

## Kinetics and Mechanism of Tetrazole Formation from 1-Adamantyl Arenesulfonates in Acetonitrile Containing Azide Ion<sup>1</sup>

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The reactions of seven 1-adamantyl arenesulfonates with 0.12–0.48 *M* solutions of tetraethylammonium azide in acetonitrile give predominantly (>80%) 1-(1-adamantyl)-5-methyltetrazole (by solvolysis followed by 1,3-addition of azide ion) and smaller amounts of the direct substitution product, 1-adamantyl azide. The product distribution is essentially independent of the identity of the arenesulfonate leaving group and it follows the mathematical form required by competition for an intermediate between azide ion and solvent. The kinetics are, except for relatively small salt effects, independent of the concentration of azide ion and the rates, with 0.08 *M* tetraethylammonium azide at 25°, are some 5–17 times slower than for corresponding ethanolyse; it is shown that this is primarily due to a reduction in the entropy of activation. At 25°, the Hammett  $\rho$  value of  $2.34 \pm 0.10$  is appreciably larger than the  $1.76 \pm 0.08$  for ethanolysis, consistent with the usual magnification of leaving-group effects upon going from a protic to an aprotic solvent. As in ethanolysis, there is a deviation from "normal" behavior in that the *m*-nitro derivative reacts faster than the *p*-nitro derivative.

In hydroxylic solvents, azide ion has for many years been used as a probe for the mechanism of the solvolysis of added substrates.<sup>2–8</sup> In particular, for reactions proceeding *via* an intermediate carbonium ion or ion pair, the ratios of the second-order rate coefficients for capture by either solvent or azide ion have been logarithmically plotted against the solvolysis rates to give stability–selectivity linear free energy correlations.<sup>3,4</sup> The more stable carbonium ions show both the faster rates of formation and also the greater selectivity toward nucleophilic capture.

In hydroxylic solvents, the rapid deprotonation of the first formed oxonium ion (to give a relatively stable alcohol or ether) by another solvent molecule, by the azide ion, or by the leaving group prevents complications which could otherwise arise from further reaction of the oxonium ion, as in the case of attack by dioxane when such reaction cannot operate.<sup>5</sup> However, the presence of this acidic proton can lead, as pointed out by Ritchie,<sup>6</sup> to complications of a different type, in that the possibility exists of a general base catalysis to the capture of the carbonium ion intermediate by the solvent. Ritchie was discussing primarily reactions of relatively stable carbonium ions and he concentrated on the characteristics of general base catalysis by the trapping agent. Harris<sup>9,10</sup> has suggested that, for relatively reactive carbonium ions formed during solvolysis, the catalyst is more likely to be the departing anion, with capture occurring at the solvent-separated ion-pair stage. Evidence has also been presented that, in the solvolysis of benzhydryl derivatives, the intervention by added azide ion can occur at the solvent-separated ion-pair stage.<sup>7,8,11</sup>

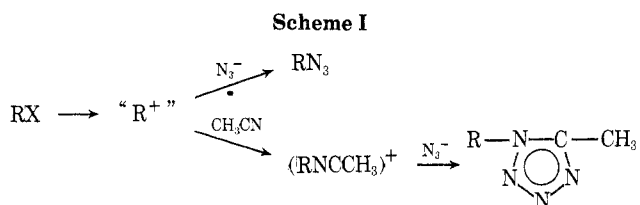
Since azide ion incorporation values cannot be taken by themselves as an indication of mechanism,<sup>3</sup> studies with 1-adamantyl and 2-adamantyl derivatives are especially useful; bimolecular attack on 1-adamantyl derivatives is prevented by the cage structure and steric hindrance to an SN2 transition state for 2-adamantyl derivatives leads to little, if any, nucleophilic assistance to its substitution reactions.<sup>12,13</sup> The more subtle details of the substitution mechanisms for adamantyl derivatives are not firmly established, but it is clear that an initial ionization is followed by subsequent attack upon a carbonium ion or ion pair; controversy exists regarding the importance of ion-pair return in these systems and, consequently, as to whether ionization<sup>14</sup> or interconversion of intimate to solvent-separated ion pairs<sup>15</sup> is rate determining.

A study has been made<sup>3</sup> of the influence of azide ion upon the solvolysis of 1-adamantyl bromide and 2-adamantyl tosylate in 80% ethanol at 75°. In both instances a modest rate increase was observed, consistent with a salt effect upon a unimolecular solvolysis, and, even with concentrations of sodium azide as high as 0.06 *M*, very little adamantyl azide was formed. Corresponding studies in dipolar aprotic solvents would be of interest. Hydrogen bonding to the departing anion within the solvent-separated ion pair (and general base catalysis) would not be operative and, since these solvents are usually less nucleophilic than hydroxylic solvents and anions dissolved in them are (owing to lack of hydrogen-bonded solvation) considerably more nucleophilic than in hydroxylic solvents, one would predict increased amounts of azide relative to solvolysis product.

A semiquantitative study has been made<sup>16</sup> with 1-adamantyl bromide and sodium azide in dimethyl sulfoxide, dimethylformamide, and hexamethylphosphoramide. Even after 3 days at 100°, no reaction was detected in the latter two solvents but, in dimethyl sulfoxide, a 29.6% yield of 1-adamantyl azide was isolated after 2 days and this rose only to 35.2% after 14 days; about 30% 1-adamantanol was also isolated after water treatment, presumably by hydrolysis of the initial solvolysis product,<sup>17</sup> 1-adamantoxymethylsulfonium ion (1-AdOSMe<sub>2</sub>)<sup>+</sup>. The very slow increase in 1-adamantyl azide production after the initial 2-day period suggests that it is primarily formed concurrent with the solvolysis product rather than, as the authors suggested,<sup>16</sup> from it.

In a study of the decomposition of 1-adamantyl chloroformate in a variety of solvents, it was found that in acetonitrile capture of intermediate 1-adamantyl carbonium ions by solvent could compete with collapse to 1-adamantyl chloride; addition of water led to the isolation of *N*-(1-adamantyl)acetamide.<sup>18</sup> However, on remaining in solution for several days, the solvent-capture product underwent replacement of acetonitrile by chloride ion to convert to the alternate 1-adamantyl chloride.<sup>19</sup> The solvolysis product could also be captured by 1,3-addition of azide ion to give 1-(1-adamantyl)-5-methyltetrazole.<sup>19</sup> Indeed, it has been found that even nitrilium cations such as *N*-ethylacetone-trilium ion, which could readily undergo SN2 displacement of nitrile by azide ion, preferentially undergo 1,3-addition.<sup>20</sup> Azide ion in acetonitrile does therefore represent a very useful aprotic system for both kinetic and product partitioning studies. The two possible products, alkyl azide and 1-alkyl-5-methyltetrazole (*via* solvolysis), both consume azide in their production and, since azide is basic to

resorcinol blue (Lacmoid) in aprotic solvents,<sup>21</sup> acid-base titration can be used to monitor the overall kinetics of reaction. Gas chromatography can be used to determine the product ratio. Remaining noncommittal at this stage concerning the actual intermediate (or intermediates) which are trapped, the situation for an ionization reaction will be as in Scheme I.



The substrates employed in the investigation reported at this time are 1-adamantyl benzenesulfonate and six para or meta-substituted derivatives. The kinetic studies can be compared to parallel ones which were carried out in a hydroxylic solvent, ethanol,<sup>22</sup> and the product ratios can be compared with those obtained for competition between azide ion and solvent for 1-adamantyl bromide and 2-adamantyl tosylate in 80% ethanol<sup>3,23</sup> and related to the mechanism proposed to explain the nature of the partitioning between the two components of the solvent for a series of 2-adamantyl arenesulfonates in aqueous ethanol.<sup>9</sup>

## Results

**Kinetics of Reaction of 1-Adamantyl Arenesulfonates in Acetonitrile Containing Azide Ion.** Acid-base titration was used to follow the disappearance of azide ion<sup>21</sup> and, since the reduction in azide ion concentration is accompanied by a corresponding reduction in 1-adamantyl arenesulfonate concentration, first-order rate coefficients (specific rates) for the reaction of 1-adamantyl arenesulfonate could be calculated. Within experimental error, these coefficients remained constant throughout each run. A study was made, at 25.0°, with varying tetraethylammonium azide concentrations and with 0.1 *M* initial concentrations of the parent 1-adamantyl benzenesulfonate plus the *p*-methoxy, *p*-chloro, *p*-bromo, and *p*-nitro derivatives; a corresponding study was made of the *p*-methyl derivative at 39.6°. A small increase in the specific rate of reaction of the 1-adamantyl arenesulfonate ( $k^{\text{expt}}$ ) was linearly related to the increase in the initial tetraethylammonium azide concentration and the data were treated according to the equation  $k^{\text{expt}} = k_0(1 + b[\text{NET}_4\text{N}_3])$ ; values for  $k_0$  and  $b$  are reported within Table I.

The  $b$  values are of the same order of magnitude as those previously reported<sup>23</sup> for 2-adamantyl tosylate in 75% aqueous dioxane (3.5) and 80% aqueous ethanol (3), values which were assumed to reflect salt effects. In order to determine whether this explanation applies to the present systems, several runs were carried out with 0.1 *M* 1-adamantyl *p*-toluenesulfonate and 0.08 *M* tetraethylammonium azide at 39.6°. Addition of either tetraethylammonium perchlorate or tetraethylammonium *p*-toluenesulfonate led to rate increments which were, within experimental error, identical with those obtained upon adding an identical concentration increment of tetraethylammonium azide (Table II), confirming that the acceleration is indeed due to a salt effect. The similar behavior of the azide and *p*-toluenesulfonate salts is consistent with the lack of perturbation throughout each run, when azide ion is being replaced by arenesulfonate ion.

In view of the relatively small sensitivity of the rate to salt concentration, it was decided that, rather than carry

**Table I**  
Kinetic Parameters for Reaction of 0.1 *M* 1-Adamantyl Arenesulfonates in Acetonitrile, Containing Various Concentrations of Azide Ion, at 25.0°

Substituent	$[\text{NET}_4\text{N}_3], M$	$10^6 k_0, \text{sec}^{-1}^a$	$b, M^{-1} \text{sec}^{-1}^a$
<i>p</i> -OMe	0.08–0.30	1.49 ± 0.07	1.6 ± 0.1
<i>p</i> -Me	0.08–0.40		1.4 ± 0.1 <sup>b</sup>
None	0.08–0.30	4.49 ± 0.16	1.4 ± 0.1
<i>p</i> -Cl	0.06–0.30	20.2 ± 2.9	2.1 ± 0.1
<i>p</i> -Br	0.08–0.24	21.6 ± 1.8	2.5 ± 0.2
<i>p</i> -NO <sub>2</sub>	0.08–0.30	235 ± 23	4.1 ± 0.2

<sup>a</sup> From intercept and slope of plots of experimental first-order rate coefficients vs.  $[\text{NET}_4\text{N}_3]$ , with associated standard errors;  $k^{\text{expt}} = k_0(1 + b[\text{NET}_4\text{N}_3])$ . <sup>b</sup> At 39.6° and including some experiments with  $[\text{NET}_4\text{N}_3] = 0.08 M$  and added  $\text{NET}_4\text{OTs}$  or  $\text{NET}_4\text{ClO}_4$ ; calculated according to  $k^{\text{expt}} = k_0(1 + b[\text{salt}])$ ; see Table II.

**Table II**  
Influence of Added Tetraethylammonium Salts upon the Specific Rate of Reaction of 0.1 *M* 1-Adamantyl *p*-Toluenesulfonate with 0.080 *M* Tetraethylammonium Azide in Acetonitrile at 39.6°<sup>a</sup>

$[\text{NET}_4\text{X}]$	$10^5 k_1, \text{sec}^{-1}$						Registry no.
	0.000	0.040	0.080	0.160	0.240	0.320	
X = OTs	1.59 <sup>c</sup>	1.70	1.71	2.01		2.27	733-44-8
X = ClO <sub>4</sub>	1.59 <sup>c</sup>	1.64	1.74	1.95	2.19		2567-83-1
X = N <sub>3</sub> <sup>b</sup>	1.59 <sup>c</sup>	1.68	1.71	2.04			993-20-4

<sup>a</sup> Values are averages of two or more runs; standard error associated with each run was usually less than 3% of the value. <sup>b</sup> Total  $\text{NET}_4\text{N}_3$  concentration minus 0.080 *M*. <sup>c</sup> From Table III.

out for each system at each temperature a series of runs at several salt concentrations and then extrapolate the specific rates back to very low salt concentration, it would be less time consuming and also slightly more accurate (magnification of errors due to extrapolation avoided) to choose, as a standard medium for further kinetic studies, acetonitrile containing 0.08 *M* tetraethylammonium azide. Values for the specific rate of reaction under these standard conditions of 1-adamantyl benzenesulfonate and the *m*-nitro derivative at 25° and for the *p*-methoxy, *p*-methyl, *p*-chloro, *p*-bromo, and *p*-nitro derivatives at several temperatures within the range 15–60° are reported within Table III together with activation parameters for those derivatives studied over a range of temperatures.

**Product Studies of the Reactions of 1-Adamantyl Arenesulfonates in Acetonitrile Containing Azide Ion.** Studies were carried out at 25.0° in acetonitrile solution containing 0.12 *M* tetraethylammonium azide for the unsubstituted 1-adamantyl benzenesulfonate and for the *p*-methoxy, *p*-methyl, *p*-chloro, *p*-bromo, *m*-nitro, and *p*-nitro derivatives. Studies were also made at higher concentrations, ranging up to 0.48 *M*, for the unsubstituted compound and for the *p*-nitro derivative. The reactions were allowed to go to completion (3 weeks or less) and the products were analyzed by glpc. In all cases, small amounts of 1-adamantanol were found and in several instances it was shown that this concentration of 1-adamantanol was present as an impurity within the initial reaction mixtures. Commercial 1-adamantanol and authentic samples of 1-adamantyl azide<sup>19</sup> and 1-(1-adamantyl)-5-methyltetrazole<sup>19</sup> were available for calibration purposes.

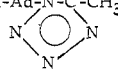
The product data are reported in Table IV, together with values for the competition factor ( $\alpha$ ),  $d[1-\text{AdN}_3]/d[\text{tetrazole}] = \alpha[\text{N}_3^-]/19.1$ , relating the second-order rate coefficients for capture of an intermediate by azide ion and by

**Table III**  
**First-Order Rate Coefficients at Various Temperatures<sup>a,b</sup> and Enthalpies ( $\Delta H^*$ ) and Entropies ( $\Delta S^*$ ) of Activation for Reaction of 0.1 M 1-Adamantyl Arenesulfonates in Acetonitrile Containing 0.0800 M Tetraethylammonium Azide**

Substituent	$10^5 k_1, \text{sec}^{-1}$						$\Delta H^*_{298},^h$ kcal/mol	$\Delta S^*_{298},^h$ eu	Registry no.
	15.0°	25.0°	30.0°	35.0°	40.0°	50.0°			
<i>p</i> -OMe		0.165		0.670	1.07	3.84	23.2 ± 0.5	-8.2 ± 1.8	43049-41-8
<i>p</i> -Me	0.0925 <sup>c</sup>	(0.251) <sup>d</sup>	0.351 <sup>e</sup>		1.59 <sup>f</sup>	5.07	23.0 ± 0.2	-7.6 ± 0.8	16200-57-0
None		0.470							43049-43-0
<i>p</i> -Cl	0.492	2.38		9.24	13.4	45.4	23.0 ± 0.5	-2.4 ± 1.6	43049-45-2
<i>p</i> -Br		2.57	4.60		14.5	47.5	21.7 ± 0.2	-3.5 ± 0.8	43049-46-3
<i>m</i> -NO <sub>2</sub>		47.9							43049-47-4
<i>p</i> -NO <sub>2</sub>	10.8 <sup>g</sup>	33.5		105	176		21.0 ± 0.4	-3.7 ± 1.2	43049-48-5

<sup>a</sup> Values are averages of two or more runs; standard error for the first-order rate coefficient associated with each run was less than 4% of its value. <sup>b</sup> Using Hammett  $\sigma$  values from ref 28, a Hammett  $\rho$  value at 25.0° of  $2.34 \pm 0.10$  was calculated; omitting the point for *m*-NO<sub>2</sub>, a corresponding value of  $2.26 \pm 0.08$  was obtained. <sup>c</sup> At 18.4°. <sup>d</sup> Interpolated from an Arrhenius plot of data at other temperatures. <sup>e</sup> At 28.4°. <sup>f</sup> At 39.6°. <sup>g</sup> At 16.7°. <sup>h</sup> Errors quoted are standard errors.

**Table IV**  
**Percentage Composition of Product from Reaction of 0.1 M 1-Adamantyl Arenesulfonates within Acetonitrile Containing Tetraethylammonium Azide at 25.0° and Calculated Values for  $\alpha$ , the "Competition Factor"**

Substituent	[NEt <sub>4</sub> N <sub>3</sub> ]	% composition of product			$\alpha^{b,c}$
		1-AdOH <sup>a</sup>	1-AdN <sub>3</sub>	1-Ad-N-C-CH <sub>3</sub> 	
<i>p</i> -OMe	0.12	4.1	2.3	93.6	6.6
<i>p</i> -Me	0.12	6.4	2.2	91.4	6.3
None	0.12	2.1	2.8	95.1	8.0
	0.16	2.9	3.8	93.4	6.8
	0.20	1.8	5.1	93.0	6.8
	0.24	3.1	6.4	90.6	7.1
	0.30	1.5	7.5	91.0	6.3
	0.36	2.7	8.9	88.5	6.2
<i>p</i> -Cl	0.12	1.1	2.2	96.7	6.1
<i>p</i> -Br	0.12	8.2	2.4	89.4	7.2
<i>m</i> -NO <sub>2</sub>	0.12	3.2	2.3	94.5	6.5
<i>p</i> -NO <sub>2</sub>	0.12	2.7	2.4	94.9	6.7
	0.24	7.0	5.7	87.3	6.5
	0.36	9.4	7.9	82.8	5.7
	0.48	7.9	10.5	81.6	5.7

<sup>a</sup> In several instances it was shown, by glpc, that these same percentages of 1-adamantanol were present as impurity within the initial reaction mixtures. <sup>b</sup> Defined by  $d[1\text{-AdN}_3]/d[\text{tetrazole}] = \alpha[\text{N}_3^-]/19.1$  (see ref 24). <sup>c</sup> Based on all entries, the average value is  $6.6 \pm 0.6$ ; based on experiments with 0.12 M NEt<sub>4</sub>N<sub>3</sub>, the average value is  $6.8 \pm 0.6$ .

the solvent acetonitrile (considered as being 19.1 M). In calculating competition factor values, allowance was made for consumption of azide ion within both of the competing product-formation steps.<sup>24</sup>

### Discussion

The Hammett  $\rho$  values of  $2.34 \pm 0.10$ , using all the data points, and  $2.26 \pm 0.08$ , using only the para-substituted derivatives (omitting the *m*-nitro value), are appreciably larger than the corresponding values of  $1.76 \pm 0.08$  and  $1.65 \pm 0.07$  obtained in ethanolysis.<sup>22</sup> This provides yet another example of the magnification of leaving-group effects observed on transfer of a reaction from a protic to an aprotic solvent.<sup>25,26</sup> As for the ethanolysis,<sup>22</sup> the *m*-nitro derivative

reacted faster than the *p*-nitro derivative, presumably once again owing to a solvent effect upon the substituent constants.<sup>27</sup> The Hammett  $\sigma$  values (substituent constants) necessary to place the *m*-NO<sub>2</sub> and *p*-NO<sub>2</sub> derivatives upon the Hammett plot were calculated as +0.80 and +0.73, quite similar to the values of +0.78 and +0.69 obtained in ethanol<sup>22</sup> and quite different from the generally accepted values<sup>28</sup> of +0.71 and +0.78.

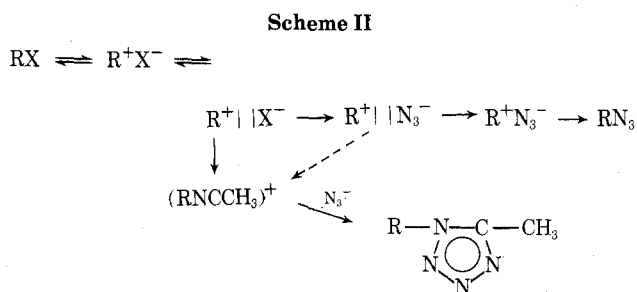
The actual rates, at 25°, varied from 16.5 times slower than in ethanol for the *p*-methoxy derivative to 4.4 times slower than in ethanol for both the *m*-nitro and *p*-nitro derivatives. A comparison of the activation parameters (Table III) with those obtained in ethanol<sup>22</sup> shows that, in general, the energy of activation values are comparable (22.0–23.8 kcal/mol in ethanol), with on the average slightly lower values in acetonitrile. Parallel to what was shown for the related ionization reactions of *tert*-butyl derivatives,<sup>26</sup> the slower reaction in acetonitrile results from a considerable lowering of the entropy of activation; for the 1-adamantyl arenesulfonates considered within Table III, the entropies of activation are some 3–8 eu less than for the corresponding ethanolyses.

Analysis of the data reported in Table IV shows that a reasonably constant value is obtained for the competition factor and the production of 1-adamantyl azide and 1-(1-adamantyl)-5-methyltetrazole obeys the mathematical form predicted for a competition for an intermediate between azide ions and solvent molecules. The competition factor has an average value of  $6.6 \pm 0.6$ , which can be compared to values, for competition between the water component and azide ion in 80% ethanol at 75%, of 2.5 for 1-adamantyl bromide and 1.7 for 2-adamantyl *p*-toluenesulfonate.<sup>3</sup> It must, however, be borne in mind that, in aqueous ethanol, it has been shown that the product partitioning is sensitive to the nature of the leaving group<sup>9</sup> and especially large leaving-group effects upon product partitioning are operative if one is comparing arenesulfonates and halides.<sup>10,29</sup> There can be no doubt, however, that even with a common leaving group all three values would remain very small (for substrates producing relatively stable carbonium ions, competition factors as large as  $10^3$  have been observed<sup>3</sup>). It is somewhat surprising that a change in solvent from 80% aqueous ethanol to acetonitrile does not lead to an appreciable increase in value. There is evidence that both components of 80% ethanol are considerably more nucleophilic than acetonitrile<sup>8,30</sup> and, in addition, anions have their nucleophilicities considerably increased on transfer

from a protic to an aprotic solvent, presumably owing to elimination of hydrogen-bonded solvation.<sup>33</sup>

The answer to this apparent anomaly may well lie in the competition occurring not for free carbonium ions but for carbonium ions within a solvent-separated ion pair, in which case the mathematical form will parallel that operative for attack on free carbonium ions but, assuming that the solvent molecules capturing the carbonium ion are from the one or two<sup>34</sup> solvent molecules separating the ions, the physical significance of the competition factor value will be quite different. It was shown several years ago that, in the solvolysis of benzhydryl derivatives, capture by added azide ions is probably at the solvent-separated ion-pair stage,<sup>7,8</sup> and, more recently, it has been shown that in 80% ethanol, 2-adamantyl arenesulfonate solvolysis probably also involves capture of the carbonium ion (to give either ether or alcohol) at the solvent-separated ion-pair stage.<sup>9,10</sup> Also, the suggestion that the reactions involve rate-determining conversion from the intimate (contact) to the solvent-separated ion pair<sup>15</sup> would be consistent with capture at this stage. It should be pointed out that one otherwise attractive scheme, involving either collapse with a solvent molecule within the solvent-separated ion pair or separation to give a free carbonium ion which is usually captured by azide ion, is not consistent with the experimental finding of a dependence of the product ratio upon azide ion concentration. While several schemes are possible, it is necessary for the azide ion to be actively involved in forming 1-adamantyl azide, rather than for it to be passively waiting for the production of an intermediate which then prefers to react with azide ion rather than solvent.

A competition at the solvent-separated ion-pair stage would be expected to be strongly biased in favor of solvolysis. Not only are the solvent molecules strategically located but additional bias in their favor can result, in the case of protic solvents, from general base catalysis to the solvolysis<sup>6</sup> by the departing anion.<sup>9,10</sup> For competition between acetonitrile and azide, one can explain our experimental results as in Scheme II. For consistency with the observed mathematical form, it is necessary to assume that little collapse of the carbonium ion with the solvent occurs in  $R^+||N_3^-$  and that this entity usually proceeds to  $RN_3$ . Under these conditions, low values for the competition factor would not be surprising and, indeed, the theoretical lower limit of unity<sup>3</sup> which would result from competition for a free carbonium ion between free azide ions and solvent will not apply for a competition of this type and values below unity and all the way down to zero could be observed.<sup>35</sup>



The explanation given<sup>9,10</sup> for the variation in product ratio between ether and alcohol, upon varying the substituent within a series of para-substituted 2-adamantyl arenesulfonates, in terms of hydrogen bonding to the anion being assisted both by electron-supplying substituents and by the presence of two hydrogens in water (cyclic intermediate) as opposed to only one in ethanol requires that, in a

mixture of two aprotic solvents, a constant value would be observed for the ratio. An experiment of this type has not yet been performed but the constant product ratio observed, in the present study, for competition between an aprotic solvent, acetonitrile, and added azide ion is consistent with the hydrogen-bonding explanation for variations within mixed protic solvents.<sup>9,10</sup>

### Experimental Section

**Materials.** Acetonitrile was purified as described previously.<sup>36</sup> The preparation and characterization of the 1-adamantyl arenesulfonates has previously been described.<sup>22,37</sup> Samples of 1-adamantyl azide and 1-(1-adamantyl)-5-methyltetrazole, for use as standards, were available from a previous study.<sup>19</sup>

Tetraethylammonium azide was prepared from commercially available tetraethylammonium hydroxide (15% in water) and a solution of hydrazoic acid in either benzene or chloroform.<sup>38</sup> The aqueous layer was evaporated to dryness under reduced pressure and the impure tetraethylammonium azide residue was recrystallized from acetone and dried at 100° under vacuum for 12 hr. The dried salt was immediately dissolved in acetonitrile and the concentration of the solution was determined by titration of aliquots, in acetone against a standardized solution of methanolic hydrogen chloride, using resorcinol blue (Lacmoid) as indicator.<sup>21</sup>

**Kinetic Procedures.** Solutions of tetraethylammonium azide in acetonitrile of the required concentration were made by appropriate dilution of a stock solution and added to weighed amounts (to make an approximately 0.1 M solution) of the appropriate 1-adamantyl arenesulfonate, contained within a 25-ml volumetric flask and maintained at the desired temperature. After temperature equilibration, the reaction was monitored by transfer at convenient time intervals of 2-ml aliquots into acetone and the remaining azide ion concentration was determined by titration, as indicated above. Changes in azide ion concentration were equated to corresponding changes in the concentration of the sulfonate esters and rate coefficients for disappearance of the 1-adamantyl arenesulfonate were obtained by use of the standard form for the integrated first-order rate coefficient. Three illustrative runs are given in Table V.

**Product Studies.** These were usually carried out using samples of 1-adamantyl arenesulfonates from which several portions had been removed for kinetic studies. Owing to the sensitivity of these compounds to moisture,<sup>39</sup> a small amount of acid had developed within the samples and they were recrystallized from ether. This recrystallization removed the acid but, if anything, the 1-adamantanol was concentrated. However, control experiments showed the 1-adamantanol concentration to remain unchanged during reaction and these samples, all containing less than 10% 1-adamantanol, were acceptable for use in the product studies. In one instance, for a reaction of 1-adamantyl *p*-chlorobenzenesulfonate, a freshly prepared analytically pure sample was used and only 1.1% 1-adamantanol was detected within the products; this gives an approximate measure of the extent of interaction with moisture during preparation of a reaction mixture. Control experiments showed that 1-adamantyl azide and 1-(1-adamantyl)-5-methyltetrazole do not interconvert under the experimental conditions.

The glpc analysis was carried out using a Varian Aerograph Series 1700 instrument, equipped with a thermal conductivity detector and a Sargent Recorder, Model SRG (with disc integrator). A 2 ft × 0.25 in. column packed with 30% SE-30 on 80 mesh Chromosorb W was maintained initially at 85° and the instrument was temperature programmed so that the column temperature had risen to no higher than 225° at the time of elution of the tetrazole (at higher temperatures decomposition was observed).

Use of authentic samples showed that the plausible components (in order of elution) were as follows: acetonitrile, 1-adamantanol, 1-adamantyl azide, *N*-(1-adamantyl)acetamide<sup>18,40</sup> (from possible capture of the solvolysis product by adventitious moisture), unreacted 1-adamantyl arenesulfonate, and 1-(1-adamantyl)-5-methyltetrazole. Good peak separation was obtained under the experimental conditions. After completion of reaction with excess tetraethylammonium azide, only 1-adamantanol (concentration unchanged from that present originally), 1-adamantyl azide, and 1-(1-adamantyl)-5-methyltetrazole were detected, in the proportions reported in Table IV. In calculating the competition factors, the initial concentration of 1-adamantyl arenesulfonate entered into the equation<sup>24</sup> was corrected for the 1-adamantanol impurity.

In a few cases the crude reaction product was isolated by parti-

Table V

A. Temperature, 39.6°; 2-ml Aliquots; [C <sub>10</sub> H <sub>15</sub> OTs], 0.100 M; [NEt <sub>4</sub> N <sub>3</sub> ], 0.080 M; Titers, Milliliters of 0.0198 M Methanolic HCl						
Time, sec	0	7200	10,800	15,900	21,400	26,000
Titer	7.81	6.76	6.40	5.71	5.08	4.65
10 <sup>5</sup> k <sub>1</sub> , sec <sup>-1</sup>		1.60	1.46	1.54	1.56	1.52
Time, sec	34,900	40,800	49,600			
Titer	3.74	3.24	2.52			
10 <sup>5</sup> k <sub>1</sub> , sec <sup>-1</sup>	1.57	1.57	1.60			
B. Temperature, 39.6°; 2-ml Aliquots; [C <sub>10</sub> H <sub>15</sub> OTs], 0.100 M; [NEt <sub>4</sub> N <sub>3</sub> ], 0.080 M; [NEt <sub>4</sub> ClO <sub>4</sub> ], 0.040 M; Titers, Milliliters of 0.0198 M Methanolic HCl						
Time, sec	0	7200	10,800	14,900	20,400	
Titer	7.76	6.72	6.22	5.68	4.99	
10 <sup>5</sup> k <sub>1</sub> , sec <sup>-1</sup>		1.60	1.62	1.64	1.67	
Time, sec	25,700	35,600	39,800	48,500		
Titer	4.47	3.55	3.03	2.27		
10 <sup>5</sup> k <sub>1</sub> , sec <sup>-1</sup>	1.64	1.67	1.70	1.74		
C. Temperature, 25.0°; 2-ml Aliquots; [C <sub>10</sub> H <sub>15</sub> OSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -p-NO <sub>2</sub> ], 0.100 M; [NEt <sub>4</sub> N <sub>3</sub> ], 0.080 M; Titers, Milliliters of 0.0156 M Methanolic HCl						
Time, sec	0	169	390	575	777	1012
Titer	9.58	8.95	8.15	7.59	6.97	6.23
10 <sup>5</sup> k <sub>1</sub> , sec <sup>-1</sup>		31.7	32.0	31.0	31.1	31.8
Time, sec	1212	1423	1607			
Titer	5.84	5.28	4.92			
10 <sup>5</sup> k <sub>1</sub> , sec <sup>-1</sup>	32.3	32.5	31.8			

tion between water and ether and evaporation of the ether. The relatively small amounts of 1-adamantyl azide (and 1-adamantanol?) could be removed by sublimation under reduced pressure at 40°, to leave a residue of 1-(1-adamantyl)-5-methyltetrazole.<sup>19</sup> Alternatively, the crude reaction product could be separated by chromatography on a column containing neutral alumina. The 1-adamantyl azide<sup>16,19</sup> was eluted using benzene, followed by elution of the tetrazole<sup>19</sup> using 50:50 hexane-benzene or chloroform.

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- This is also apparent from the results reported earlier.<sup>3</sup> Competition factors of 2.5 and 1.7 were obtained for 1-adamantyl bromide and 2-adamantyl *p*-toluenesulfonate in 80% ethanol containing azide ion, when competition between water and azide ion was considered. Consideration of competition between the ethanol of the solvent and the azide ion leads to corresponding values of 2.4 and 4.7. Taken at their face value these latter values are in conflict with the ones reported earlier for the azide ion and water competition and they suggest the 2-adamantyl carbonium ion to be more stable than the 1-adamantyl carbonium ion. The valid conclusion is, of course, that one cannot directly compare, in this solvent, product studies obtained using bromides with those using *p*-toluenesulfonates.<sup>10</sup> Accordingly, even if one accepts that competition factors with azide ion in 80% ethanol at 75° can be related to those in 80% acetone at 25°, the inclusion of product-partitioning data for bromides and, especially, *p*-toluenesulfonates on a stability-selectivity plot for chlorides<sup>3</sup> is, at best, a very approximate procedure.
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