.161	-0.362	
90-40% Acetone (6) <sup>d</sup>	0.899	-0.097	0.998
90-40% Acetone (6) <sup>e</sup>	0.821	+0.023	0.996
90-70% HFIP (3)	1.258	-0.552	1.000
All (28) <sup>d</sup>	1.032	-0.126	0.991
All (28) <sup>e</sup>	0.987	-0.047	0.987

<sup>a</sup>Data from Table 1. <sup>b</sup>Number of data points. <sup>c</sup>Correlation coefficient.

<sup>d</sup>Using  $Y_{OTs}$  values for 90 and 80% acetone calculated as in footnote g of Table 1.

<sup>e</sup>Using  $Y_{OTs}$  values for 90 and 80% acetone calculated as in footnote h of Table 1.

Combining the present results with data from the literature, it is possible to compare the solvolyses of three 2-adamantyl sulfonate esters of the type  $2AdOSO_2CH_2X$ , where X is H<sup>15</sup>, CF<sub>3</sub><sup>34</sup>, or CH<sub>2</sub>NMe<sub>3</sub><sup>†</sup> (the present study); specific rates of solvolysis in 50% ethanol at 25.0°C are  $0.096 \times 10^{-5}s^{-1}$  for X = H (extrapolated<sup>15a</sup> from data at higher temperatures),  $8.17 \times 10^{-5}s^{-1}$  for X = CF<sub>3</sub><sup>34</sup>, and  $9.53 \times 10^{-5}s^{-1}$  for X = CH<sub>2</sub>NMe<sub>3</sub><sup>†</sup> (Table 1). In terms of substitution within the methyl group of 2-adamantyl ethanesulfonate, one trimethylamino group has almost exactly the same influence as three fluorine atoms. In terms of substitution within the methyl group of 2-adamantyl methanesulfonate, both a CF<sub>3</sub> and a CH<sub>2</sub>NMe<sub>3</sub><sup>†</sup> group produce very close to a one hundred fold increase in the rate of solvolysis. For

the presumably  $S_N2$  hydrolysis of butyl [2]betylate at 35.0°C, the specific rate was 16 times that estimated from data<sup>35</sup> for butyl methanesulfonate hydrolysis.<sup>28</sup> That the betylate/mesyate rate ratio is higher for a solvolysis of the 2-adamantyl esters than for a solvolysis of the butyl esters is to be expected from the previously observed<sup>23</sup> larger leaving group effects for the ethanolysis of a series of sulfonate esters when the  $S_N1$  rather than the  $S_N2$  mechanism operates.

Supporting the proposal that the solvolyses of 2-adamantyl sulfonate esters with a remote positive charge parallel closely the solvolytic behavior of uncharged sulfonate esters, it has been shown<sup>36</sup> that the product partitioning during solvolysis in a 2,2,2-trifluoroethanol-ethanol mixture is virtually identical for the 2-adamantyl mesyate ion<sup>36</sup> and 2-adamantyl *p*-toluenesulfonate.<sup>37</sup>

## EXPERIMENTAL

**Materials.** The purifications of acetone,<sup>31</sup> ethanol,<sup>31</sup> methanol,<sup>31</sup> 1,1,1,3,3,3-hexafluoro-2-propanol,<sup>38</sup> and 2,2,2-trifluoroethanol<sup>39</sup> were as previously described. 2-Adamantanol (Aldrich), 2-chloroethanesulfonyl chloride (Aldrich) and methyl trifluoromethanesulfonate (Aldrich) were used as supplied.

**2-Adamantyl ethenesulfonate.** Following a previously reported general procedure,<sup>28</sup> 2-Adamantanol (3.05 g, 0.020 mol) was dissolved in 150 ml of ice-cold  $CH_2Cl_2$  and 2-chloroethanesulfonyl chloride (6.52 g) and ice-cold  $Et_3N$  (7.08 g) were added. After 30 min, the mixture was washed with cold 10% aqueous  $Na_2CO_3$  (3 x 100 mL) and  $H_2O$  (100 mL). The  $CH_2Cl_2$  layer was dried (anhyd.  $MgSO_4$ ) and the solvent evaporated. The crude product (3.98 g, 82%) was used without further purification;  $^1H$  NMR ( $CDCl_3$ )  $\delta_A$ 6.56,  $\delta_B$ 6.39,  $\delta_C$ 6.06 (each 1 H):  $J_{AB}$  = 16.6 Hz and  $J_{AC}$  = 9.6 Hz, 4.74 (s,  $CHOSO_2CH=CH_2$ ), 2.2-1.2 (m, 14 H).

**2-(2-Adamantoxysulfonyl)-N,N,N-trimethylethanaminium trifluoromethanesulfonate(2-adamantyl [2]betylate triflate).** 2-Adamantyl ethenesulfonate (0.727 g; 3.0 mmol) was dissolved in 25 ml of ice-cold  $CH_2Cl_2$  and  $Me_2NH$  (1 mL) was added. After 10 min, the solvent and excess  $Me_2NH$  were removed by evaporation. The resulting 2-adamantyl 2-(dimethylamino)ethanesulfonate was immediately dissolved in  $CH_2Cl_2$  (25 mL) and methyl trifluoromethanesulfonate (0.37 mL, 1.1 equiv) was added. After 15 min, the solvent was evaporated and the residue triturated with ether. Filtration gave a solid product (0.95 g; 70%); mp 122-130° (dec). Several batches were prepared and used directly in the kinetic runs. Recrystallization of a portion from acetonitrile gave an off-white solid: mp 125-130° (dec);  $^1H$  NMR ( $CD_3CN$ )  $\delta$ 4.96 (s, 1 H), 3.72 (s, 4 H), 3.11 (s, 9 H), 2.3-1.6 (m, 14 H); IR  $\nu_{max}$  (KBr) includes strong peaks at 1255, 1168, 1032, 918  $cm^{-1}$ . Anal. Calcd for  $C_{16}H_{28}NO_6F_3S_2$ : C, 42.56; H, 6.25; N, 3.10. Found: C, 42.51; H, 6.38; N, 3.21.

Kinetic Procedures. The kinetic runs were carried out by removing, at suitable time intervals, 5 mL portions from 30 mL of solution, except for the runs in HFIP-containing solvents, when 1 mL portions were removed from 10 mL of solution. The portions were quenched by addition to 25 mL of acetone, cooled to solid CO<sub>2</sub>-acetone slush temperature and containing Lacmoid (resorcinol blue) indicator. The acid previously produced was titrated against a standardized solution of sodium methoxide in methanol. First-order rate coefficients were calculated from the integrated form of the rate equation and all values from duplicate runs were averaged to give the values reported in Tables 1 and 2. For runs with half lives of longer than 16 h, the time to ten half lives (infinity titer) was reduced by addition of a portion to 5 mL of water and allowing to stand overnight at 50° prior to addition of the 25 mL of acetone and titration in the usual manner.

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