Solvolysis Mechanisms. Kinetic Solvent Isotope Effects for Alkyl Tosylates in Acetic Acid and Acetic Acid-d^1

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Abstract: Since kinetic solvent isotope effects for H_2O vs. D_2O are largely independent of alkyl group structure, it seemed important to determine whether the same held true in acetic acid, a solvent widely studied as a solvolytic medium and more acidic but less nucleophilic than water. Isotope effects, k_H/k_D, with standard deviations of a few percent (temperatures in parentheses) are: benzyl *p*-toluenesulfonate (OTs), 1.10 (70), 1.07 (80), 1.04 (95); (*p*-MeOPh)C(Me)$_2$CH$_2$OTs, 1.10 (60), 1.12 (70), 1.10 (80); methyl-OTs, 1.03 (95); 1-adamantyl-OTs, 1.06 (15), 1.05 (30), 1.04 (40). These isotope effects are only slightly temperature dependent over the ranges studied, appearing to exhibit the usual Arrhenius trend to slightly lower effects at higher temperatures. The isotope effects appear to be the same at any given temperature for all substrates except adamantyl. These results extend the near independence of water solvent isotope effects to acetic acid. It is suggested that the data are most consistent with mutually compensating changes in isotope effects associated with nucleophilic and electrophilic solvent participation with different substrates. The isotope effects for adamantyl appear to be significantly low when temperature is taken into account, and it is suggested that the recently proposed mechanism for adamantyl and other rear-side blocked substrates, rate-determining formation of solvent-separated ion pair, is the probable cause.

Solvent kinetic isotope effects can be a powerful tool in the study of reaction mechanisms and may involve both primary and secondary contributions.[2-4] Extensive studies in water, particularly by Robertson,[2] have given small isotope effects, k_{H_2O}/k_{D_2O}, on the order of 1.05–1.40, strongly indicating no primary contribution (rate-determining hydrogen transfer), in contrast to what is observed in hydrolysis of carboxylic acid derivatives, where isotope effects are usually around 2.5 or higher.[4-7] There is a rather remarkable lack of dependence of the isotope effects for hydrolysis of simple aliphatic substrates upon the nature of the alkyl group, though there is a dependence on leaving group in that halides give 1.2–1.4 but sulfonates give 1.05–1.10.[2] Such observations may be explained if the transition states are similar with respect to solvent participation for all substrates, primary, secondary, and tertiary, or they may be explained by mutually compensating effects such that substrates which have stronger nucleophilic participation by solvent have weaker electrophilic participation.[3] A trend toward compensation is not unexpected since primary substrates probably have relatively tight transition state structures with considerable nucleophilic participation and incomplete leaving group bond rupture, whereas tertiary substrates or other types which have the potential for carbonium ion stabilization probably have looser transition state structures with little nucleophilic participation but also nearly complete bond rupture, i.e., nearly ion pair like.[8-11]

There is a large body of information on solvent effects in solvolytic reactions at saturated carbon atoms,[12-20] but the blend of nucleophilic and electrophilic participation has been difficult to evaluate.[20]

We therefore felt it would be valuable to study kinetic solvent isotope effects in a solvent other than water. Since mixed solvents present additional problems of interpretation, we wished to use a single solvent, one that had been studied extensively in its protiated form, and one that differed significantly from water in its properties. The solvent chosen for this work was acetic acid, which is considerably more acidic (electrophilic) and considerably less basic (nucleophilic) than water.

Solvent kinetic isotope effects have been measured for acetic[21,22] and formic[23] acids, but these studies involved acid catalysis and are thus not comparable with our work.

Experimental Section[1b]

Melting and boiling points are uncorrected. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del. Wayne-Kerr Autobalance Precision Bridge B331 and Universal Bridge B221 were used for conductivity measurements. A Kewanee drybox was used for preparation of solvents and solutions and was filled with oxygen-free prepurified nitrogen at all times, with open dishes of phosphorus pentoxide and potassium hydroxide inside.

Protium oxide was laboratory distilled water redistilled from potassium permanganate before use.

Deuterium oxide (99.7 atom % D) was obtained from General Dynamics Corp., Liquid Carbonic Division.

Acetic acid-*d* was prepared from acetic anhydride and deuterium oxide. All glassware was dried at least 10 hr at 200°C before use, then placed in a desiccator or drybox while hot. Where it was not possible to dry glassware in this way, it was rinsed at least twice with deuterium oxide before use. Deuterium oxide and 1 mol % excess of acetic anhydride (Baker Analytical Reagent) were mixed and allowed to stand in the drybox for ca. 10 hr. The mixture was refluxed at least 4 hr, then distilled through a 45-cm column packed with 6-mm i.d. glass helices. The fraction collected at a reflux ratio 4/1, bp 117–117.3°C, was used for kinetics. The whole system was under a nitrogen atmosphere during reaction and distillation. Deuterium analysis gave 24.70 atom % excess D,[24] corresponding to 98.8% isotopic purity.

Acetic acid was prepared by exactly the same procedure used for acetic acid-*d*, using protium oxide. Thus the solvents used in the solvolytic studies were made under exactly the same conditions.

Benzyl *p*-toluenesulfonate was prepared by reaction of benzyl alcohol with *p*-toluenesulfonyl chloride in ether in the presence of powdered potassium hydroxide.[25,26] The dried ethereal solution of product was concentrated on a rotary evaporator at room temperature. When the concentrated solution was cooled in a dry ice bath, a copious precipitate of fine, white needles was obtained. The crystals were rapidly filtered and recrystallized at least four times from petroleum ether (bp 30–60°C) to constant mp 58–58.5°C, yield 75% (lit.[27] mp 57.8°, yield 38%; lit.[28] mp 58.5–58.9°C, yield 80%). The ester, stored in anhydrous ether at 0°C, is stable for years. Small portions were recrystallized for use as needed.

***p*-Methoxyneophyl *p*-toluenesulfonate** was prepared by dimethylation of *p*-methoxybenzyl cyanide, hydrolysis to (α,α-dimethyl-*p*-methoxybenzyl)acetic acid, reduction with lithium aluminum hydride, and reaction of the resulting alcohol with *p*-toluenesulfonyl chloride.[29,30] The hydrolysis procedure was carried out in a high-pressure bomb with aqueous methanolic potassium hydroxide; best yield was obtained at 160°C (150 atm) for 65 hr. Also,

Table I. Rate Constants and Kinetic Solvent Isotope Effects for Solvolysis of Alkyl Tosylates in Acetic Acid and Acetic Acid-*d*, Each Containing 1% Acetic Anhydride, at Various Temperatures[a]

Alkyl tosylate	T, °C	k_{H}, sec^{-1}	k_{D}, sec^{-1}	$k_{\mathrm{H}}/k_{\mathrm{D}}$[b]
Benzyl	70.20	$4.64 \pm 0.03 \times 10^{-4}$	$4.22 \pm 0.02 \times 10^{-4}$	1.10 ± 0.01
	80.03	$1.110 \pm 0.006 \times 10^{-3}$	$1.040 \pm 0.018 \times 10^{-3}$	1.07 ± 0.02
	94.90	$3.57 \pm 0.15 \times 10^{-3}$	$3.42 \pm 0.10 \times 10^{-3}$	1.04 ± 0.05
p-Methoxyneophyl	60.01	$5.25 \pm 0.08 \times 10^{-4}$	$4.77 \pm 0.10 \times 10^{-4}$	1.10 ± 0.03
	70.20	$1.31 \pm 0.11 \times 10^{-3}$	$1.17 \pm 0.10 \times 10^{-3}$	1.12 ± 0.03
	80.03	$3.26 \pm 0.05 \times 10^{-3}$	$2.97 \pm 0.17 \times 10^{-3}$	1.10 ± 0.05
Methyl	94.90	$1.03 \pm 0.05 \times 10^{-6}$	$1.00 \pm 0.07 \times 10^{-6}$	1.03 ± 0.05
1-Adamantyl	14.90	$1.41 \pm 0.02 \times 10^{-4}$	$1.33 \pm 0.03 \times 10^{-4}$	1.06 ± 0.03
	30.01	$1.13 \pm 0.01 \times 10^{-3}$	$1.08 \pm 0.02 \times 10^{-3}$	1.05 ± 0.02
	39.9	$3.70 \pm 0.03 \times 10^{-3}$	$3.55 \pm 0.04 \times 10^{-3}$	1.04 ± 0.01

[a] Rate constants are given with standard deviations; should be read as $(4.64 \pm 0.03) \times 10^{-4}$, etc. [b] Isotope effects are given with standard deviations.

the toluenesulfonate was made using powdered potassium hydroxide and ether, as described in the previous paragraph.[25,26] The product was recrystallized from petroleum ether (bp 30-60°C) to constant mp 50-51.5°C (lit.[31] 53-54°C).

1-Adamantyl *p*-toluenesulfonate was prepared by a modification of the procedure of Schleyer and Nicholas,[32] which gave purer material.

Glassware was rigorously dried as described above for making acetic acid-*d*. A 1 l., three-necked, round-bottomed flask was equipped with magnetic stirrer, addition funnel, condenser fitted with a drying tube, and nitrogen gas inlet. The system was flushed with prepurified nitrogen at least 30 min before introducing any chemicals, and continuously during the reaction.

A solution of 1.2 g (8 mmol) of 1-adamantyl alcohol (Aldrich) in 50 ml of sodium-dried benzene was added to a magnetically stirred mixture of 1 g (excess) of sodium dispersion[33] in 50 ml of dry benzene. Addition was made over 2 hr, and the mixture was refluxed for another hour. Sodium alcoholate formed on the surface of the sodium particles; when the formation of alcoholate was complete, the sodium particles coagulated into a single lump, and the solution became clear. After the mixture cooled to room temperature, a solution of 3.0 g (11.8 mmol) of freshly recrystallized *p*-toluenesulfonyl chloride in 50 ml of dry benzene was added over 1 hr; then the mixture was refluxed for 4 hr. The solution became dark gray and the sodium lump separated into particles.

Upon standing at room temperature for 24 hr, the salts and sodium had settled to the bottom of the flask. The solution was filtered by using filtering aid, the salts were washed with ice-cold petroleum ether (bp 30-60°C), and the combined filtrate was concentrated using a rotary evaporator at room temperature until the volume was 10 ml.

Treating the 10 ml of product solution with 10 ml of dry pyridine for 5 min, pouring into ice-cold water (100 ml), followed by extracting with ether (three times, each 50 ml), washing with ice-cold water (five times), drying with anhydrous potassium carbonate, and evaporating the solvent gave a yellow, oily product. Crystallization of the product from petroleum ether (bp 30-60°C) at −70° (dry ice-acetone bath), filtration, and washing the yellowish crystals with ice-cold petroleum ether very quickly gave white crystals of 1-adamantyl tosylate. After two recrystallizations,[34] and drying under vacuum for at least 1 hr, 0.96 g (40% yield) of product (crude yield, 51%) was obtained: mp 72-74°C; NMR δ_{H} ($\mathrm{Me_4Si}$) 1.63 (s, 6 H, δ protons), 2.18 (s, 9H, β and γ protons), 2.42 (s, 3 H, methyl), 7.27 (d, 2 H, aromatic), 7.78 (d, 2 H, aromatic) ppm.

Anal. Calcd for $\mathrm{C_{17}H_{22}O_3S}$: C, 66.66; H, 7.19; S, 10.55; Cl, 0.00. Found: C, 66.50; H, 7.04; S, 10.89; Cl, 0.00.

Methyl *p*-toluenesulfonate (Matheson Coleman and Bell, reagent grade) was distilled through a 40 × 2.5 cm spinning-band column at a reflux ratio of 4/1. The fraction boiling at 139°C (3.5 mm) [lit.[35] bp 161°C (10 mm); lit.[36] 129.0°C (2.2 mm)] was used for kinetics.

Conductivity Measurements. A specially constructed conductivity cell of ca. 2.8-ml volume, with circular platinum electrodes 0.8 cm in diameter, set 0.5 cm apart, with inclined rather than parallel arms (to decrease magnetic interference between leads), and with a long neck 0.5-cm o.d. having a Teflon stopcock (giving very low surface area and volume vaporization while in the constant temperature bath), was used. The electrodes were not platinized. All solvents were transferred into the cell by using needles and syringes. After use, the cell was cleaned with distilled water and acetone and dried with a stream of prepurified nitrogen just before use. It was rinsed twice with the solution to be measured before being filled.

Benzyl and *p*-methoxyneophyl tosylates were kept at 0°C in anhydrous ether, and just enough material for a kinetic run was taken, dried on a vacuum line for 5-7 min at room temperature, and transferred into the drybox. 1-Adamantyl tosylate, stored in crystalline form at 0°C, was dried and handled analogously.

Measurements were carried out in a vigorously stirred silicone oil bath, controlled to ±0.002°C and calibrated with a NBS certified thermometer. A linear relationship was found between conductivity and concentration of *p*-toluenesulfonic acid in the concentration range observed in the kinetic experiments.

Conductivity increased with time in kinetic experiments as a result of production of *p*-toluenesulfonic acid. Good first-order kinetics was observed for each substrate. Initial concentrations were on the order of 10^{-3} *M*. Rate constants were obtained with a nonlinear least-squares computer program. At least four runs, and in most cases seven or eight, were carried out to give the reported mean rate constants.

Results

The observed rate constants and resulting isotope effects are given in Table I. Methyl tosylate was studied at only one temperature because it was so slow as to give poor data below 95°C, and there were apparently problems with the solvent or other factors which also give poor data above 95°C. Temperatures for other substrates were dictated by their reactivities. While there are clearly experimental limitations to getting kinetic data of high reproducibility in this solvent system, and a great deal of effort was required to obtain the present results, we felt that the general conclusions and comparisons of pure acetic acid with water which we can now demonstrate made it desirable to carry out such a difficult project. Because of rapid rates, the problems were particularly noticeable for *p*-methoxyneophyl tosylate at 70 and 80°C. It was possible to obtain isotope effect values with considerably lower standard deviations by carrying out reactions pairwise and simultaneously for deuterated and undeuterated acetic acid. Therefore, isotope effects for these two cases were calculated from pairs of runs, and then these isotope effects were averaged and their standard deviations reported in Table I. This procedure should give a better estimate of the accuracy of these isotope effects and is justified by the fact that some unknown but imperfectly controlled variable is at work in runs carried out at different times but does not affect the isotope effects determined simultaneously as greatly as it affects individual rate constants.

The temperature dependences of the isotope effects are small and follow an Arrhenius type relationship, as expected.[3] The temperature effect in the benzyl case is too steep for a nonanomalous temperature dependence, but this is very probably just experimental error. Examination of the data shows that all the isotope effects are nearly equal at comparable temperatures, except those for adamantyl tosylate, which would extrapolate to very low values at temperatures of 70–95°C, where the other substrates were studied. Certainly there may be some differences between substrates in isotope effects and in their temperature dependences—the temperature dependence appears to be substantial for benzyl but negligible for *p*-methoxyneophyl—but these small effects are within experimental error.

Discussion

The isotope effects observed are small and almost certainly secondary.[2-4] It was not clear prior to our experiments whether acetic acid would be the same as water in not having a primary contribution since acetic acid might be expected to be a much better acid catalyst for solvolyses of alkyl derivatives than water.

The values of around 10% or less are close to those observed for various sulfonates in water and considerably less than the 20–40% isotope effects observed in water for alkyl halides.[2] This seeming near-equality of isotope effects in acetic acid and in water suggests a similarity in the numbers of solvent protons and their degree of involvement in activation of substrates for solvolysis in the two solvents.

Relative independence of isotope effects upon alkyl group is now seen in acetic acid, thus demonstrating that the phenomenon is not restricted to water.[2] Since methyl tosylate seemingly must involve significant nucleophilic participation by solvent, whereas the anchimerically assisted *p*-methoxyneophyl tosylate[29,31] cannot, it would appear from the similarity of the isotope effects that they cannot be determined largely by nucleophilic assistance. If anything, the isotope effect for *p*-methoxyneophyl appears to be larger. On the other hand, the present understanding and theory of solvent isotope effects in water indicate that there should be a significant isotope effect ($k_H/k_D > 1$) associated with significant nucleophilic interaction generating a partial positive charge on the proton-bearing nucleophilic solvent oxygen atom.[3,4] This phenomenon should exist in acetic acid as well. It is expected that electrophilic interaction would produce an isotope effect in the same direction ($k_H/k_D > 1$) through stronger hydrogen bonding in the transition state than in the reactant.[3,4] Thus, if methyl tosylate has a significant isotope effect arising from the expected significant nucleophilic interaction, it would appear to have a lowered contribution from electrophilic interaction compared with *p*-methoxyneophyl since if anything the isotope effect for the former is lower than that for the latter at the same temperature. It is therefore suggested that the data for benzyl, *p*-methoxyneophyl, and methyl tosylates are most consistently explained by the compensation effect discussed above.[3,8-11] In these terms, methyl would have a tight transition state, with significant nucleophilic participation but only partial tosylate rupture and thus reduced electrophilic participation. Benzyl would have a looser transition state, with less nucleophilic but more electrophilic participation than methyl. *p*-Methoxyneophyl would have virtually nonexistent nucleophilic participation but would have a transition state closely resembling the rearranged carbonium ion, leaving tosylate almost completely ruptured and therefore involving strong electrophilic participation. The nucleophilic and electrophilic contributions to such solvent isotope effects in acetic acid or water are not expected to be changing in precisely compensating ways with changes in alkyl group, but it is suggested that there is sufficient cancellation through such compensating effects to obliterate any trends of isotope effect with structure or reactivity.

We would like to emphasize that the interpretation of isotope effects is rather independent of mechanistic schemes and the existence of various ion-pair intermediates. These effects probe only the rate-determining transition state. Similar transition states will give similar isotope effects regardless of whether one system shortly thereafter encounters a "Boltzmann hole" on its energy surface and thus necessarily populates some type of intermediate, while the other system does not encounter such a hole, or encounters a different one. In general, widely different mechanisms will give different transition states, but a gradual trend of transition state structure and intermediate stability is expected for changes in reactant structure. In addition, since ion pairs are generally high-energy intermediates (relative to reactants and products), the consequences of the Hammond postulate[9,37] are that transition states for the formation and the decomposition of such intermediates all resemble that intermediate in structure, and therefore resemble each other. The position of many types of transition states along a reaction path, with respect to the position of the intermediate (prior to or after that transition state), may be difficult to determine using techniques which probe transition state structures.

1-Adamantyl tosylate appears to have conspicuously lower isotope effects upon extrapolation to the temperature where the other substrates were studied. If the interpretation of the other data is correct, a mechanistic difference may be indicated. We believe that this result is nicely consistent with the recent proposals that adamantyl and other systems totally incapable of accepting rear-side nucleophilic assistance must solvolyze by rate-determining formation of solvent-separated ion pair.[16,17] The lower isotope effect may result from the significant involvement of fewer molecules of acetic acid, perhaps only one, in the rate-determining step for this adamantyl mechanism than in the cases of the other substrates we have studied.

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References and Notes

(1) (a) Supported by the National Science Foundation through Grants GP-2937, GP-6047, GP-8685, and GP-34,491X. (b) For further details, cf. T. S.-C. C. Huang, Ph.D. Dissertation in Chemistry, University of Pennsylvania, 1971.
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(34) When more recrystallizations were done, the melting point was not improved and it was found that more tosylate had been hydrolyzed back to the alcohol; therefore, further recrystallization was abandoned.
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Rearrangement of Nonamethylbicyclo[3.2.1]octa-3,6-dien-2-yl Cation to the Corresponding [3.3.0] Cation

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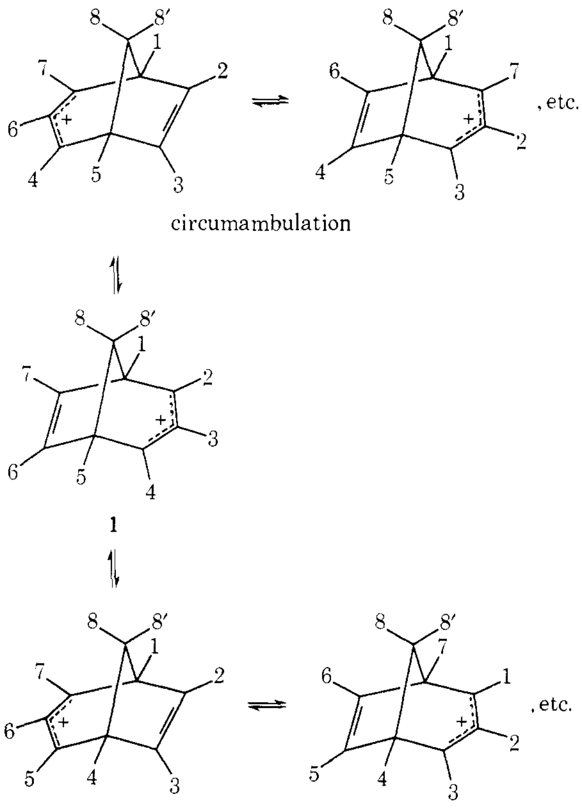
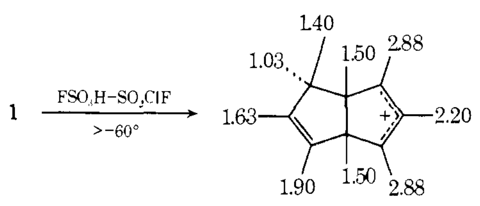
Abstract: The title ion **1**, which in FSO_3H-SO_2ClF undergoes rapid degenerate rearrangements below −60°, rearranges irreversibly above that temperature to the 1,2,3,4,5,6,7,8,8-nonamethylbicyclo[3.3.0]octa-3,6-dien-2-yl ion, **2**. The mechanism involves a cyclopropylcarbinyl–cyclopropylcarbinyl type of rearrangement (A → D); labeling experiments eliminate an alternative mechanism involving a 1,2-methyl shift. Ion **2** incorporates deuterium on standing in trifluoroacetic acid-*d*. Eventually all nine methyls become labeled, but they do so at different rates, and a mechanistic scheme is suggested to account for the results. These studies delineate preferred paths for carbonium ions which have several alternatives for rearrangement; attention is drawn to the importance of bishomoantiaromaticity as a factor in these rearrangements.

In a previous paper[1] we described two rapid degenerate rearrangements which the nonamethylbicyclo[3.2.1]octa-3,6-dien-2-yl cation (**1**) undergoes below −60° in FSO_3H-SO_2ClF. The faster of these is a circumambulatory process which is NMR-observable; the three carbons which bear methyl groups 1, 5, 8, and 8′ circumambulate about the five carbons which bear methyls 2, 3, 4, 6, and 7 in such a manner that these five methyls equilibrate, as do methyls 8 and 8′, but methyls 1 and 5 remain unique. The slower process, detected only by deuterium labeling studies, equilibrates methyls 1 through 7, and methyls 8 and 8′; it is most simply rationalized via a 1,2-bridge shift. Both processes are illustrated in Scheme I. Circumambulation has a $\Delta H^\ddagger$ of 7.4 kcal/mol, whereas the $\Delta H^\ddagger$ for bridge shift is somewhat higher, but less than 17.8 kcal/mol.

Scheme I



On standing in FSO_3H-SO_2ClF at or above −60°, ion **1** rearranges to the [3.3.0] ion **2**. In this paper we discuss in detail the mechanism of this rearrangement.[2]



2

Results and Discussion

Structure of Ion 2. Because of the circumambulatory process, the ^1H NMR spectrum of **1** at −60° or above consists of only three peaks, a sharp singlet at δ 1.27 due to equilibrating methyls 8 and 8′, a sharp singlet at δ 1.52 due to methyls 1 and 5, and a broad singlet at δ 2.20 due to equilibrating methyls 2, 3, 4, 6, and 7. Gradually, with a rate constant of 1.9 ± 0.2 × 10^{-4} sec^{-1} at −52°, this spectrum is replaced by one with seven peaks, assigned as shown in