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Solvent Ionizing Power. Comparisons of Solvolyses of 1-Adamantyl Chlorides, Bromides, Iodides, and Tosylates in Protic Solvents

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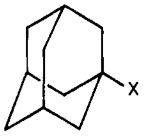
Solvolytic rate constants for 1-adamantyl iodide (1-AdI) in binary aqueous mixtures of ethanol, methanol, acetone, trifluoroethanol, and hexafluoroisopropyl alcohol and in acetic and formic acids are reported. Additional kinetic data for solvolyses of 1-adamantyl halides in 97% w/w hexafluoroisopropyl alcohol/water were obtained by using a microconductivity cell (volume, ca. 0.4 mL). Kinetic data for iodine-catalyzed solvolyses of 1-AdI in methanol/water mixtures are also reported. A scale of solvent ionizing power for iodides (Y_I) is defined by $\log (k/k_0)_{1\text{-AdI}} = Y_I$, where k is the rate constant for solvolysis of 1-AdI in any solvent at 25 °C relative to 80% v/v ethanol/water (k_0). Correlations of Y_I and similarly defined scales for tosylates (Y_{OTs}) and bromides (Y_{Br}) with data for chlorides (Y_{Cl}) show variations in slopes attributed to charge delocalization in the leaving group (slopes, Cl > Br > I > OTs); acidic solvents show significant deviations from the correlation lines. The effect of iodine catalysis increases as solvent ionizing power decreases, consistent with formation of the charge delocalized leaving group I_3^-. Y_I does not correlate satisfactorily with Kosower's Z values for aqueous and alcohol solvents, and the range of Z values is substantially greater in energy terms than the corresponding range of Y_I values. Our data provide qualified independent support for a recent proposal by Swain et al. that only two solvent properties correlate the *major* solvent effect on rates, equilibria and spectra.

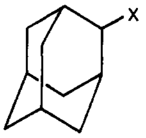
The concept of solvent ionizing power (Y) has proved useful for interpreting the mechanisms of heterolytic reactions in protic media.[1-5] Values of Y are defined by eq 1, in which k/k_0 refers to solvolysis rates at 25 °C in any solvent (k) relative to 80% v/v ethanol/water (k_0). When RX (eq 1) is *tert*-butyl chloride, m = 1.000 defines the

$$\log (k/k_0)_{RX} = mY \tag{1}$$

original Y values of solvent ionizing power for each solvent.[5a] These Y values were found to be unsuitable for correlating solvolytic rate data for tosylates,[3c,6] so Y_{OTs} values were defined by eq 1 with RX = 2-adamantyl tosylate (II, X = OTs) and m = 1.00.[3c] To separate the effects of nucleophilic solvent assistance (S_N2 character) from those due to solvation of the leaving group, it is necessary to compare solvolyses having the same leaving group.[1a] However, the inadequacies of the original Y values for correlating solvolytic rate data for tosylates cannot be attributed solely to leaving group effects (chloride vs. tosylate). A comparison of solvent effects on the reactivity of *tert*-butyl chloride with 1-adamantyl chloride (I, X = Cl), along with other evidence, showed that solvolyses of *tert*-butyl chloride were sensitive to nucleophilic solvent assistance (S_N2 character).[2r,3d,4e] To remove this nucleophilic contribution from the original Y values and to allow for leaving group effects, a scale of solvent ionizing power for chlorides (designated Y_{Cl}) was defined by eq 1 with RX = 1-adamantyl chloride (I, X = Cl). An analogous scale for bromides (Y_{Br}) was also defined.[3d]



(I)



(II)

Solvent effects on the reactivity of I and II (X = OTs) are almost identical,[3a] and so very similar Y_{OTs} values could be defined by eq 1 with RX = 1-adamantyl tosylate (I, X = OTs) and m = 1.00. Because I (X = OTs) solvolyzes about 10^5 times faster than II (X = OTs) and both are strongly prone to S_N1 reactions, it is possible to examine systematically the solvent effects on S_N1 reactivity for a wide range of leaving groups using the adamantyl framework as a relatively "constant" alkyl group.[3a] Kinetic data for reactive leaving groups (e.g. perchlorate,[4c] tosylate[3c,f,4b,7]) have been obtained from solvolyses of II, in addition to data for I (X = Cl,[3d] Br,[3d,8,9] OMs,[3a] and OTs).[4a] We now

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Table I. Rate Constants for Solvolyses of 1-Adamantyl Iodide (I, X = I)[a]

solvent	temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
80% EtOH	100.1	$(3.52 \pm 0.04) \times 10^{-4}$		
	75.0	$(3.28 \pm 0.04) \times 10^{-3}$	23.7	−6.7
	25.0^{c}	9.0×10^{-7}		
	25.0^{c,d}	8.45×10^{-7}	23.2	−8.6
	25.0^{c,e}	$(5.8 \pm 0.2) \times 10^{-7}$		
50% EtOH	25.0	$(3.55 \pm 0.05) \times 10^{-5}$		
20% EtOH	25.0	$(2.79 \pm 0.04) \times 10^{-3}$		
H_2O^{f}	25.0	$(1.01 \pm 0.02) \times 10^{-2}$		
100% MeOH	75.0^{g}	$(7.03 \pm 0.15) \times 10^{-5}$		
	60.0^{g}	$(1.15 \pm 0.02) \times 10^{-5}$	27.1	0.0
	60.3^{e,h}	$(1.4 \pm 0.1) \times 10^{-5}$		
	50.0^{g,h}	$(3.14 \pm 0.01) \times 10^{-6}$		
	25.0^{c}	8.4×10^{-8}		
80% MeOH	50.0	$(8.99 \pm 0.11) \times 10^{-5}$		
	35.0	$(1.40 \pm 0.01) \times 10^{-5}$	24.5	−1.4
	25.0^{h}	$(3.31 \pm 0.01) \times 10^{-6}$		
	25.0^{i}	$(3.4 \pm 0.1) \times 10^{-6}$		
60% MeOH	50.0	$(1.17 \pm 0.01) \times 10^{-3}$		
	25.0^{j}	$(5.4 \pm 0.1) \times 10^{-5}$	22.9	−1.2
40% MeOH	45.0	$(6.72 \pm 0.02) \times 10^{-3}$		
	25.0	$(6.08 \pm 0.11) \times 10^{-4}$	22.0	0.6
20% MeOH	25.0^{j}	$(3.41 \pm 0.05) \times 10^{-3}$		
80% $(CH_3)_2CO$	75.0^{g}	$(1.22 \pm 0.02) \times 10^{-4}$		
	50.0^{g}	$(8.61 \pm 0.11) \times 10^{-6}$	23.1	−10.5
	25.0^{c}	3.9×10^{-7}		
60% $(CH_3)_2CO$	50.0	$(1.79 \pm 0.01) \times 10^{-4}$		
	25.0	$(9.28 \pm 0.12) \times 10^{-6}$	22.1	−7.5
	25.0^{k}	$(9.1 \pm 0.2) \times 10^{-6}$		
40% $(CH_3)_2CO$	50.0	$(2.69 \pm 0.01) \times 10^{-3}$		
	25.0	$(1.56 \pm 0.03) \times 10^{-4}$	21.2	−4.7
20% $(CH_3)_2CO$	25.0	$(1.76 \pm 0.08) \times 10^{-3}$		
	25.0^{k}	$(1.82 \pm 0.02) \times 10^{-3}$		
10% $(CH_3)_2CO$	25.0^{l}	$(3.54 \pm 0.25) \times 10^{-3}$		
5% $(CH_3)_2CO$	25.0^{l}	$(5.4 \pm 0.8) \times 10^{-3}$		
97% CF_3CH_2OH	25.0	$(9.6 \pm 0.1) \times 10^{-5}$		
70% CF_3CH_2OH	25.0	$(2.38 \pm 0.04) \times 10^{-4}$		
50% CF_3CH_2OH	25.0	$(4.3 \pm 0.1) \times 10^{-4}$		
CH_3CO_2H	100.5^{m,n}	$(2.7 \pm 0.3) \times 10^{-5}$		
	81.1	$(3.9 \pm 0.2) \times 10^{-6}$	25.5^{o}	−11.6
	25.0^{c}	3.6×10^{-9}		
HCO_2H	25.0^{n}	$(2.5 \pm 0.5) \times 10^{-5}$		

[a] Determined conductimetrically in duplicate except where otherwise noted; errors shown are average deviations. [b] Percent EtOH, MeOH, and $(CH_3)_2CO$ refer to ethanol/water (v/v), methanol/water (v/v), and acetone/water (v/v) respectively; percent CF_3CH_2OH and percent $(CF_3)_2CHOH$ refer to trifluoroethanol/water (w/w) and hexafluoroisopropyl alcohol/water (w/w), respectively. [c] Calculated from data at other temperatures. [d] Data from ref 8. [e] Determined titrimetrically; solution buffered with 0.015 M 2,6-lutidine. [f] Containing <0.1% acetone. [g] Solution buffered with ca. 10^{-3} M lutidine. [h] Single measurement of rate constant. [i] Determined titrimetrically in duplicate; one of the solutions contained an excess of sodium thiosulfate. [j] Triplicate measurement of rate constant. [k] Independent measurement in duplicate. [l] Quadruplicate measurement of rate constant. [m] Triplicate measurement of rate constant. [n] Determined titrimetrically; solution initially contained 0.015 M sodium acetate. [o] ±2 kcal/mol.

Table II. Rate Constants for Solvolyses of 1-Adamantyl (1-AdX) and *tert*-Butyl (*t*-BuX) Halides in 97% Hexafluoroisopropyl Alcohol/Water[a]

halide	temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1-AdCl	14.0^{b}	$(3.90 \pm 0.03) \times 10^{-4}$		
	25.0^{b,c}	$(1.09 \pm 0.01) \times 10^{-3}$	15.1	−21.6
	35.0^{b}	$(2.53 \pm 0.01) \times 10^{-3}$		
1-AdBr	15.0^{d}	$(3.85 \pm 0.01) \times 10^{-3}$		
	25.0^{d,e}	$(9.68 \pm 0.01) \times 10^{-3}$	14	−21
	35.0^{d,f}	$(1.98 \pm 0.02) \times 10^{-2}$		
1-AdI	13.8^{d}	$(1.36 \pm 0.01) \times 10^{-3}$		
	25.0^{d}	$(4.00 \pm 0.02) \times 10^{-3}$	15.2	−18.8
	35.0^{d}	$(9.03 \pm 0.06) \times 10^{-3}$		
	25.0^{g}	$(4.23 \pm 0.10) \times 10^{-3}$		
	25.0^{b,h}	$(4.03 \pm 0.02) \times 10^{-3}$		
t-BuBr	25.0^{i}	$(2.17 \pm 0.01) \times 10^{-2}$		
	25.0^{j}	$(2.20 \pm 0.03) \times 10^{-2}$	16.2	−11.7

[a] As Table I; measurements using the microconductivity cell (volume, ca. 0.4 mL) except where stated otherwise. [b] Substrate dissolved by sonication prior to the kinetic run. [c] Previously reported rate constant $k = (9.7 \pm 0.5) \times 10^{-4}$, ref 13. [d] Substrate dissolved by injecting in dioxan solution (1 μL containing 0.15 mg of substrate). [e] Previously reported rate constant $k = (9.1 \pm 0.2) \times 10^{-3}$, ref 13. [f] Rate constant may be unreliable (too low) because the substrate may have dissolved during the kinetic run. [g] Independent measurement using a different batch of solvent and a larger conductivity cell (volume ca. 3 mL). [h] Single measurement. [i] Injected 2 μL of neat liquid. [j] Reference 13.

Table III. Approximate Catalytic Effects of 10^{-3} M Iodine (+10^{-4} M HI) on Solvolyses of 1-Adamantyl Iodides in Aqueous Methanol at 25 °C

solvent	background oxidation[a] k, s^{-1}	catalytic solvolysis[b] k, s^{-1}	catalytic rate factor[c]
20% MeOH	$(6.3 \pm 0.7) \times 10^{-6}$	$(3.4 \pm 0.4) \times 10^{-3}$	1.0
40% MeOH	$(5.7 \pm 1.2) \times 10^{-5}$	$(3.3 \pm 0.2) \times 10^{-3}$	5.4
60% MeOH	$(2.3 \pm 0.4) \times 10^{-4}$	$(4.1 \pm 0.5) \times 10^{-4}$	8
80% MeOH[d]	$(5 \pm 2) \times 10^{-5}$	$(5.0 \pm 0.5) \times 10^{-5}$	15

[a] Oxidation of methanol by iodine—no adamantyl iodide present. [b] A correction of conductance readings for the competing background oxidation was required for 60% MeOH and 80% MeOH. [c] Ratio of first-order rate constants for catalytic solvolysis (previous column) and for uncatalyzed solvolysis (Table I). [d] Catalytic solvolysis rate determined in triplicate.

report an extensive kinetic study of solvolyses of 1-adamantyl iodide (I, X = I), which has previously been examined only in 80% ethanol/water.[8] Because iodide ion is larger than bromide and chloride and is the least electronegative anion of the above series, we can assess the significance of specific anion solvation during heterolytic reactions.

Parallel with the further development of Y values, there has been increasing emphasis on solvatochromism, e.g., in the solvent effects on the electronic spectra of pyridinium ions (III) leading to Z values,[10] or pyridinium N-phenolates leading to $E_T(30)$ values.[11] Both Z and $E_T(30)$ are relatively well-defined single parameters, which have been applied extensively as measures of solvent polarity.[11b] Solvent effects on spectra also form the basis of the *multiparameter* treatment of Kamlet and Taft including π^* (solvent dipolarity), α (hydrogen bond donor), and β (hydrogen bond acceptor)—see eq 2.[12] However it is not

$$\log k = \log k_0 + s\pi^* + a\alpha + b\beta \qquad (2)$$

yet clear to what extent scales based on solvatochromism are suited to probing the microscopic changes in solvation occurring *during* heterolytic reactions. Our data for 1-adamantyl iodide provide the first direct comparison between a solvatochromic scale (Z) and a scale of solvent

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ionizing power based on solvolysis rates (Y) in which the anion is identical (iodide).

Results

Kinetic data for solvolyses of 1-adamantyl iodide obtained conductimetrically and/or titrimetrically are shown in Table I. Additional kinetic data for solvolyses of various halides in 97% w/w hexafluoroisopropyl alcohol/water were obtained (Table II) conductimetrically in a microconductivity cell (volume, ca. 0.4 mL). The effects of 10^{-3} M iodine on the rates of solvolyses were examined (Table III) to assess the kinetic effects of the small amounts of iodine ($<10^{-5}$ M) formed during standard conductimetric runs. Formation of iodine was reduced by addition of base (2,6-lutidine or sodium acetate) and/or by removal of oxygen. Experimental procedures were similar to those previously described.[3a,d,6] except that much more use was made of ultrasonics to ensure that substrates were rapidly dissolved before kinetic data were obtained. Ultrasonics were also employed to degas partially the solvents used for kinetics in pure methanol. However, significant quantities of iodine ($<10^{-3}$ M) were produced during titrimetric kinetics runs (initial substrate concentrations, ca. 0.005 M), but acceptable kinetic runs were followed conductimetrically (initial substrate concentrations, $<10^{-3}$ M). Formation of iodine during formolyses and acetolyses was minimized by deoxygenation under vacuum (either by ultrasonics or by freeze, evacuate, purge with nitrogen, freeze etc cycles). Although $<2 \times 10^{-4}$ M I_2 was produced from 5×10^{-3} M adamantyl iodide, unsatisfactory infinity titres were obtained. These reactions appear to be reversible, even when buffered, as previously reported for similar reactions.[3d,5b] Selected reactions were studied with exclusion of light, but no significant changes in rate constants were observed.

Iodine-catalyzed solvolyses in aqueous methanol were studied under conditions where the iodine concentration remained almost constant (10^{-3} M), whilst the background conductivity increased even in the absence of adamantyl iodide. The latter process was partially suppressed by 10^{-4} M hydrogen iodide and was accelerated by 2,6-lutidine. Presumably iodine oxidized methanol and was partially hydrolyzed to HOI, which may also oxidize methanol. Iodine may also be regenerated by reaction with oxygen. Catalyzed solvolysis rates similar to those reported in Table III were obtained in the absence of 10^{-4} M hydrogen iodide. From similar studies of iodine-catalyzed reactions in 50% and 80% ethanol/water (with and without added HI) it appears that ethanol is oxidized more rapidly than methanol. We were unable to obtain reliable data even in the absence of 1-adamantyl iodide—after a period of linear change the conductance increased rapidly.

Discussion

Kinetic Data. Our results include several revisions of previously published rate constants. For solvolysis of 1-adamantyl iodide in 80% ethanol/water at 25 °C (Table I), the discrepancy appears to be due to extrapolation error and possibly to iodine catalysis. For solvolyses of adamantyl chloride and bromide in 97% hexafluoroisopropyl alcohol/water at 25 °C, the small discrepancies may be explained by improved techniques for obtaining a thoroughly dissolved substrate (Table II). The remarkably good results obtained with the microconductivity cell (volume, ca. 0.4 mL) counters the cost disadvantage of solvolyses in hexafluoroisopropyl alcohol. To obtain such good precision data with the microcell, it was necessary to equilibrate the solvent and substrate in the cell overnight at the required temperature. Even then the first kinetic run was, in seven cases, significantly less reliable (ca. 5% error) than the following two kinetic runs. It appears that control of surface adsorption effects may be critically important in applications requiring microconductivity cells, which inevitably have a high surface/volume ratio. Interestingly, some of the earlier kinetic studies by conductivity employed as much as 1 L of solvent (e.g., water).[14] It is necessary for volatile solutes (e.g., *tert*-butyl chloride) to minimize the vapor space above the solvent,[15] but large volumes of solvent now appear to be unnecessary.[16]

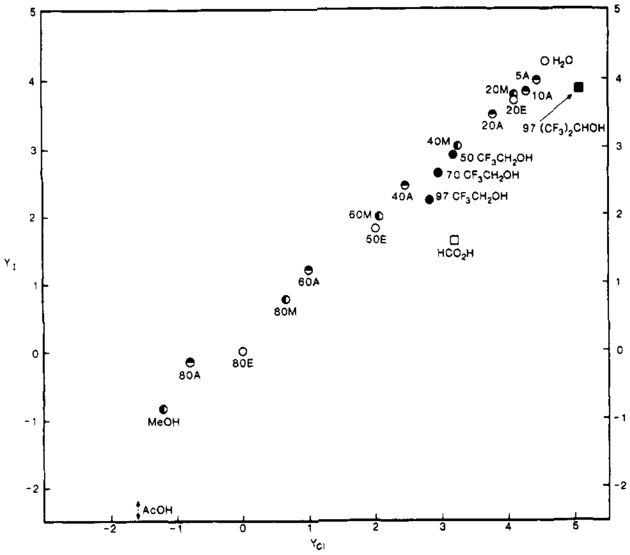

Figure 1. Correlation of logarithms of solvolysis rates for 1-adamantyl chloride (I, X = Cl) vs. 1-adamantyl iodide (I, X = I) at 25 °C. Data from Table I and ref 3d, expressed as Y_{Cl} or Y_I values according to eq 1.

The main significance of the results in Table III is evidence that iodine catalysis would not be expected to contribute significantly to the observed solvolysis rate constants (Table I), except for the possibility of a small (ca. 20%) contribution for 100% methanol. Of the mechanisms for iodine catalysis discussed recently,[17] we favor formation of a molecular complex (1-adamantyl triiodide) followed by solvolysis.[18] This accounts for the reduction in catalytic effects as the solvent ionizing power increases (Table III), because an increase in the size of the leaving group decreases m (eq 1, see also discussion below); also the formation constants for triiodides probably increase as the alcohol content of the solvent increases.[17] Similar results were obtained for iodine-catalyzed solvolyses of *tert*-butyl iodide in aqueous ethanol.[17] The slightly greater catalytic effects reported for 1-adamantyl iodide compared with *tert*-butyl iodide may be due to a higher formation constant for 1-adamantyl triiodide, following the trend observed for simpler alkyl systems;[18a] consequently, we question the recent proposal[17] that a change in mechanism occurs. Oxidation of alcohols by iodine has received little attention,[19] but our results are in qualitative agreement with more extensive studies of the oxidation of alcohols by bromine.[20]

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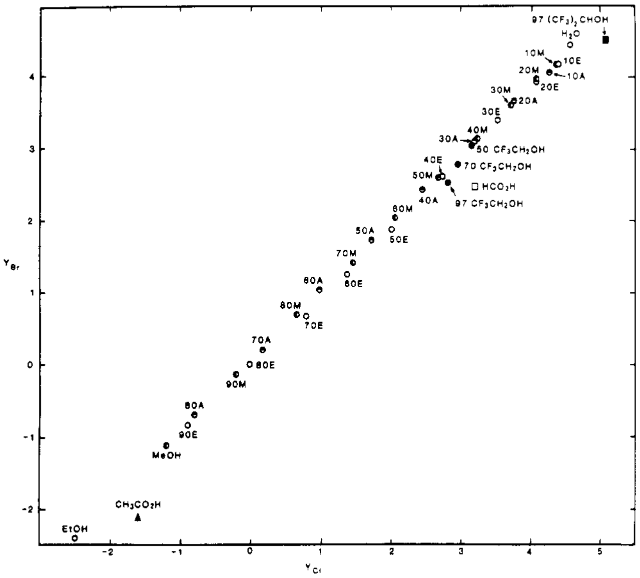

Figure 2. As for Figure 1, except correlation of Y_{Cl} vs. Y_{Br} (data from ref 3d).

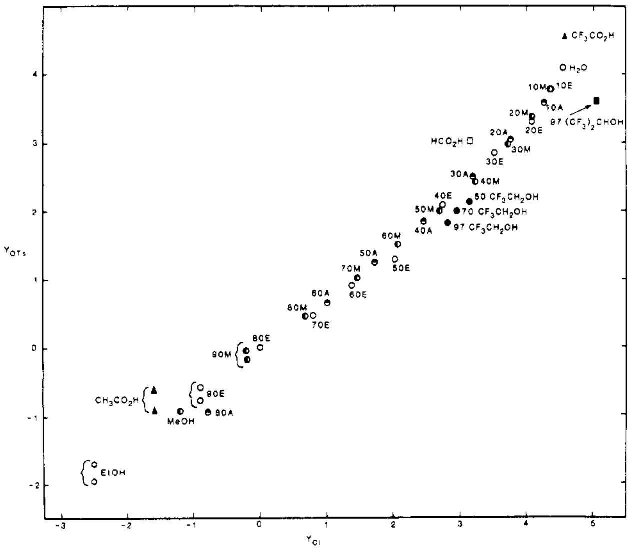

Figure 3. As for Figure 1 except Y_{Cl} vs. Y_{OTs} (data from ref 3a and 3c). Additional Y_{OTs} values for EtOH, CH_3CO_2H, 90E, 90M, and 80A defined from data for 1-adamantyl tosylate (I, X = OTs)—ref 4a.

Y_{I} values can be defined by eq 1 with RX = 1-adamantyl iodide (I, X = I). A plot of all experimentally derived Y_{I} values vs. Y_{Cl} (Figure 1) provided additional Y_{I} values for ethanol/water, methanol/water, and acetone/water by linear interpolation or limited extrapolation (Table IV). This approach to the calculation of additional data for restricted ranges of solvents is supported by similar correlations of Y_{Br} and Y_{Cl} (Figure 2) and of Y_{I} and Y or log k for *tert*-butyl iodide.[21] Iodide/bromide rate ratios (Table IV) vary with solvent ionizing power and are less than unity for the relatively acidic solvents.

Table IV. Summary of Solvolysis Data for 1-Adamantyl Iodides. New *Y* Values for Iodides (Y_{I}) and Iodide/Bromide Rate Ratios[a]

	1-adamantyl-I		
solvent[b]	10^6k, s^{-1}	Y_{I}	$k_{\text{1-AdI}}/k_{\text{1-AdBr}}$
100% EtOH	0.0037[d]	−2.2[d]	3.7
90% EtOH	0.09[d]	−0.81[d]	2.3
80% EtOH	0.58	0.00	2.1
70% EtOH	2.97[e]	0.71[e,f]	2.2
60% EtOH	9.63[e]	1.22[e]	1.9
50% EtOH	35.5	1.79	1.7
40% EtOH	167[g]	2.46[g]	1.4
30% EtOH	858[g]	3.17[g]	1.2
20% EtOH	2790	3.68	1.2
10% EtOH	5170[h]	3.95[h]	1.2
H_2O	10100	4.24	1.3
100% MeOH	0.084	−0.84	4.0
90% MeOH	0.60[i]	0.01[i]	3.0
80% MeOH	3.37	0.76	2.4
70% MeOH	16.7[i]	1.46[i]	2.3
60% MeOH	54	1.97	1.7
50% MeOH	200[i]	2.54[i]	1.8
40% MeOH	608	3.02	1.6
30% MeOH	1580[i]	3.43[i]	1.4
20% MeOH	3410	3.77	1.4
10% MeOH	5910[j]	4.01[j]	1.4
80% $(CH_3)_2CO$	0.39	−0.17	6.5
70% $(CH_3)_2CO$	2.23[k]	0.58[k]	4.5
60% $(CH_3)_2CO$	9.2	1.20	3.1
50% $(CH_3)_2CO$	38.3[k]	1.82[k]	2.5
40% $(CH_3)_2CO$	156	2.43	2.0
30% $(CH_3)_2CO$	570[k]	2.99[k]	1.6
20% $(CH_3)_2CO$	1790	3.49	1.4
10% $(CH_3)_2CO$	3540	3.79	1.1
5% $(CH_3)_2CO$	5400	3.97	
97% CF_3CH_2OH	96	2.22	1.0
70% CF_3CH_2OH	238	2.61	1.4
50% CF_3CH_2OH	430	2.87	1.4
97% $(CF_3)_2CHOH$	4000	3.84	0.41[l]
CH_3CO_2H	0.0036	−2.2[m]	0.6[n]
HCO_2H	25	1.6	0.4

[a] Kinetic data from Table I and *Y* values defined by eq 1 with *m* = 1.00 and RX = 1-adamantyl iodide at 25 °C, except where stated otherwise. [b] As in Table I. [c] Kinetic data for 1-adamantyl bromide from ref 3d. [d] By extrapolation of data for 80% and 50% EtOH in a plot of Y_{I} and Y (ref 5b). [e] Interpolated from a plot of Y_{I} and Y_{Cl} for 80% and 50% EtOH. [f] Interpolation from a plot of Y_{I} and Y (see footnote e) gives $Y_{\mathrm{I}} = 0.64$. [g] As footnote *e*, but including 20% EtOH; the equation is $Y_{\mathrm{I}} = 0.900Y_{\mathrm{Cl}} - 0.009$ (correlation coefficient 0.9999). [h] As footnote *g*, except extrapolated. [i] Interpolated from a plot of Y_{I} and Y_{Cl} for 100%, 80%, 60%, 40%, and 20% MeOH; the equation is $Y_{\mathrm{I}} = 0.870Y_{\mathrm{Cl}} + 0.189$ (correlation coefficient 0.9999). [j] As footnote *i* except extrapolated. [k] Interpolated from a plot of Y_{I} and Y_{Cl} for 80%, 60%, 40%, 20%, 10%, and 5% $(CH_3)_2CO$; the equation is $Y_{\mathrm{I}} = 0.792Y_{\mathrm{Cl}} + 0.451$ (correlation coefficient 0.9997). [l] Kinetic data from Table II. [m] From considerations of possible experimental errors in $\Delta H^{\ddagger}$ (Table I) and temperature extrapolation errors; a value of $Y_{\mathrm{I}} = -2.5$ could be justified. [n] At 100 °C.

Comparison of *Y* Scales of Solvent Ionizing Power. Data for Y_{I}, Y_{Br}, and Y_{OTs} are plotted against Y_{Cl} in Figures 1–3. The more acidic solvents, CH_3CO_2H and HCO_2H (Figures 1–3) and CF_3CO_2H (Figure 3), deviate significantly from the correlation lines for aqueous alcohols. Although most of these deviations are relatively small, they are consistent in that the leaving groups containing the more electronegative charge-carrying elements react slightly faster than expected; the order OTs > Cl > Br > I is consistent with greater electrophilic assistance by these acidic solvents, which follows the order of electronegativity of the appropriate atoms: O in tosylates > Cl in chlorides etc.[5c] Consequently, the largest deviations would be observed in a plot of Y_{OTs} against Y_{I}. An important feature of the correlations with Y_{Cl} (Figures 1–3) is that the *electrophilic effects are much smaller than those previously calculated from the rate ratio* $[k_{\mathrm{EW}}/k_{\mathrm{RCO_2H}}]_Y$, a measure of the deviations between the data for carboxylic acids and the correlation line for ethanol/water based on the original *Y* values. For solvolyses of 2-adamantyl tosylate (II, X = OTs), $[k_{\mathrm{EW}}/k_{\mathrm{HCO_2H}}]_Y$ increases from 0.04[3f] to 0.3 and $[k_{\mathrm{EW}}/k_{\mathrm{AcOH}}]_Y$ increases from 0.2[3f] to 0.5, when

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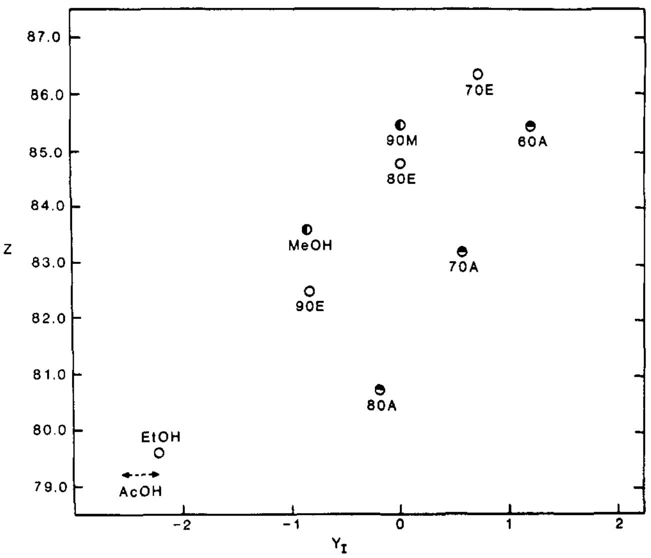


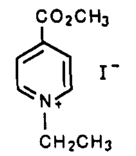
Figure 4. As for Figure 1 except Y_I vs. Z values based on solvatochromism of IIIa (data from ref 10).

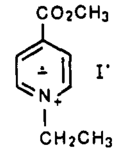
the reference Y scale is changed from the original Y to Y_{Cl}.

The curvature of the ethanol/water line for tosylates (Figure 3) is much greater than for the corresponding mesylates[6] and appears to be due to a subtle solvation difference between the aryl group for tosylates and the methyl group for mesylates in highly aqueous media.[6] Consequently it is highly questionable whether any mechanistic significance can be attached to the apparent deviation of 97% $(CF_3)_2CHOH$ from the main correlation line (Figure 3). All of the other data points for fluorinated alcohols are close to a line through data for all aqueous media (Figures 1–3). Relative to Y_{Cl}, the slopes of the correlation lines for *all* data points shown in Figures 1–3 are Y_{Br}, 0.96 ± 0.02, Figure 2, Y_I, 0.85 ± 0.05, Figure 1, Y_{OTs}, slope 0.80 ± 0.02, Figure 3; lower slopes (m values, eq 1) appear to arise from negative charge delocalization in developing anions (depending on ionic radii)[22] and from positive charge delocalization in carbocations (depending on the degree of nucleophilic or anchimeric assistance[3b,c]).

The *order* of solvent ionizing power based on solvolyses of adamantyl substrates (Figures 1–3) appears to depend only to a small extent on the leaving group. If the Y_{OTs}, Y_I, and Y_{Br} values are scaled to correspond to Y_{Cl} values (by dividing each Y_X value by the slope of the appropriate correlation line), most of the scaled Y_X values for a specific solvent agree within 0.5 (exceptions include CH_3CO_2H, range of scaled Y_X values 1.6, HCO_2H, range 1.2, and 50% CF_3CH_2OH, range 0.9). These results suggest that there may be one major electrostatic effect attributable to differences in solvent ionizing power but that other more subtle effects contribute to each Y_X scale (e.g., small differences in electrophilic assistance and/or hydrogen bonding and differences in solvation of aryl and alkyl groups in tosylates and mesylates[6]).

Correlations Based on Solvatochromism for Single Indicators. The data for Y_I (Table IV) permit the first comparison between a scale of solvent ionizing power and a solvatochromic scale Z,[10] having the same anion (iodide). The results (Figure 4) show a large and *systematic* dispersion between the correlation lines for the three aqueous binary mixtures. Although the electronic transition on which the Z scale is based is concentration dependent,[23] apparently this does not lead to large *random* errors in Z values. The slopes of these three lines are significantly greater than unity when Y_I values are expressed in kcal/mol ($\Delta Y_I = 1.0 \equiv 1.4$ kcal/mol). A similar result was obtained in a comparison of Y_{OTs} and $E_T(30)$,[3a] but in this case the anions were not identical. If it is assumed that charge development in an S_N1 reaction is almost complete[24] and that the transition state is in equilibrium with the solvent,[15] the solvatochromic scales predict erroneously large solvent effects. These results can be reconciled as follows. Kosower proposed for polar solvents that there was a region of strongly oriented solvent molecules (a cybotactic region) stabilizing the ion pair in the ground state (IIIa) and destabilizing the excited state (IIIb).[10] He argued that destabilization of the excited state (relative to the energy in the gas phase or in isooctane as solvent) was approximately equal to stabilization of the ground state. Accordingly, the energy range of Z values should be approximately double the range of Y_I values—for the series EtOH → 70% EtOH the range of Z values is 6.8 kcal/mol and the corresponding range of Y_I values is 4.1 kcal/mol. These results suggest, as might have been expected, that the stabilization of the ion pair ground state (IIIa) may be *greater than* destabilization of the neutral excited state (IIIb).


(IIIa)


(IIIb)

Presumably, if Z values are expected to be good models for microscopic solvation effects occurring *during* heterolytic reactions, it is important that destabilization of the excited state (IIIb) makes a relatively small contribution to the observed solvatochromism. In contrast, a recent study of the thermodynamics of solution and ionization of an ion pair closely related to IIIa showed that even the ground-state ion pair was *destabilized* on transfer to more polar solvents and that the excited state was highly destabilized.[25a] However, such measurements will include various solvation effects of absolute significance which change relatively little during the process ground state → excited state or transition state.[25b] Attempts have been made to dissect some of these solvation effects (e.g., to separate the cavity term[24]), but other nonelectrostatic effects (e.g., hydrophobic interactions) and some electrostatic effects will still be common to both ground and excited states. This argument suggests that dissecting thermodynamic data into contributions from initial states and transition states may be misleading.

Multiparameter Correlations. We can compare our results (Figures 1–3) with those expected from studies of π^*, α, and β (eq 2). It has previously been assumed that β can be associated with solvent nucleophilicity,[26a] but it now appears[26b] that correlations with β will be restricted to solutes capable of hydrogen bond donation. Y values should be correlated with π^* and α.[3a,12a] We have shown that rate data in 97% CF_3CH_2OH and 97% $(CF_3)_2CHOH/H_2O$ are very similar to data for the corre-

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sponding pure solvents.[3b] Thus, we *have* Y values for five hydroxylic solvents having a wide range of values for hydrogen bond donation α[12b] [e.g., H_2O (1.17), CH_3OH (0.93), C_2H_5OH (0.83), CF_3CH_2OH (1.51), and $(CF_3)_2CHOH$ (1.96)] spanning a wide variety of leaving groups. These five solvents show such minor deviations from our correlation lines (Figures 1–3) that separation of these Y values into π and α terms would be very difficult to justify. Also, if the deviations of the fluorinated solvents from the correlation line for Y_{OTs} vs. Y_{Cl} (Figures 3) are significant, they are in the *opposite direction* from that predicted by the high α of $(CF_3)_2CHOH$ and the greater electronegativity of oxygen. However, it may be argued that the carboxylic acids show sufficiently large deviations from our correlations that a separate adjustable parameter (e.g., α) could be justified to account for the specific effects of hydrogen bonding to the various leaving groups. Unfortunately reliable α values for carboxylic acids are not yet available.

Our approach is based on eq 3, an extension of eq 1 with l representing the substrate's sensitivity to solvent nucleophilicity (N).[3c] Values of N are derived from model

$$\log (k/k_0)_{RX} = mY + lN \qquad (3)$$

S_N2 reactions with appropriate correction for the mY term (eq 3).[3c,27] Values of l vary from 1 (defined for solvolyses of methyl tosylate at 50 °C) to 0 for 2-adamantyl tosylate (II, X = OTs) and parallel the susceptibilities to S_N2 reactions.[3b,c,28]

In an impressive recent study, Swain et al.[29] have correlated a wide range of solvent dependent properties (rates, equlibria, and spectra)—eq 4. In eq 4, a and b are the

$$\log k = aA + bB + c \qquad (4)$$

substrate's sensitivities to the solvent's tendency for anion solvation (acity, A) and cation solvation (basicity, B), respectively; nominally c represents the rate of reaction in *n*-heptane ($A = B = 0$), although it is a free adjustable parameter for 66 of the 77 data sets because only 11 of the data sets included experimental data for heptane. Kevill has replied to Swain's criticisms of eq 3 and has questioned the suitability of eq 4 for solvolytic reactions,[30] but one aspect merits further emphasis. Swain et al. stated explicitly that B solvation *included* cation solvating tendency and nucleophilicity and they implied that A solvation *excluded* them.[29] In practice their computer program appears to have allocated some solvent nucleophilicity effects to reduced or even negative sensitivity to acity (e.g., solvolyses of methyl tosylate), *reflecting the tendency for strongly acidic solvents to be weak nucleophiles*. Conversely some A solvation could be treated as a reduced sensitivity to B. The resulting correlations fit an outstanding range of data,[29] but some unreliable a and b values lead to extraordinary predictions.[30]

Two equations (3 and 4), in which only two solvent properties are required to correlate major solvent effects, differ mainly in the physical significance of the derived parameters. Y and N (eq 3) are defined by model reactions and an assumption that acetic and formic acids have the same N value,[3c,27,30] whereas many sets of *two* combinations of A and B could be derived from eq 4. Swain et al.[29] associated $A + B$ with solvent polarity and noted that this correlated with Y values; our plots support this view except for CF_3CO_2H—the discrepancy can be explained by the dependence of $A + B$ on solvent nucleophilicity.[31] Unfortunately Swain et al. did not include fluorinated alcohols in their work and much of the current data common to eq 3 and eq 4 refer to solvents having similar N values.

With the limited usefulness of α values (eq 2, discussed above), there is now considerable justification for applying a single solvent parameter for correlating and interpreting kinetic data for heterolytic reactions in protic media.[2,3] For such reactions, the magnitudes of many solvation effects may change little during the process: initial state → transition state.[25b] Also the charges requiring solvation are very close together at the reaction site. Particularly high precision correlations can be attained if comparisons are restricted to reactions having the same leaving group (e.g., tosylate[3b,c,4d]). An important practical reason for having one solvent parameter for ionizing power (or a family of similar parameters, one for each leaving group) is that kinetic data are rarely obtained in a sufficiently diverse range of solvents to justify a multiparametric analysis. This limitation is compounded by the tendency of solvent properties to bunch, e.g., there are many solvent series where ionizing power is almost exactly proportional to solvent nucleophilicity.[32]

If only one solvent parameter is utilized, rate ratios for solvolytic reactions in solvents having the same Y value and different nucleophilicities can provide evidence for nucleophilic solvent assistance.[3f,5c,33] The following pairs of solvents appear to be well suited to such studies: (i) 97% w/w $(CF_3)_2CHOH/H_2O$ and 10% v/v $(CH_3)_2CO/H_2O$, which have very similar Y_{OTs} and Y_I values; (ii) 97% w/w CF_3CH_2OH/H_2O and 40% v/v $(CH_3)_2CO/H_2O$, which have very similar Y_{OTs} and Y_{Br} values; (iii) 97% w/w $(CF_3)_2CHOH/H_2O$ and H_2O have very similar Y_{Br} values; (iv) 97% w/w CF_3CH_2OH/H_2O and 40% v/v $EtOH/H_2O$ have very similar Y_{Cl} values. Such rate ratios in solvents of constant ionizing power can be abbreviated as $[k_{AW}/k_{HFIP}]_Y$, $[k_{AW}/k_{TFE}]_Y$, $[k_W/k_{HFIP}]_Y$, and $[k_{EW}/k_{TFE}]_Y$, respectively. Alternatively, solvolyses can be positioned in the S_N2–S_N1 spectrum between methyl and 2-adamantyl solvolyses by using the Q equation.[3b,3c]

Conclusion

Y scales of solvent ionizing power based on solvolyses of adamantyl substrates (Y_{Cl}, Y_{Br}, Y_I, and Y_{OTs}—see eq 1) are closely similar, in contrast to the original Y scale based on solvolyses of *tert*-butyl chloride. The main effect of changes in leaving groups is that the sensitivities of the solvolyses to changes in solvent ionizing power are reduced as the size of the leaving group is increased (a reduction in electrostatic effects probably due to charge delocalization in the developing anion). More subtle solvent effects are also present but, with the possible exception of carboxylic acid solvents, these are not of sufficient magnitude to warrant the introduction of further adjustable solvent parameters (e.g., α, eq 2). They are sufficient to justify separate Y values for each leaving group. Subtle differences in solvation effects occur even within families of similar leaving groups (e.g., the sulfonates, tosylates, and mesylates); in such cases it should be possible to choose one standard leaving group (e.g., tosylate) and to convert other data by using appropriate rate ratios (e.g., from rate data for mesylates to rate data for tosylates by using tosylate/mesylate rate ratios). We agree with Swain et al.[29]

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that the *major* solvent effects on reactivity can be correlated with two solvent parameters, in our work Y and solvent nucleophilicity N; however we disagree on how the two solvent properties are extracted from the experimental data to give a physically significant empirical model of solvation effects on reactivity in protic media. The solvent polarity scales based on solvatochromism appear to be less suitable for probing heterolytic reactivity, possibly because of contributions from solvation effects which destabilize excited states.

Experimental Section

Chemicals. 1-Adamantyl iodide (I, X = I) was prepared and purified by literature procedures mp 75–77 °C (lit.[8,17] mp 75–76 °C). Trifluoroethanol, hexafluoroisopropyl alcohol, and ethanol were purified as described previously.[3d] Commercially available samples of acetone, dioxan and methanol (Fisons, dried and distilled), acetic acid (BDH, Aristar), and formic acid (BDH, AR) were used directly. Acetone, ethanol, and methanol samples were shown by Karl Fischer titration to contain <0.015% water. Distilled water was stored in glass bottles before use.

Kinetic Methods. The equipment and techniques described previously [3a,d] were adopted with the following additions and modifications. The microconductivity cell, constructed by A. M. Willis, had Pt/Pyrex seals (satisfactory close to 25 °C) with two 6 × 4 mm bright Pt electrodes 4 mm apart—cell volume, ca 0.4 mL, cell constant, 2.26 cm^{-1}. The ultrasonic bath was a Kerry type PUL55 (power, 50/100 W average/peak), and samples were sonicated for 2–15 min. Formolyses and acetolyses were studied in 0.005 M degassed solutions (initially with 0.015 M sodium acetate added) in 25-mL Wheaton bottles sealed with Teflon-faced butyl disks. Aliquots (1 mL) were withdrawn by using a Hamilton gas-tight syringe; formolyses were quenched in 4 mL of AR acetic acid,[34] and the excess of base was titrated with 0.01 M AR perchloric acid in acetic acid (derivative method, weak setting on Radiometer RTS822 autotitrator). Iodine solutions were freshly made in tetrahydrofuran before injection into methanol/water solvents. Iodine concentrations were obtained by adding solid KI (BDH, AR) equivalent to at least 0.1 M and monitoring the absorbance of I_3^- at 285 or 350 nm[35] (Pye Unicam SP1800 spectrophotometer); calibrations were made for a standard solvent (e.g., 60% methanol/water).

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Registry No. 1-AdCl, 935-56-8; 1-AdBr, 768-90-1; 1-AdI, 768-93-4; *t*-BuBr, 507-19-7; iodide, 20461-54-5.

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Reaction of Polycyclic Aromatic Hydrocarbons (PAH) with Nitrogen Dioxide in Solution. Support for an Electron-Transfer Mechanism of Aromatic Nitration Based on Correlations Using Simple Molecular Orbital Theory

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Eight unsubstituted, polycyclic aromatic hydrocarbons (PAH) were allowed to react with nitrogen dioxide in dichloromethane at 25 °C, and relative rate constants were obtained by direct competition techniques. The rate constants depend markedly on substrate structure, with over a 10^4 difference in rate constants between the least reactive (benzene) and most reactive (perylene) compounds studied. The major products formed from most substrates are nitroaromatics. Anthracene, however, also reacts with nitrogen dioxide to form appreciable amounts of 9,10-anthraquinone. Linear free energy relationships were determined between rate data and molecular orbital parameters based on models involving rate-determining σ-complex formation or electron-transfer (ET) reactions. Based on the better correlations obtained using the latter model, it is suggested that the more easily ionized PAH undergo nitration by an ET mechanism. Values of absolute rate constants for the nitration of three of the PAH (as measured by stopped-flow) also are reported and correlate well with our relative rate constants. The formation of 9,10-anthraquinone is suggested to result from the trapping of the intermediate anthracene radical-cation by water.

The nitration of aromatic molecules in solution is among those reactions that are taught to students in their first exposure to organic chemistry. The subject has been extensively reviewed in basic textbooks, in the advanced literature,[2] and in monographs.[3,4] Most nitrations have been carried out in strongly acidic, polar media, and under these conditions the nitrating species is generally regarded as the nitronium ion.[5] Although less frequently discussed in textbooks, nitrations also can be carried out both in solution and in the gas phase by nitrogen dioxide (or its dimer, dinitrogen tetraoxide).[5–19] The high concentrations

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