

Communication

Additional Solvent Ionizing Power Values for Binary Water-1,1,1,3,3,3-Hexafluoro-2-propanol Solvents

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Abstract: Determinations of the specific rates of solvolysis of 1-adamantyl bromide and 1-adamantyl iodide in 1,1,1,3,3,3-hexafluoro-2-propanol-water mixtures, in conjunction with earlier reported values in 80% ethanol, have led to additional YBr and YI solvent ionizing power values. These new values will be especially important in avoiding multicollinearity when the extended Grunwald-Winstein equation (extended by addition of a term involving solvent nucleophilicity) is used to correlate solvent-induced changes in the specific rates of solvolyses involving a bromide or iodide ion leaving group.

Keywords: 1-adamantyl bromide, 1-adamantyl iodide, 1,1,1,3,3,3-hexafluoro-2-propanol, Grunwald-Winstein equation, solvent ionizing power.

1. Introduction

The one-term Grunwald-Winstein equation (eqn 1) [1] was developed to correlate the specific rates of solvolytic displacements proceeding by a unimolecular ionization pathway ($S_N1 + E1$ reactions).

$$\log(k/k_o) = mY + c \quad (1)$$

In eqn 1, k and k_o represent the specific rates of solvolysis of a substrate in a given solvent and in the standard solvent (80% ethanol-20% water v/v), Y is a scale of solvent ionizing power, m is the

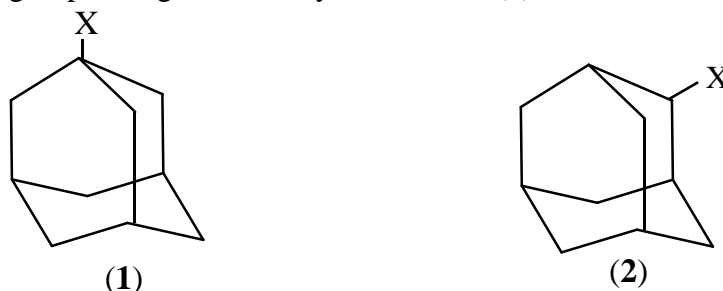
sensitivity towards changes in the solvent ionizing power value and c is a (usually small) constant (residual) term. The original Y scale was developed using *tert*-butyl chloride as the standard substrate (m value set at unity).

For the correlation of bimolecular solvolytic displacements, where the solvent also functions as a nucleophile in the rate-determining step; it was proposed that a second variable should be added (eqn 2) [2], where N is a measure of solvent nucleophilicity and l is the sensitivity towards changes in its value.

$$\log(k/k_0) = lN + mY + c \quad (2)$$

Only in 1976 did an extensive listing of N values (the N_{OTS} scale) become available [3], based on the specific rates of solvolysis of methyl *p*-toluenesulfonate (tosylate). More recently, an N_T scale based on the solvolyses of the *S*-methylidibenzothiophenium ion has been developed [4, 5].

A further development as regards solvent ionizing power scales involved the recognition that the Y scale based on *tert*-butyl chloride solvolyses included a nucleophilic component [6-9], which could be avoided by the use of the bridgehead 1-adamantyl chloride [6] as the standard substrate. Further, the solvent ionizing power scale was found to be leaving-group dependent and scales have been independently determined for several leaving-groups (X) and termed, in general, Y_X scales [10]. These have been determined, for relatively poor leaving groups using 1-adamantyl derivatives (1) and for relatively good leaving groups using 2-adamantyl derivatives (2).



The application of eqn 2 is usually with the incorporation of the N_T scale of solvent nucleophilicity and the appropriate Y_X scale for the leaving group X .

An important aspect of the use of eqn. 2 is that, for the majority of the binary solvent mixtures used as the solvents, as the Y_X -value increases on increasing the water content, the N_T value decreases approximately linearly and multicollinearity can be a major problem. Indeed, if, as historically was often the case, a study of the solvolyses of a substrate is restricted to ethanol-water, methanol-water, acetone-water, and dioxane-water mixtures, multicollinearity is unavoidable [11, 12]. Fortunately multicollinearity problems can be avoided by the incorporation of fluoroalcohol-containing solvents and 2,2,2-trifluoroethanol (TFE)-water and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)-water mixtures are strongly recommended systems for incorporation into any study involving the application of eqn. 2 [5, 10]. TFE-ethanol mixtures are also frequently used [13]. The fluoroalcohol-containing binary systems make an essential contribution because of the quite different relationships between N_T and Y_X values relative to those for the other four mixed solvent systems mentioned above. For example, in TFE- H_2O mixtures, as N_T increases the Y_X values show a modest *increase* [5,10].

Fewer Y_X values are available for HFIP- H_2O mixtures and the review by Bentley and Llewellyn lists a Y_X value for the important chloride, bromide, and iodide leaving groups only for a 97% HFIP (w/w)

content. A subsequent extension of the previous [6,10] kinetic study of 1-adamantyl chloride solvolyses has led to the availability of Y_{Cl} values for more aqueous HFIP-H₂O mixtures [8]. In the present study, we determine the specific rates of solvolysis of 1-adamantyl bromide and 1-adamantyl iodide in these more aqueous mixtures, which allows the determination of the corresponding Y_{Br} and Y_I values.

2. Results and Discussion

The specific rates of solvolyses were determined, at 25.0°C, for 1-adamantyl bromide and 1-adamantyl iodide in 97%, 90%, 70%, and 50% HFIP (weight-weight basis, with other component water). The values (Table 1) for 97% HFIP are in very good agreement with earlier determinations [14,15]. The specific rates are the averages from at least four independent kinetic runs. The specific rates are reported within Table 1, together with the calculated Y_{Br} and Y_I values and, for comparison, previously reported [6, 8] Y_{Cl} values.

Table 1. Specific rates of solvolyses of 1-adamantyl halides^a in 80% ethanol and HFIP-H₂O mixtures at 25.0°C and new solvent ionizing power values (Y_X).

solvent ^b	1-AdBr ^c			1-AdI ^d			1-AdCl
	rate constant, s ⁻¹	N ^e	Y_{Br}	rate constant, s ⁻¹	N ^e	Y_I	Y_{Cl} ^f
80EtOH	2.8×10^{-7g}		0.00	5.8×10^{-7h}		0.00	0.00
97HFIP	$(9.1 \pm 0.2) \times 10^{-3i}$		4.51 ^g	$(4.00 \pm 0.02) \times 10^{-3h}$		3.84 ^h	5.08 ^g
	$(9.68 \pm 0.01) \times 10^{-3h}$		4.54	-			
	$(9.37 \pm 0.06) \times 10^{-3}$	4	4.52	$(4.27 \pm 0.06) \times 10^{-3}$	4	3.87	5.17
90HFIP	$(2.29 \pm 0.05) \times 10^{-3}$	5	3.91	$(1.63 \pm 0.03) \times 10^{-3}$	4	3.45	4.31
70HFIP	$(1.09 \pm 0.04) \times 10^{-3}$	4	3.59	$(1.24 \pm 0.07) \times 10^{-3}$	4	3.33	3.83
50HFIP	$(1.06 \pm 0.04) \times 10^{-3}$	4	3.58	$(1.25 \pm 0.05) \times 10^{-3}$	4	3.33	3.80

^a With associated standard errors. ^b 80EtOH on volume-volume basis and HFIP-containing solvents on weight-weight basis, other component is H₂O. ^c Concentration of $8.1 \times 10^{-4} M$. ^d Concentration of $6.6 \times 10^{-4} M$. ^e Number of determinations. ^f From ref. 8. ^g Data from ref. 6. ^h Data from ref. 14. ⁱ Data from ref. 15.

Differences in Y_X values for a given solvent are believed to be primarily due to differences in electrophilic solvent assistance [6] and the halide series, showing a reduction in electrophilicity as one moves down the periodic table, is a useful one for assessing the significance of the specific anion solvation [14].

It was found [14] that, while 1-adamantyl iodide reacts in most solvents faster than 1-adamantyl bromide, the rates become essentially identical in 97% TFE and the order was reversed in the most acidic solvents studied: 97% HFIP, acetic acid, and formic acid. In the present study (Table 1), we find the bromide to be the more reactive in both 97% HFIP and 90% HFIP. The rates would become equal at about 77% HFIP and the iodide is 14% and 18% more reactive in 70% and 50% HFIP. Clearly, there is a balance between the resistance of the carbon-halogen bond towards heterolysis and the magnitude of the superimposed electrophilic assistance from the solvent.

When the comparison is made in terms of Y_x values, it is important to realize that, for a given solvent, the Y_x values are relative to the behavior of that particular 1-AdX substrate in 80% ethanol. Variations in Y_x values for different leaving groups will have components both from differences in interactions in the solvent under consideration *and* from differences in interactions in the 80% ethanol. However, the observation that the 1-AdI/1-AdBr specific rate ratio varies only from 2.3 in 90% EtOH to 1.9 in 60% EtOH [14] suggests that interactions in ethanol-rich ethanol-water mixtures are similar for different halides. In contrast, appreciably larger variation (0.46 to 1.14) is observed over the similar concentration range of 97% HFIP to 70% HFIP, consistent with the dominant influence of differences in the interactions of the various 1-adamantyl halides with a more electrophilic fluoroalcohol-rich solvent.

In addition to the obvious utility in correlations using eqn 1, the presently reported Y_{Br} and Y_I values for HFIP-H₂O mixtures will be especially useful in extended Grunwald-Winstein equation (eqn 2) treatments of solvolyses involving displacement of bromide or iodide ion. In conjunction with available N_T values for the solvents [4,5], they will assist in promoting a good mix of solvent types. This will avoid the high degree of multicollinearity present when only specific rates determined in binary mixtures of water with acetone, dioxane, ethanol, and methanol are available.

3. Experimental

The 1-adamantyl bromide (Aldrich, 99%) and 1-adamantyl iodide (Aldrich, 98%) were used as received. The 1,1,1,3,3,3-hexafluoro-2-propanol (Aldrich, 99+%) was purified as previously described [15]. The apparatus, allowing rapid response to changes in conductivity [16], has been previously described [17]. Typically, the determinations of the specific rates were made after the injection of 4.0 μ l of a 10% (weight-weight) solution of the substrate in dry acetonitrile into the conductivity cell containing 2.00mL of the solvent mixture.

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References and Notes

1. Grunwald, E.; Winstein, S. The Correlation of Solvolysis Rates. *J. Am. Chem. Soc.* **1948**, *70*, 846.
2. Winstein, S.; Grunwald, E.; Jones, H.W. The Correlation of Solvolysis Rates and the Classification of Solvolysis Reactions into Mechanistic Categories. *J. Am. Chem. Soc.* **1951**, *73*, 2700.
3. Schadt, F.L.; Bentley, T.W.; Schleyer, P.v.R. The S_N2-S_N1 Spectrum.2. Quantitative Treatments of Nucleophilic Solvent Assistance. A Scale of Solvent Nucleophilicities. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
4. Kevill, D.N.; Anderson, S.W. An Improved Scale of Solvent Nucleophilicity Based on the Solvolysis of the S-Methyldibenzothiophenium Ion. *J. Org. Chem.* **1991**, *56*, 1845.

5. Kevill, D.N. Development and Uses of Scales of Solvent Nucleophilicity. In *Advances in Quantitative Structure-Property Relationships*, Vol 1; Charton, M., Ed.; JAI Press: Greenwich, CT, **1996**; pp 81-115.
6. Bentley, T.W.; Carter G.E. The S_N2-S_N1 Spectrum. 4. Mechanism for Solvolyses of *tert*-Butyl Chloride: A Revised Y Scale of Solvent Ionizing Power based on Solvolyses of 1-Adamantyl Chloride. *J. Am. Chem. Soc.* **1982**, *104*, 5741.
7. (a) Bentley, T.W.; Bowen, C.T.; Parker, W.; Watt, C.I.F. S_N2 Character of Solvolyses of *tert*-Butyl Halides and of Trifluoroacetolyses of Secondary Alkyl Sulfonates. *J. Am. Chem. Soc.* **1979**, *101*, 2486. (b) Bentley, T.W.; Roberts, K. Weakly Nucleophilic Leaving Groups. Solvolyses of 1-Adamantyl and *t*-Bu Heptafluorobutyrate and Trifluoroacetates. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1055.
8. Kevill, D.N.; D'Souza, M.J. Additional Y_{Cl} Values and the Correlation of the Specific Rates of Solvolysis of *tert*-Butyl Chloride in Terms of N_T and Y_{Cl} Scales. *J. Chem. Res. Synop.* **1993**, 174.
9. Kevill, D.N.; Anderson, S.W.; Fujimoto, E.K. Nucleophilicity Studies of Reactions in Which the Displaced Group is a Neutral Molecule. In *Nucleophilicity*; Harris, J.M.; McManus, S.P., Eds.; Advances in Chemistry Series, No. 215, American Chemical Society: Washington, DC, **1987**; pp 269-283.
10. Bentley, T.W.; Llewellyn, G. Y_x Scales of Solvent Ionizing Power. *Prog. Phys. Org. Chem.* **1990**, *17*, 121.
11. Kevill, D.N.; Park, B.-C.; Park, K.-H.; D'Souza, M.J.; Yaakoubd, L.; Mlynarski, S.L.; Kyong, J.B. Rate and Product Studies in the Solvolyses of *N,N*-Dimethylsulfamoyl and 2-Propanesulfonyl Chlorides. *Org. Biomol. Chem.* **2006**, *4*, 1580.
12. Kaspi, J.; Rappoport, Z. Nucleophilicity and Ionizing Power in Binary Solvent Mixtures. *Tetrahedron Lett.* **1977**, 2035.
13. Kaspi, J.; Rappoport, Z. Solvolysis in 2,2,2-Trifluoroethanol-Water and 2,2,2-Trifluoroethanol-Ethanol Mixtures. Selectivity of the Intermediates and N Values. *J. Am. Chem. Soc.* **1980**, *102*, 3829.
14. Bentley, T.W.; Carter, G.E.; Roberts, K. Solvent Ionizing Power. Comparisons of Solvolyses of 1-Adamantyl Chlorides, Bromides, Iodides, and Tosylates in Protic Solvents. *J. Org. Chem.* **1984**, *49*, 5183.
15. Bentley, T.W.; Bowen, C.T.; Parker, W.; Watt, C.I.F. Evidence against Appreciable Internal Ion Pair Return in the Solvolyses of Tertiary Aliphatic Halides. Measurement of α -Methyl/Hydrogen Rate Ratios in Hexafluoropropan-2-ol-Water. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244.
16. Bentley, T.W.; Jones, R.O. Stoichiometric Solvation Effects. Part 1. New Equations Relating Product Selectivities to Alcohol-Water Solvent Compositions for Hydrolyses of *p*-Nitrobenzoyl Chloride. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2351.
17. Lee, I.; Lee, H.W.; Uhm, T.S.; Sung, D.D.; Ryu, Z.H. Solvation in Mixed Solvents (VII). Solvolysis of *tert*-Butyl Halide in Isodielectric Solvents. *J. Korean Chem. Soc.* **1988**, *32*, 85