Methanesulfonate/p-Nitrobenzoate and p-Toluenesulfonate/p-Nitrobenzoate Rate Ratios. Solvolyses of 1-Adamantyl and Benzhydryl Substrates

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Alcohols derivatized as benzoate or sulfonate esters are frequently employed as precursors of carbocationic species generated in solvolytic reactions.[1] Typically, reactivities of a series of compounds having the same leaving group are examined in individual projects. Comparisons of substituent effects on kinetic data for different benzoates OR sulfonates can readily be made,[2] but comparisons of benzoates AND sulfonates (i.e., p-nitrobenzoates and tosylates) are difficult because benzoates are about 10^8-fold less reactive than sulfonates.[3]

Improved methods for determining first-order solvolysis rate constants have extended the conveniently accessible range to fast reactions having half-lives of <1 s,[4,5] and sulfonates too unstable to be isolated at room temperature have recently been studied.[6] Also, kinetics of reactions of sparingly soluble substrates can now be examined conveniently by HPLC monitoring of the disappearance of the substrate; as the "infinity" value (equal to zero substrate concentration) can be assumed, this method is well-suited to very slow reactions.[7,8] A combination of these two

Table I. Rate Constants (k) for Solvolyses of Benzhydryl Mesylate (1, X = OMs)[a]

solvent	temp, °C	k, s^{-1}	Y_{OMs}[b]
80% EtOH[d]	−17.1	$(1.64 \pm 0.02) \times 10^{-1}$	
	−9.6	$(4.18 \pm 0.05) \times 10^{-1}$	0.0
	0.8	1.31 ± 0.01	
	25.0[c]	14.8	
90% EtOH[d]	−9.2	$(1.34 \pm 0.01) \times 10^{-1}$	−0.82
EtOH	−9.2	$(1.22 \pm 0.05) \times 10^{-2}$	−2.22

[a] Determined conductimetrically at least in duplicate; errors shown are average deviations. [b] Values at 25 °C from ref 9b; an m value of 0.78 ± 0.06 is obtained for solvolyses of 1 at −9 °C. [c] Calculated from rate constants at lower temperatures; $\Delta H^* = 15.5$ kcal mol^{-1}, $\Delta S^* = -0.9$ cal mol^{-1} K^{-1}. [d] % v/v ethanol/water.

Table II. Rate Constants (k) for Solvolyses of Benzhydryl p-Nitrobenzoate (1, X = OCOC$_6$H$_4$NO$_2$) in 80% Ethanol/Water

temp, °C	k, s^{-1}	ΔH^*, kcal/mol	ΔS^*, cal mol^{-1} K^{-1}
100.0[a]	3.48×10^{-5}		
100.3[b]	$(3.34 \pm 0.05) \times 10^{-5}$		
75.2[b]	$(2.70 \pm 0.01) \times 10^{-6}$	25.6	−11.0
59.5[b]	$(4.33 \pm 0.13) \times 10^{-7}$		
25.0[c]	4.5×10^{-9}		

[a] Determined spectrophotometrically from the rate of appearance of acid.[10] [b] Determined in duplicate by HPLC from the rate of disappearance of ester in buffered solution; the rate of appearance of acid gave slightly higher results having greater uncertainty. [c] Calculated from rate constants at higher temperatures.

Table III. Rate Constants (k) for Solvolyses of 1-Adamantyl Esters (2) in 60% v/v Ethanol/Water

leaving group (X)	temp, °C	k, s^{-1}	ΔH^*, kcal/mol	ΔS^*, cal mol^{-1} K^{-1}
OMs[a]	25.0	$(5.16 \pm 0.04) \times 10^{-2}$	17.8[b]	−4.7[b]
OMs[a]	35.0	$(1.41 \pm 0.03) \times 10^{-1}$	17.9	−4.4
OMs[a]	50.0	$(5.77 \pm 0.12) \times 10^{-1}$		
OMs[c]	75.0	4.6		
PNB[d]	129.2	$(7.76 \pm 0.2) \times 10^{-6}$		
PNB[d]	101.7	$(5.16 \pm 0.1) \times 10^{-7}$	28.8	−11.0
PNB[c]	75.0	2.5×10^{-8}		

[a] Mesylate (OMs) determined conductimetrically at least in duplicate; errors shown are average deviations. [b] Reference 4c. [c] Calculated from rate constants at other temperatures. [d] p-Nitrobenzoate (PNB) determined by HPLC from the rate of disappearance of ester in buffered solution—the rate of appearance of acid gave similar but less precise results; an additional rate constant of $(3.18 \pm 0.03) \times 10^{-6}$ was obtained for 40% ethanol/water at 101.5 °C.

methods allows reliable, direct measurements of first-order rate constants spanning at least seven orders of magnitude.

We now report rate constants for solvolyses of benzhydryl (1) and 1-adamantyl (2) p-nitrobenzoates and methanesulfonates (mesylates) in aqueous ethanol, providing the first reliable measurements of sulfonate/p-nitrobenzoate rate ratios. When combined with the known trends in substituent effects[2] and solvent effects (from the Grunwald–Winstein treatment[9]), these new data link an unusually diverse range of published kinetic data.

Results

The fast-response conductimetric method[4] was applied to solvolyses of benzhydryl mesylate (1, X = OMs) in pure

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1   2

3   4   5
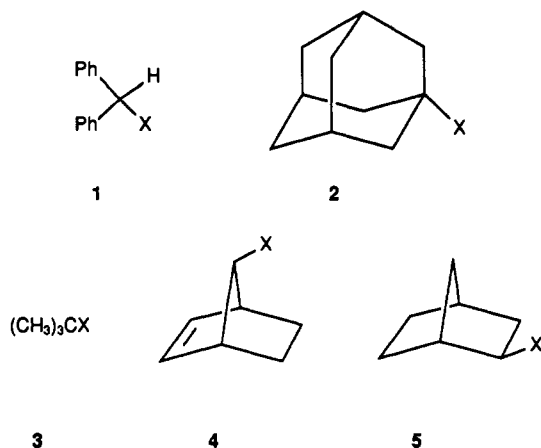
ethanol and in 90 and 80% aqueous ethanol (Table I) and to solvolyses of 1-adamantyl mesylate (2, X = OMs) in 60% aqueous ethanol (Table III). Corresponding solvolyses of *p*-nitrobenzoates (1, 2, X = OCOC$_6$H$_4$NO$_2$), investigated by HPLC, are shown in Tables II and III; these have been studied previously at high temperatures,[7,10] and the required alkyl–oxygen cleavage has been shown to be dominant by the incorporation of [18]OH$_2$ from 70% acetonitrile/water into the 1-adamantanol (2, X = OH) formed during solvolyses of 2 (X = OCOC$_6$H$_4$NO$_2$) at 150 °C.[7a] Also, in our work, ethyl *p*-nitrobenzoate (a product of acyl–oxygen fission in ethanol/water mixtures) was observed in only trace amounts (about 1%) and was stable under the reaction conditions. Reactions were buffered with 2,6-dimethylpyridine to avoid acid catalysis and to minimize buffer catalysis.[11]

Temperature extrapolations of only 25–35 °C were required to obtain the mesylate/*p*-nitrobenzoate rate ratios for solvolyses of 1 and 2 (Table IV). Tosylate/mesylate rate ratios, which are slightly solvent dependent but are close to unity,[9b] were then used to calculate tosylate/*p*-nitrobenzoate rate ratios (Table IV).

Benzhydryl tosylate 1 (X = OTs) has previously been isolated, and the preliminary rate constant of 4.5 × 10^{-3} s^{-1} in 90% THF/water at 0 °C[13] is 2–4-fold slower than we estimate from our results; tosylates are less suitable for fast kinetics because they dissolve much less rapidly than mesylates.

Discussion

Previous estimates of tosylate/*p*-nitrobenzoate rate ratios, varying nearly 3 orders of magnitude from 9.4 × 10^6 to 6.7 × 10^9,[3] have usually involved long temperature extrapolations and other assumptions linking data from three or four different sources. Our tosylate/*p*-nitrobenzoate rate ratios (Table IV) are toward the high end of the published range, significantly higher than the "rounded" value of 10^8 chosen recently.[3a] Three additional, directly determined, values are also given in Table IV.

Previous estimates of tosylate/*p*-nitrobenzoate rate ratios[3] and the literature values for substrates 3–5 (Table IV) required longer temperature extrapolations than those

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Table IV. Sulfonate/*p*-Nitrobenzoate Rate Ratios

substrate	solvent	temp, °C	rate ratio[a] OMs/OPNB	rate ratio[a] OTs/OPNB
1[b]	80% EtOH	25.0	3.3 × 10^9	3.3 × 10^9
2[c]	60% EtOH	75.0	1.9 × 10^8	1.7 × 10^8
3[d]	80% acetone	25.0	4.6 × 10^9	4.6 × 10^9
4[e]	70% dioxane	25.0		(3 × 10^8)
5[f]	97% CF$_3$CH$_2$OH	100.0	1.2 × 10^8	1.2 × 10^8

[a] Calculated from the OMs/OPNB rate ratio, assuming the OTs/OMs rate ratios (at 25 °C) given in ref 9b. [b] Kinetic data from Tables I and II. [c] Kinetic data from Table III. [d] Kinetic data for *p*-nitrobenzoate extrapolated from 125 and 100 °C[12a]) and for mesylate estimated from data in 80% ethanol/water[6] by an mY_{OMs} plot. [e] Kinetic data for *p*-nitrobenzoate extrapolated from 185, 170, and 140 °C (refs 12b and 12c) and for tosylate estimated from data in acetic acid (ref 12d) by an mY_{OTs} plot. [f] Kinetic data from refs 6 and 12e.

Table V. Temperature Dependence of Mesylate/*p*-Nitrobenzoate Rate Ratios[a]

substrate	temp, °C 25	50	75	100
benzhydryl 1[b]	3.3 × 10^9	9.0 × 10^8	3.0 × 10^8	1.1 × 10^8
1-adamantyl 2[c]	2.6 × 10^9	6.2 × 10^8	1.9 × 10^8	6.4 × 10^7

[a] Calculated by Arrhenius extrapolations. [b] Kinetic data from Tables I and II. [c] Kinetic data from Table III.

reported here for solvolyses of 1 and 2. Extrapolations using the Arrhenius equation amplify experimental errors, e.g., a 5% error at 140 °C is amplified about 5-fold at 50 °C. Also, curvature of Arrhenius plots due to heat capacity effects[14] can lead to errors of at least 100% for extrapolations from 150 to 25 °C. The latter results are based on a trial calculation for the solvolysis of methyl benzenesulfonate in water for which the heat capacity of activation (−36 cal mol^{-1} deg^{-1}) is relatively small. As ΔH^* is temperature dependent, varying in this case by 3.6 kcal/mol over a 100 °C range, extrapolations tend to give high results regardless of whether they are from higher or from lower temperatures. For our results for solvolyses of 1 and 2 (Table IV), extrapolations have been limited to 25–35 °C for each substrate, so errors should be small and will tend to cancel.

Because the activation energies for solvolyses of mesylates and *p*-nitrobenzoates differ by 10 kcal/mol, the measured rate ratios decrease significantly as the temperature is increased (Table V). The small differences in results for solvolyses of 1 and 2 (Table V) are due, at least in part, to extrapolation errors. The rate ratio for 5 (Table IV) is as expected for a value at 100 °C, and the ratio for 3 is also in satisfactory agreement with the other results. However, the rate ratio for 4 appears to be too low, perhaps because of acyl–oxygen fission in the highly unreactive *p*-nitrobenzoate (4, X = OCOC$_6$H$_4$NO$_2$). Other experimental difficulties associated with kinetic studies of unreactive 3,5-dinitrobenzoates have previously been reported.[15]

Why have previous literature estimates of tosylate/*p*-nitrobenzoate rate ratios varied so widely? Temperature effects do not account for the discrepancies.[3] Also, solvent effects on the rate ratio are expected to be small. Logarithms of rate constants for solvolyses of 1-adamantyl trifluoroacetate 2 (X = OCOCF$_3$) in aqueous acetone, ethanol, and methanol and in 97% trifluoroethanol and hexafluoro-2-propanol at 25 °C plot linearly (slope 1.04)

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vs 1- and 2-adamantyl tosylates (Y_{OTs}),[16a] and Y_{OTs} has also been shown to be a satisfactory solvent parameter for correlating rates of solvolyses of p-nitrobenzoates.[3a,16b,c]

There may be differences in strain energy released on ionization of p-nitrobenzoates and sulfonates, similar to those noted in comparisons of tertiary chlorides and p-nitrobenzoates.[7b] Tosylate/halide rate ratios for secondary and tertiary substrates are strongly influenced by steric factors.[17] The lower estimated tosylate/p-nitrobenzoate ratios (ca. 10^7) are based on an intermediate calculation of rate data for chlorides,[3a] in which data for both secondary and tertiary substrates are included. Tosylate/chloride rate ratios from secondary systems give ratios that are too small for direct comparisons with p-nitrobenzoate/chloride rate ratios from tertiary systems, and hence low tosylate/p-nitrobenzoate ratios were obtained.[3a]

Trifluoroacetates would be more suitable than chlorides as "bridges" between reactive sulfonates and unreactive p-nitrobenzoates because they are similar sterically. Also, trifluoroacetates are about as reactive as chlorides,[16a,18] and they can be prepared directly from alcohols without the possibility of carbocationic rearrangements. A minor disadvantage of trifluoroacetates is their low solubility.[16a,18b]

A rate ratio of 490 ± 20 for solvolyses of tosylates in acetic acid at 25 °C and 3,5-dinitrobenzoates in 60% acetone/water at 100 °C has previously been established for three cyclopropylcarbinyl substrates.[19] At 25 °C, 3,5-dinitrobenzoates solvolyze six times faster than p-nitrobenzoates,[11,20] which are 20–25 times more reactive than benzoates.[2c] Relative rates of solvolyses of sulfonate esters can be obtained from a compilation of data for tosylates and mesylates (see Table 5 of ref 9b) or from ρ values for solvolyses of arenesulfonates.[2a,2b]

The sulfonate/p-nitrobenzoate rate ratios discussed here are ratios of "titrimetric" rate constants. Benzhydryl p-nitrobenzoate (1, X = $OCOC_6H_4NO_2$) is known to undergo ^{18}O exchange about three times faster than solvolytic release of acid,[21] and similar observations have been made for sulfonates.[22] A note of caution[23a] about a previous assumption of constant tosylate/bromide rate ratios was based on ρ^+ values for solvolyses of 1-aryl-1-(trifluoromethyl)ethyl substrates; ρ^+ was −6.85 for tosylates[23b] and −10.3 for bromides.[23a] However, only one substituent (Me) was common to these two plots. Also, bromides are structurally less similar to tosylates than are p-nitrobenzoates.

Conclusion

Tosylate/p-nitrobenzoate solvolysis rate ratios (3 × 10^9 in 80% ethanol/water at 25 °C) are relatively insensitive to solvent and structural effects (steric and perhaps also electronic effects). The ratio varies almost 100-fold over a 100 °C range of temperatures and, allowing for this effect,

consistent results (Table IV) have been obtained for four substrates (1–3 and 5). Previous estimates of tosylate/p-nitrobenzoate rate ratios (spanning nearly 3 orders of magnitude at 25 °C) are unreliable because of the indirect comparisons required. The corresponding tosylate/3,5-dinitrobenzoate rate ratio is 5 × 10^8 at 25 °C.

Experimental Section

Chemicals. 1-Adamantyl p-nitrobenzoate (2, X = $OCOC_6H_4NO_2$) was recrystallized from ethanol, mp 188–189 °C (lit.[24] mp 185.8–186.1 °C, 1-adamantyl mesylate (2, X = OMs) was prepared as described previously,[4c,25] benzhydryl p-nitrobenzoate (1, X = $OCOC_6H_4NO_2$) was recrystallized from 50/50 hexane/acetone, mp 134–135.5 °C (lit.[26] mp 131–133 °C), and benzhydryl mesylate (1, X = OMs) was prepared in situ.[6]

Kinetics. Conductimetric procedures for fast reactions were as described previously,[4c,d,6] except that LSKIN calculations[27] were performed in a few seconds on an Amstrad PC1512 (approximately equivalent to an IBM XT). Because 1-adamantyl p-nitrobenzoate is relatively insoluble, the following procedure was adopted: the substrate (7.5 mg)[28] was mixed with dry acetonitrile (1 mL), warmed, sonicated for 10 min, and then filtered. 2,6-Dimethylpyridine (1 μL) was added to the solvolysis medium (50 mL), this solution (1.7 × 10^{-4} M) was dispensed into 5-mL ampules, and the acetonitrile solution (25.0 μL) was then added (<10^{-4} M p-nitrobenzoate). HPLC analyses required only 25.0 μL of solution, eluted with 95% methanol/water, with detection at 260 nm (A = 0.05).

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(28) Four-fold less sample could conveniently have used if the sample had been less plentiful.

Acyclic 1,4-Radical Cations. Direct Observation and Stability

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Introduction

One of the most characteristic reactions of radical ions is the unimolecular or biomolecular formation of "distonic radical ion" in which charge and radical sites are separated from each other.[1] An introduction of an electron-donating group such as a methoxyl group which stabilizes the cationic site of the distonic radical ion enhances the efficiency and the selectivity of the reaction of radical cations.[2] A typical example of the distonic radical ions is an acyclic

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