Y_X Scales of Solvent Ionizing Power

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CONTENTS

I. INTRODUCTION

The Y_X scales of solvent ionizing power are recent adaptions of the Grunwald–Winstein (GW) equation taking account of effects due to specific solvation of the leaving group X. In the original GW equation, rates of solvolyses of *tert*-butyl chloride in any solvent k relative to solvolyses in 80% ethanol–water k_0 at 25°C define the solvent ionizing power Y (1):

$$\log\left(\frac{k}{k_0}\right)_{t-\text{BuCl}} = Y \qquad (1)$$

Inclusion of a slope parameter m and an intercept c (usually very small) permits the correlation and prediction of solvolysis rates for any substrate

RX:

$$\log\left(\frac{k}{k_0}\right)_{\text{RX}} = mY + c \tag{2}$$

The background to the development of the GW equation (Equation 2) has recently been given by Grunwald (2). Applications of the GW equation were further stimulated by the later determination of additional Y values for many binary mixtures of solvents (3). Although reports of limitations of the GW equation have been appearing since the 1950s, many Y values for aqueous binary mixtures (typical cosolvents are methanol, ethanol, acetone, and dioxan) are still useful for modern correlations of rate data, because these solvent mixtures have similar nucleophilicities (4). Other correlations may be successful fortuitously because changes in solvent ionizing power may be proportional to changes in solvent nucleophilicity (5).

Alternatives to *tert*-butyl chloride as the model compound (Equation 1) have been considered for many years, as described in an earlier review (6). A systematic approach has recently been developed using solvolyses of 1-adamantyl (structure 1) and 2-adamantyl (structure 2) substrates to provide a relatively constant alkyl group, and permitting kinetic studies of a wide range of solvents and leaving groups (7). These results can be incorporated into a modified GW equation (Equation 3).

$$\log\left(\frac{k}{k_0}\right)_{\text{AdX}} = Y_X \tag{3}$$

(1)   (2)
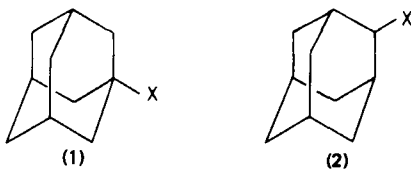
In Equation 3, k is the solvolysis rate in any solvent relative to 80% ethanol–water (k_0) for solvolyses of adamantyl-X substrates, X is the leaving group and Y_X is the scale of solvent ionizing power for the heterolytic process as shown in

$$(\text{R–X})_{\text{solvated}} \longrightarrow (\text{R}^+)_{\text{solvated}} + (\text{X}^-)_{\text{solvated}} \tag{4}$$
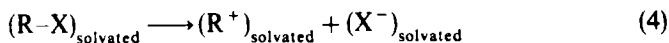
Hence in Equation 3 explicit consideration is given to effects due to changes in specific solvation of the leaving group.

Unfortunately, it has not always been possible to obtain all the required

experimental data for adamantyl substrates directly at 25°C. Extrapolations using the Arrhenius equation are frequently required. To avoid the accumulation of extrapolation errors, some Y_X values have not been defined at 25°C. Also for various reasons (e.g., low solubility of adamantyl compounds in highly aqueous media), other reference compounds have also been used.

As rapid progress has been made over the past 5 years, with major contributions from several research groups, a summary of recent progress in the development of Y_X scales is now appropriate. Emphasis will be given to kinetic data—typical products of solvolytic reactions are substitution, elimination, and/or rearrangement, with substitution predominating for solvolyses of adamantyl substrates. Previously unpublished results are also included.

II.   DEVELOPMENT OF Y_X SCALES OF SOLVENT IONIZING POWER

A.   The Y_{OTs} Scale of Solvent Ionizing Power

#### 1.   Choice of Model Substrate

One of the most frequently employed leaving groups in organic chemistry is the tosylate group (OTs where Ts = p-methylbenzenesulfonyl). Solvolyses of the bridgehead 1-adamantyl tosylate (structure 1, X = OTs) were first reported in 1961 (8). The caged structure prevents rearside attack by nucleophiles and the bridgehead structure greatly inhibits elimination. Solvolyses of 1-adamantyl substrates were considered at that time to be unexpectedly rapid (8, 9), in view of the bridgehead compounds of other ring systems then known. It has since been observed that, in the gas phase, the 1-adamantyl cation is more stable than the more flexible *tert*-butyl cation (10–12). These results cannot be explained solely by enhanced effects of alkyl group polarizability in the gas phase (13), because equilibria between stable ions in solution show $\Delta G \sim 0$ for anion exchange between *tert*-butyl and 1-adamantyl cations (14).

In contrast to the approximately 10^3-fold greater reactivity of solvolyses of *tert*-butyl substrates than 1-adamantyl substrates in ethanol (8), solvolyses in the very weakly nucleophilic solvent, hexafluoroisopropanol, occur at almost the same rate (15–17). These observations are consistent with the stable ion data discussed above. Hence, in contrast to earlier views (8, 9), it now appears that solvolyses of *tert*-butyl substrates in nucleophilic solvents (e.g., ethanol) are unexpectedly rapid. Nucleophilic solvent assistance in solvolyses of *tert*-butyl substrates can explain these observations (15–17). These results and earlier communications (18, 19) provided further impetus to the development of alternative Y scales of solvent ionizing power, replacing *tert*-butyl

chloride as the model substrate. Relative rates of solvolyses of 1-adamantyl and other bridgehead systems can be correlated using force field calculations (20, 21), further supporting the consistency of the interpretation of the kinetic data.

Although solvolyses of 1-adamantyl tosylate (structure **1**, X = OTs) were studied by several groups in the 1970s (22 25), it is relatively reactive and was investigated only in less ionizing solvents having $Y \leqslant 0$ (e.g., acetic acid, ethanol). Also 1-adamantyl tosylate is extremely sensitive to moisture (23).

The secondary 2-adamantyl system (structure **2**) provides alternative model substrates for Y_X scales. It was proposed (26) that nucleophilic solvent participation in solvolyses of 2-adamantyl substrates would be prevented because the necessary pentacoordinate intermediate or transition state (structure **3**) would be strongly hindered by the axial hydrogen atoms shown.


(3)
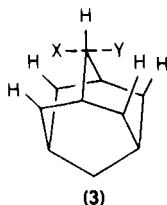
This proposal is now additionally supported by the correlations of solvolysis rates (see Fig. 1, discussed in more detail later), and by the low reactivity of 2-adamantyl sulfonates even under vigorous S_N2 reaction conditions (27, 28). The first solvolytic rate data for solvolyses of 2-adamantyl tosylate (structure **2**, X = OTs) were reported in 1970 (26, 29), and additional studies followed rapidly (30–33).

After considering various other alternative model compounds (34), solvolyses of 2-adamantyl tosylate at 25°C were chosen (35) to define a Y_{OTs} scale of solvent ionizing power based on Equation 3 for tosylates and related compounds. Many useful correlations of typical solvolysis rate data have been carried out using Y_{OTs} values (see Section IV). However, the need for additional model compounds became apparent when studies of a wider range of solvents were attempted. Because of the low solubility of 2-adamantyl tosylate in highly aqueous media, solvolyses of 2-adamantyl mesylate (X = OSO_2CH_3) were required to obtain the Y_{OTs} value for water (36).

2.   An Alternative Model Substrate for Solvolyses in Highly Aqueous Media

A more convenient substrate for solvolyses in highly aqueous media is 2-*endo*-norbornyl mesylate (2-NbOMs, structure **4**).
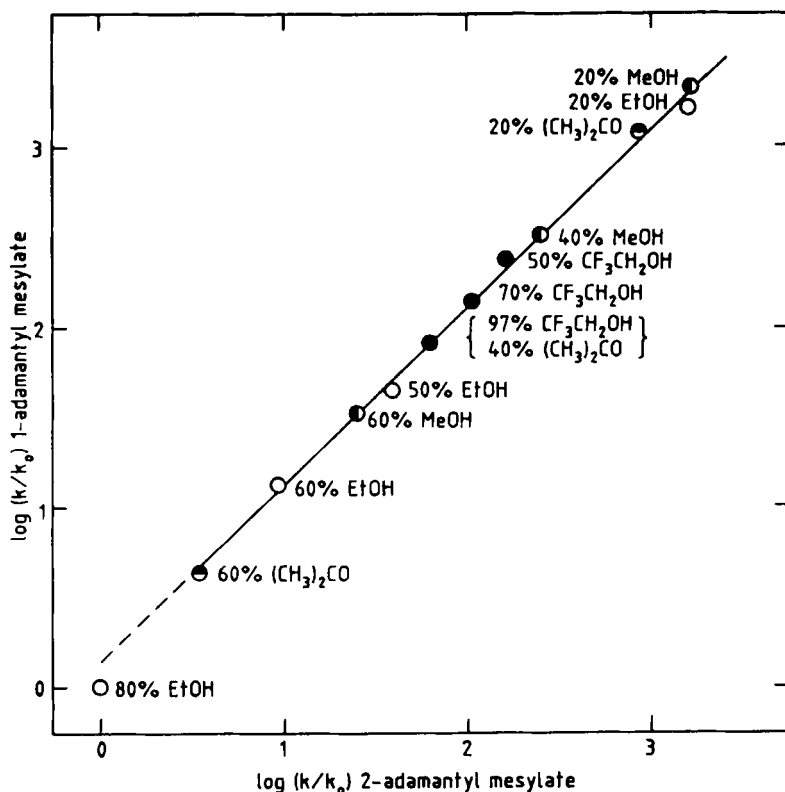
Figure 1   Correlation (Equation 7) of logarithms of solvolysis rates for 1-adamantyl mesylate versus 2-adamantyl mesylate; kinetic data from references 7 and 41 and Tables 1 and 2. Water is the cosolvent for each of the solvent mixtures; k_0 for 2-adamantyl mesylate was calculated assuming a OTs/OMs rate ratio of 1.0 for 80% ethanol–water (41), but the data point was excluded from the least-squares analysis (slope 0.982 ± 0.016, intercept 0.144 ± 0.035, $r = 0.99$).

This substrate was shown to be only weakly sensitive to nucleophilic solvent assistance (37–39) , although it was later established that S_N2 attack by stronger nucleophiles can occur (28). A relationship (Equation 5) was established for 12 solvent mixtures for which kinetic data for both

OMs
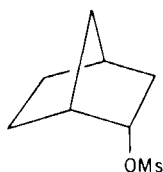
(4)

2-adamantyl tosylate and 2-*endo*-norbornyl mesylate could be obtained (40a).

$$Y_{OTs} = 1.41 \log\left(\frac{k}{k_0}\right)_{2-NbOMs} + 0.17 \qquad (5)$$

Then Y_{OTs} values could be calculated from equation (5), with knowledge of only the rate data for solvolyses of 2-*endo*-norbornyl mesylate. The Y_{OTs} value calculated (40b) for pure water was 3.78, significantly less than the previous estimate (36) of 4.1. Possible causes of this discrepancy include small changes in tosylate/mesylate rate ratios (e.g., from 0.5 to 2.1), not accounted for in Equation 5. Tosylate/mesylate rate ratios depend significantly on solvent composition and to a much lesser degree on the nature of the alkyl group (36, 41). Solvolyses of 2-adamantyl *p*-nitrobenzenesulfonate, which has a leaving group somewhat more hydrophilic than that of tosylate, were investigated to define Y_{OTs} values for aqueous acetonitrile (42); a small leaving group effect on these values is expected, and Y_{OTs} for water was found to be a slightly low value of 3.9.

Solvolyses of 2-*endo*-norbornyl mesylate were also studied to obtain Y_{OTs} values for aqueous sulfuric acid mixtures (43). An equation similar to Equation 5 was obtained using only one leaving group (tosylate), and was further refined to allow a small contribution from solvent nucleophilicity:

$$\log\left(\frac{k}{k_0}\right)_{2-NbOTs} = 0.05 N_{OTs} + 0.72 Y_{OTs} \qquad (+0.009) \qquad (6)$$

In this equation, N_{OTs} is the solvent nucleophilicity, obtained from solvolyses of methyl tosylate (35, 44), and 0.05 represents the small sensitivity of solvolyses of 2-*endo*-norbornyl tosylate to solvent nucleophilicity. Rate data for 2-*endo*-norbornyl mesylate were converted to rate data for the tosylate, using appropriate tosylate/mesylate ratios (e.g., based on solvolyses of 2-propyl for which experimental data were available for both tosylates and mesylates). This procedure (Equation 6) gave a Y_{OTs} value for pure water of 4.04, in satisfactory agreement with the value of 4.1 obtained (36) from solvolyses of 2-adamantyl mesylate. Hence, in general, it seems likely that use of Equation 6, in combination with OTs/OMs rate ratios, is a more accurate procedure than Equation 5 for dealing with the problem of low solubility of 2-adamantyl tosylate and mesylate in highly aqueous media.

3. An Alternative Model Substrate for Solvolyses in Less Polar and Aprotic Media

A second disadvantage of 2-adamantyl tosylate is its low reactivity in less polar media. When $Y_{OTs} < 0$ solvolyses become inconveniently slow and

extrapolations of rate data from data at higher temperatures are then required. As Y_{OTs} decreases, uncertainties in these extrapolations increase. Eventually there comes a point where it is better to define an alternative model substrate and to accept the additional uncertainty in overlapping results for the two substrates. Solvolyses of 1-adamantyl mesylate are approximately 10^5 times faster than solvolyses of 2-adamantyl mesylate or tosylate (7). Hence, long extrapolations from kinetic data at high temperatures (> 50°C) are not required, but in some cases small extrapolations from kinetic data at lower temperatures are required.

Also, compared with 1-adamantyl tosylate, more rapid solvolyses of the mesylate can be examined because the mesylate dissolves quickly (7). Using a rapid injection conductimetric technique (45) and temperature extrapolations from 0 to 25°C, the range of accessible experimental data can be extended from

TABLE 1
Rate Constants for Solvolyses of 1-Adamantyl Mesylate (1) (X = OMs)

	Rate Constants $(k, s^{-1})^a$				$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Solvent	$-10°C$	$0°C$	$10°C$	$25°C$	kcal mole^{-1}	cal mole^{-1} K^{-1}
40% EtOH			0.136	0.63	16.6	-3.9
80% MeOH				0.0102		
60% MeOH		0.00798		0.144	18.2	-1.5
40% MeOH	0.0263	0.088^b	0.279	1.33^c	16.9	-1.2
20% MeOH	0.151	0.534		8.7^c	17.5	4.5
90% (CH$_3$)$_2$CO				2.42×10^{-5}		
80% (CH$_3$)$_2$CO				4.63×10^{-4}		
97% CF$_3$CH$_2$OH				0.35^d	14.7	-11.4
				0.37^e	14.1	-13.4
				$0.92^{c,f}$	17.6	0.4
97% (CF$_3$)$_2$CHOH	1.65^g			$22^{c,h}$	$(11)^h$	$(-16)^h$
CH$_3$CO$_2$H^i				6.2×10^{-4}		
HCO$_2$H			1.2^j	5.0^c	15	-4

^{a}Determined conductimetrically at least in duplicate; errors $< \pm 5\%$, typically $\pm 2\%$; solvent compositions refer to % v/v solvent–water, except for fluorinated alcohols, which are in % w/w.

^{b}Single measurement of rate constant; three other attempts gave less precise data and up to 10% lower values.

^{c}Calculated from rate data at lower temperatures.

^{d}Reference 7, error ± 0.2.

^{e}Single measurements of rate constant: °C, k, s^{-1}; 30.0°C, 0.516; 34.6°C, 0.77; 39.8°C, 1.15; 46.0°C, 1.86 ± 0.14 (triplicate measurement), hence calculated for 70°C, $k = 9.3$.

^{f}Tosylate data extrapolated from $-10°C$ (reference 47); hence calculated for 70°C, $k = 52.4$.

^{g}Error ± 0.2; average of five measurements with larger than normal errors ($\pm 10\%$) because of high amplification of signals.

^{h}Assumed value for $\Delta H^{\ddagger}$; see trend of Table III in reference 7.

^{i}Determined titrimetrically in duplicate.

^{j}Also at 5.5°C, $k = (7.6 \pm 0.2) \times 10^{-1}$.

$Y_{OTs} \leqslant 0$ to $Y_{OTs} \sim 3$, for example to 20% (v/v) ethanol–water (7). More detailed experimental studies of similarly difficult solvolyses with improved equipment have shown that the experimental technique is reliable (46), and further studies of 1-adamantyl mesylate (Table 1) now extend the earlier work (7).

Because of these improvements in experimental technique, almost the same upper limit of solvent polarity ($Y_{OTs} \sim 3$) is now accessible via 1-adamantyl mesylate as is accessible via 2-adamantyl tosylate. (For this substrate, insurmountable solubility problems in aqueous media remain.) In retrospect it would probably have been advantageous to have chosen 1-adamantyl mesylate as the main model substrate for a $Y_{sulfonate}$ scale of solvent ionizing power. These solvolyses would link better to solvolyses of 2-*endo*-norbornyl mesylate (see above), and the question of σ-bridging in solvolyses of 2-adamantyl (48, 49) would not be directly relevant. On the other hand, considerably more rate data are available in the literature for tosylates than for mesylates. Also, although 1-adamantyl mesylate is relatively easy to prepare (50), it decomposes on storage even in the freezer. Solutions may be more stable (51)–even 1-adamantyl triflate can be stored in hexane if a small amount of 2, 6-di-*tert*-butyl pyridine is added as a stabilizer (52).

Fortunately, it is possible to overlap Y_{OTs} scales based on solvolyses of 1- and 2-adamantyl sulfonates. The first approach was to convert data for solvolyses of 1-adamantyl mesylate to tosylate data by estimating OTs/OMs rate ratios. A plot (7) of logarithms of rate data for eight calculated rates of solvolyses of 1-adamantyl tosylate and four directly determined rate constants (23) versus $Y_{2-AdOTs}$ gave a slope of $1.08 \pm 0.02(r = 0.998)$. It has been pointed out that this plot is "mildly curved" (53). For $Y_{OTs} < 0$, solvolyses of 2-adamantyl tosylate are very slow ($k < 10^{-8} s^{-1}$) and may be subject to extrapolation errors. Assigning a slope of 1.00 to solvolyses of 1-adamantyl tosylate permits calculation of some revised and some additional Y_{OTs} values (7, 54). However, more recent studies (40b) have indicated a significantly higher slope of 1.15 (1/0.868) based exclusively on tosylate data—ignoring extrapolation errors, we estimate an uncertainty of about 10% in this plot. Fortuitously, exactly the same slope has recently been reported (52) for solvolyses of 1- and 2-adamantyl tresylates ($X = OSO_2CH_2CF_3$) in eight solvents.

To remove the ambiguities associated with OTs/OMs rate ratios in our earlier work (7), we have obtained additional rate data for solvolyses of 2-adamantyl mesylate (Table 2).

To reduce uncertainties due to extrapolation errors in data for 2-adamantyl mesylate, only values corresponding to $Y_{OTs} > 0$ were considered. Data for 12 solvents (Figure 1, p. 125) give

$$\log\left(\frac{k}{k_0}\right)_{1-AdOMs} = 0.982 \log\left(\frac{k}{k_0}\right)_{2-AdOMs} + 0.144 \qquad (r = 0.999) \qquad (7)$$

TABLE 2
Rate Constants for Solvolyses of 2-Adamantyl Mesylate (2) (X = OMs)

Solvent[a]	Rate Constants $(10^5 k, \mathrm{s}^{-1})$[b]				$\Delta H^{\ddagger}$ (kcal mole^{-1})	$\Delta S^{\ddagger}$ cal mole^{-1} K^{-1}
	75°C	50°C	40°C	25°C		
97% CF$_3$CH$_2$OH	42.9	3.18		0.154[c]	22.6	−9.4
70% CF$_3$CH$_2$OH	96.1	6.24		0.257[c]	23.8	−4.3
50% CF$_3$CH$_2$OH	197	11.3		0.404[c]	24.9	0.3
97% (CF$_3$)$_2$CHOH			49	10.4[d]	18.6	−14.5
HCO$_2$H		65[e]		2.66[e]	23.9	0.6

[a]Solvent compositions for fluorinated alcohols are in % w/w, with water cosolvent.
[b]Determined conductimetrically at least in duplicate; errors $< \pm 5\%$, typically $\pm 2\%$.
[c]Calculated from rate data at lower temperatures.
[d]Error ± 0.2, literature $k = (1.13 \pm 0.03) \times 10^{-4} \mathrm{s}^{-1}$ (reference 45).
[e]Determined titrimetrically.

Within experimental uncertainty, the slope is very close to 1.000. *These results support the application of Equation 3 to the determination of consistent Y_X scales of solvent ionizing power, based on solvolyses of either 1-adamantyl-X or 2-adamantyl-X.* When the two model substrates give different Y_X values, it is difficult to assess quantitatively the possible contributing factors such as experimental errors, extrapolation errors, minor solvation differences or minor mechanistic changes (e.g., σ-bridging, ion pair return). If the positive intercept in Equation 7 is reliable, the plot (Figure 1) may indeed be part of a shallow curve (53), and this would explain why others (52) have obtained higher slopes when Y_{OTs} values < 0 are included. Some revised judgements of "best" Y_{OTs} values have been made for the compilations given later (Section VI), including the recommendation that 1-adamantyl tosylate be used as the model substrate for $Y_{OTs} < 0$. Because of the unit slope of Figure 1 and the likelihood of close similarity of OTs/OMs rate ratios for 1- and 2-adamantyl, the Y_{OTs} scale is now very strongly related to solvolyses of 1-adamantyl tosylate. Since solvolyses of 2-adamantyl tosylate occur concurrently with ^{18}O-scrambling of sulfonyl oxygens (55), it would be interesting to see whether 1-adamantyl tosylate or mesylate behaved similarly.

Our work described above has been directed toward a definition of one "general-purpose" scale of solvent ionizing power for sulfonates termed Y_{OTs}. Many other Y scales have also been proposed (Section VI), including (56) a Y_{OMs} scale for mesylates based on our earlier data (7). A Y_{OMs} scale for mesylates can be justified; for instance, mesylate data is easier to obtain in highly aqueous media (see above); mesylate is a leaving group different from tosylate, and relative rates for these two sulfonates are slightly solvent dependent. However, coexistence of Y_{OTs} and Y_{OMs} scales is a precedent likely

to lead to proliferation of similar Y_X scales for only slightly different leaving groups. An alternative approach, using rate ratios for leaving groups (e.g., k_{OBs}/k_{OTs} or k_{OTs}/k_{OMs}), has been used for many years to compare data for different sulfonates; rate data for a particular sulfonate can be converted to rate data for a "similar" sulfonate. If, as seems likely from available data (e.g., references 32, 36, 41), these leaving group ratios depend to only a small extent on the alkyl group of the substrate,* only one Y_X scale for "similar" sulfonates would be required.

Solvolytic reactions can also be used to define the ionizing power of aprotic solvents. Data for solvolytic elimination of p-toluenesulfonic acid from p-methoxyneophyl tosylate (structure 5, Z = OMe) has previously been used for this purpose (57).

$$Z - \underset{\text{(5)}}{\bigcirc} - \overset{\overset{\text{Me}}{|}}{\underset{\underset{\text{Me}}{|}}{C}} - CH_2\,OTs$$

(5)
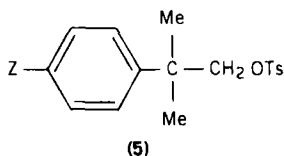
Similarly, an adamantyl scale could be derived from elimination of N_2O from 2-adamantyl azoxytosylate (structure 6) (58).


(6)
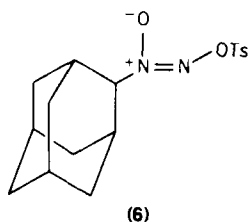
Solvolyses of 1-adamantyl tosylate may also be studied in aprotic solvents such as acetonitrile (59) and amides (60).

B. Comparisons of Y and Y_X Scales

The various Y_X scales based on Equation 3 are summarised in Section VI. Because of the high reactivity of 2-adamantyl triflate (structure **2**, X =

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*Hammett ρ values for ethanolyses of esters having various sulfonate leaving groups at 70°C for different alkyl groups are as follows: methyl ($\rho = 1.32 \pm 0.05$), ethyl ($\rho = 1.30 \pm 0.07$), 2-propyl ($\rho = 1.55 \pm 0.07$), 2-adamantyl ($\rho = 1.80 \pm 0.05$). Values for 1-adamantyl are virtually the same as for 2-adamantyl (32). For brosylates and tosylates the difference in σ values is 0.4, and the calculated OBs/OTs rate ratios vary from 3.3 to 5.2, depending on ρ.

OSO$_2$CF$_3$

(7)
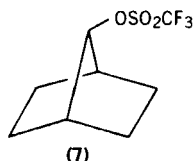
OSO_2CF_3) (61), solvolyses of 7-norbornyl triflate (structure 7) provided the first extensive Y_{OTf} data (62). These Y_{OTf} values are substantially lower than corresponding Y_{OTs} values for fluorinated alcohols and carboxylic acid solvents. Although solvolyses of 7-norbornyl and 2-adamantyl substrates are similar in that they are only weakly sensitive to solvent nucleophilicity (63), different Y_{OTf} values have been obtained for the two triflates (62, 64, 65). Additional kinetic data for solvolyses of 2-adamantyl triflate are shown in Table 3, and data are now available for a wide range of solvents at 25°C. For consistency, we now suggest that Y_{OTf} values should be based on solvolyses of 2-adamantyl triflate (64, 65) at 25°C; these Y_{OTf} values are closer to corresponding Y_{OTs} values. The Y_X values derived from solvolyses of other sulfonates, such as pentafluorobenzenesulfonates (66), $OSO_2CH_2CF_3$ (tresylates) (52, 67), and 2-AdOSO$_2$CH$_2$CH$_2$NMe$_3^+$ (68) are very similar to Y_{OTs}. The anomalous behaviour of triflate may be associated with the weakly basic nature of the leaving group (62). For example, electrophilic assistance by hydrogen bonding may be reduced. It may be significant that $\Delta S^{\ddagger}$ values for 2-adamantyl triflate (Table 3) are more positive than for corresponding tosylates and mesylates (Table 2). Incorporation of an extra CH$_2$ as in tresylates (52, 67),

TABLE 3
Rate Constants for Solvolyses of 2-Adamantyl Triflate (2) (X = OSO$_2$CF$_3$)

Solvent[a]	Rate Constants (k, s^{-1})[a]				$\Delta H^{\ddagger}$ kcal mole^{-1}	$\Delta S^{\ddagger}$ cal mole^{-1} K^{-1}
	−20°C	−10°C	0°C	25°C		
97% CF$_3$CH$_2$OH			0.0081	0.16	18.8	0.7
97% CF$_3$CH$_2$OH[b]		0.0021	0.0079[c]	0.15[c]	18.3	−0.9
70% CF$_3$CH$_2$OH			0.0186	0.45	20.1	7.3
50% CF$_3$CH$_2$OH			0.030	0.94	22	14
97% (CF$_3$)$_2$CHOH	0.0268	0.107	0.345	5.5[c,d]	17.2	2.5
HCO$_2$H			0.035	0.75	19.3	5.5

[a]Determined conductimetrically in duplicate, unless stated otherwise; errors $< \pm 5\%$; solvent compositions for fluorinated alcohols are % w/w alcohol–water; the triflate was dissolved in acetonitrile before being injected into the thermostatted solvent.
[b]Reference 65.
[c]Calculated from rate data at other temperatures.
[d]Previous approximate value (reference 65) $k = \sim 8\,s^{-1}$.

or retaining the CF_3 group but in trifluoroacetates (17), leads to much better correlations with Y_{OTs}.

The Y_X values for $X = Cl$, Br, and I are similar, but show two consistent effects. Relative to Y_{Cl} slopes of correlations versus other Y_X scales are Y_{Br} (0.96), Y_I(0.85), and Y_{OTs} (0.80); these trends are explained by *electrostatic effects* due to charge delocalization on anions of different sizes (69). This first effect on slopes
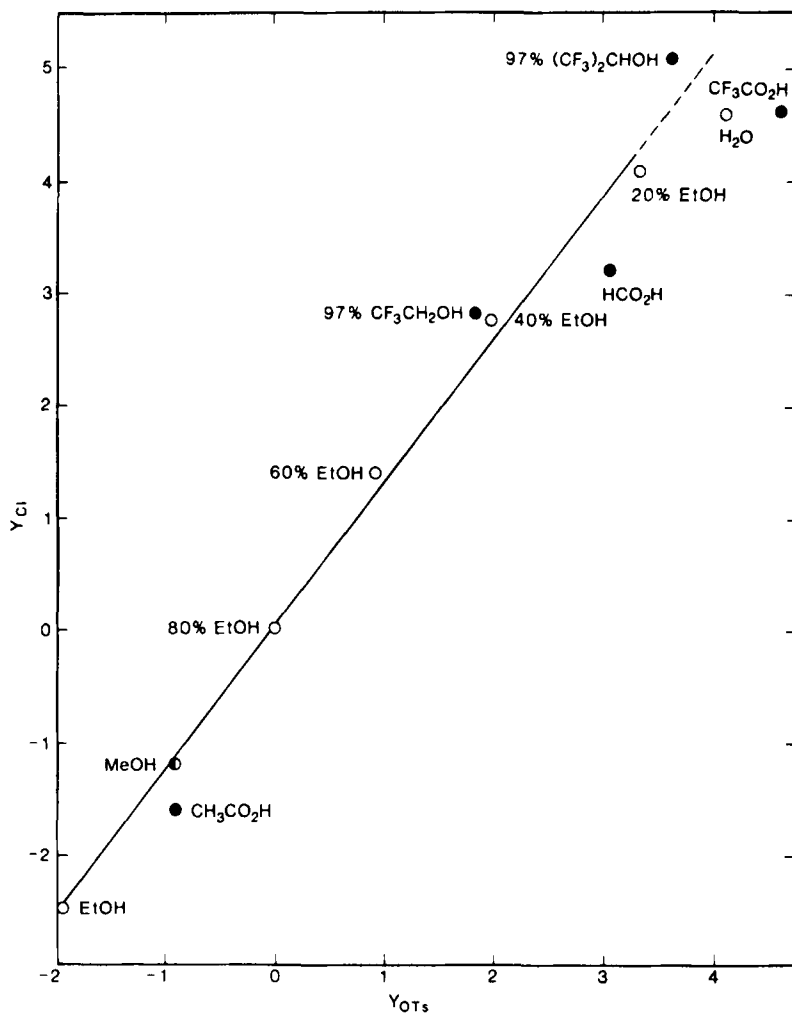
Figure 2 Correlation of Y_{Cl} versus Y_{OTs}. The correlation line is fitted to the open circles excluding pure water (slope $= 1.28 \pm 0.04$, $r = 0.998$), data from Tables 5 and 8.

(m) is most apparent in solvolyses of picrates (65), a leaving group on which the negative charge can be highly delocalized. Deviations from the main trend lines occur for carboxylic acid solvents, presumably because of *electrophilic assistance*: OTs > Cl > Br > I (69, 70). This second effect is illustrated in the Y_{Cl} versus Y_{OTs} plot (Fig. 2), in which the Y_{OTs} values for CH_3CO_2H, HCO_2H, and CF_3CO_2H are higher than expected from the data points for ethanol–water mixtures. In contrast, data points for fluorinated alcohols [CF_3CH_2OH and $(CF_3)_2CHOH$] deviate slightly in the opposite direction. For solvolyses of 1-adamantyl substrates, a Y_{Cl} versus Y_{OMs} plot (not published) shows the same trends.

From calculations of chlorine kinetic isotope effects, strong hydrogen bonding to the incipient chloride ion has been suggested for ethanol–water mixtures (71). A corresponding amount of electrophilic solvent assistance
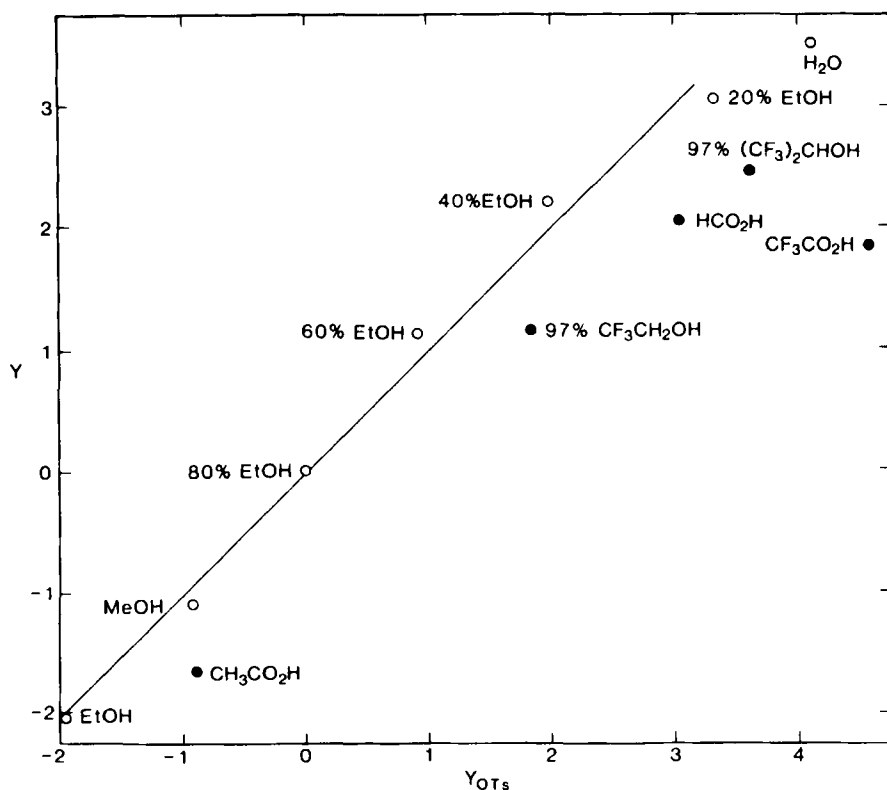
Figure 3   Correlation of Y versus Y_{OTs}. The correlation line is fitted to the open circles excluding pure water (slope $= 1.00 \pm 0.05$, $r = 0.995$); data from Tables 5 and 6.

between initial and transition states is accepted, and Y_X values probably include different amounts of assistance for each solvent; thus, Y_X is a blend of electrostatic and electrophilic solvation effects for which one adjustable parameter (m) is adequate in most cases for quantitative correlations (exceptions include carboxylic acid solvents for all leaving groups and also perhaps fluorinated alcohols for triflate leaving groups). Additional adjustable parameters are being investigated, for example, an α scale of hydrogen bond donation (72), but unfortunately reliable α values are not yet available for the most appropriate solvents (carboxylic acids).

In addition to the two major solvation effects (electrostatic and electrophilic), more specific solvation effects occur in Y_{OClO_3} and Y_{Pic} (54, 65) particularly in high percentage acetone-water mixtures.

The original Y values are compared with Y_{OTs} in Fig. 3; marked deviations for both fluorinated alcohols and carboxylic acids can be explained by nucleophilic solvent assistance in solvolyses of the model substrate *tert*-butyl chloride (15, 16). An alternative explanation (73) using the solvatochromic method is that, in fluorinated alcohols, solvolyses of *tert*-butyl chloride have a lower sensitivity to solvent electrophilicity (measured by the hydrogen bond donation parameter α) than solvolyses of 1-adamantyl chloride (15) or 2-adamantyl tosylate (Fig. 3). According to this explanation, Y values are a blend of π^* (solvent dipolarity) and α (74), but it is not explained why the additional electrophilicity term for fluorinated alcohols is *absent* in comparisons of Y_{OTs} with Y_{Cl} (Fig. 2) as well as with Y_{Br}, Y_I, and Y_{Pic} (65). Also, for solvolyses of alkyldimethylsulfonium ions, solvent electrophilicity is relatively unimportant and the effects of the low nucleophilicities of fluorinated alcohols can be observed (16).

Because many aqueous binary mixtures (excluding fluorinated alcohols) have very similar nucleophilicites, the original Y values are closely related to Y_X values, for example $Y \simeq 0.75\ Y_{Cl}$ (see column 5 of Table 8, later) and $Y \simeq Y_{OTs}$ (e.g., data for the solvent range ethanol–20% ethanol water shown in Fig. 3).

III. DEVELOPMENT OF MECHANISTIC CRITERIA

A. Correlations of Solvolysis Rates
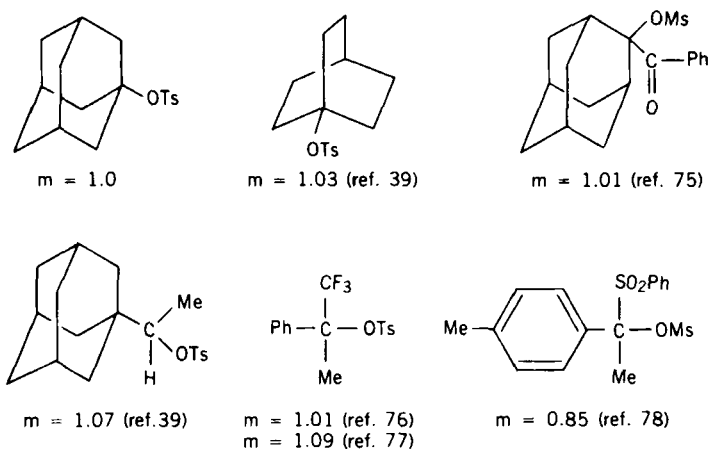
The simplest useful equation incorporating Y_X values is

$$\log\left(\frac{k}{k_0}\right)_{RX} = mY_X + c \tag{8}$$

This equation can be applied in the same way as for Equation 2, and has the

advantage that explicit consideration is given to effects due to specific solvation of the leaving group X. As most of the recent work has been done with X = OTs or a similar sulfonate, correlations using Y_{OTs} will be described.

Equation 8 will successfully correlate solvolysis rate data under the following three circumstances:

1. Sterically hindered substrates reacting by S_N1 (limiting) mechanisms give *m* values close to 1.00 (Scheme 1);

$$m = 1.0 \qquad m = 1.03 \text{ (ref. 39)} \qquad m = 1.01 \text{ (ref. 75)}$$

$$m = 1.07 \text{ (ref.39)} \qquad m = 1.01 \text{ (ref. 76)} \qquad m = 0.85 \text{ (ref. 78)}$$
$$\qquad\qquad\qquad m = 1.09 \text{ (ref. 77)}$$

Scheme 1

2. Substrates reacting by neighbouring group participation (k_Δ processes) give *m* values significantly less than 1.00, probably because of delocalization of positive charge (39, 79).

3. Substrates reacting by nucleophilic solvent assistance (k_s processes) also give *m* values significantly less than 1.00, probably because of delocalization of positive charge onto the attacking nucleophile (35, 80). These correlations are successful for solvents of similar nucleophilicities (e.g., ethanol–water mixtures give m_{EW} values) (34, 81) and are fortuitous for solvents where changes in Y are proportional to changes in solvent nucleophilicity (5).

A more general equation (9) incorporates terms for the sensitivity

$$\log\left(\frac{k}{k_0}\right)_{ROTs} = lN_{OTs} + mY_{OTs} \qquad (9)$$

(l) of the substrate to nucleophilicity (N_{OTs}), defined by

$$N_{OTs} = \log\left(\frac{k}{k_0}\right)_{CH_3OTs} - 0.3\,Y_{OTs} \tag{10}$$

The background to studies of solvent nucleophilicity has recently been reviewed (44), including consideration of alternative N scales (82–84). Briefly, Equation 10 arises from Equation 9 by substituting $l = 1$ and $m = 0.3$ for solvolyses of methyl tosylate (35). The choice of $m = 0.3$ is still being debated (44, 85), and an alternative value of 0.55 has been suggested (85), but it is agreed that consistent correlations can be obtained using N_{OTs} (85). One justification for $m = 0.3$ was the similar nucleophilicities of acetic and formic acids determined in liquid sulfur dioxide – the N_{PW} scale (86). Setting the N_{OTs} values for these two solvents to be equal gives $m = 0.3$ (actually 0.306) from Equation 9, using data for methyl and 2-adamantyl tosylates (i.e., Y_{OTs}) in acetic and formic acids (35). Although we have now recommended a revised Y_{OTs} for acetic acid (Section II.A.3), the definition of N_{OTs} using $m = 0.3$ (Equation 10) need not be changed; m would be 0.283 if acetic and formic acids were assumed to have equal nucleophilicities.

Equations 11 and 12 have also proved useful (4, 35, 39) because only one adjustable parameter is required.

$$\log\left(\frac{k}{k_0}\right)_{ROTs} = Q \log\left(\frac{k}{k_0}\right)_{2-AdOTs} + (1-Q)\log\left(\frac{k}{k_0}\right)_{CH_3OTs} \tag{11}$$

$$\log\left(\frac{k}{k_0}\right)_{ROTs} = Q' \log\left(\frac{k}{k_0}\right)_{2-AdOTs} + (1-Q')\log\left(\frac{k}{k_0}\right)_{2-PrOTs} \tag{12}$$

The success of Equations 11 and 12 indicates that m and l (Equation 9) may not be independent. An increase in sensitivity to solvent nucleophilicity (l) may *cause* a decrease in sensitivity to solvent ionizing power (m) (34, 35), and relationships between m, l, and Q are as follows:

$$l = \frac{1-m}{0.7} \tag{13}$$

$$l = 1 - Q \tag{14}$$

$$m = 0.3 + 0.7Q \tag{15}$$

Freely adjusted l and m values from Equation 9 often fit Equation 13, even for solvolyses of benzyl tosylate (87), which from an initial study with limited data appeared not to fit Equation 13 (35). Allyl tosylate gives $m = 0.53$ and $l = 0.81$ (85) in approximate agreement with Equation 13.

These detailed studies of relatively simple aliphatic and alicyclic substrates established general trends and helped to define "normal" expected behavior. A disadvantage is that a wide range of solvolytic data is needed for the correlations using Equation 9 (particularly solvents having a diversity of N and Y values); typically data for about 10 solvents can be obtained, but an even wider range would be beneficial.

B. Mechanistic Information from a Restricted Number of Solvents

Useful information can be obtained from data for a few solvents using Equation 8. As 80% v/v ethanol–water is the standard solvent for correlations, it is desireable to obtain this result experimentally. Additional data in the range 100% ethanol to 40% v/v ethanol- water give m_{EW}; the exact value would depend on the range of solvents studied because the plots may be slightly curved. If data in the region of $Y_{OTs} \sim -1$ were conveniently accessible, useful information could be obtained from the rate ratio $k_{90\% EtOH}/k_{AcOH}$, which refers to solvents of similar Y_{OTs} and different N_{OTs} values. For 1-adamantyl tosylate, this ratio is 1.38. Significantly higher ratios would be evidence for nucleophilic solvent assistance (88). More exactly, the ratio $[k_{EW}/k_{AcOH}]_{Y(OTs)}$ could be evaluated (34, 81, 88) by interpolating the ethanol–water plot to $Y_{OTs} = -0.9$, the value for acetic acid. Similarly, a ratio $[k_{EW}/k_{HCO_2H}]_{Y(OTs)}$ may be investigated (88), but the relevant ethanol–water composition is $< 30\%$ v/v. Studies of tosylates become difficult in this region. (Mesylates are a more soluble alternative.)

Another useful rate ratio is $k_{40\% EtOH}/k_{97\% CF_3CH_2OH}$ (89). This ratio is relatively independent of leaving group solvation by electrophilicity effects, as shown by the following data:

2-Adamantyl tosylate, $k_{40\% EtOH}/k_{97\% CF_3CH_2OH}$ $= 1.38$
1-Adamantyl mesylate, $k_{40\% EtOH}/k_{97\% CF_3CH_2OH}$ $= 1.76$
1-Adamantyl chloride, $k_{40\% EtOH}/k_{97\% CF_3CH_2OH}$ $= 0.83$
1-Adamantyl bromide, $k_{40\% EtOH}/k_{97\% CF_3CH_2OH}$ $= 1.23$
1-Adamantyl trifluoroacetate, $k_{40\% EtOH}/k_{97\% CF_3CH_2OH}$ $= 1.01$

Few applications of this mechanistic probe have been published to date, but the "Raber–Harris probe" (90, 91) is based on the same principles. In this approach, solvolyses are investigated in three or more compositions of both ethanol–water and trifluoroethanol water. If Equation 8 correlates all of the data satisfactorily, nucleophilic solvent assistance is judged to be unimportant. When solvent nucleophilicity is significant, separate correlation lines of greatly different slopes are required for each of the two solvent pairs.

Other rate ratios have also been applied to mechanistic interpretations. The rate ratio $k_{97^\circ{}_o(CF_3)_2CHOH/H_2O}/k_{HCO_2H}$ depends strongly on solvent nucleophilicity, varying from 0.017 for CH_3OTs to 3.7 for 2-AdOTs (92), and can be applied when more nucleophilic solvents undergo competing pathways. The rate ratio $k_{80^\circ{}_o EtOH}/k_{97^\circ{}_o CF_3CH_2OH}$ depends on both m and l (Equation 9), but was useful (93) in cases where $m > 0.6$ and l is small. In these cases nucleophilic solvent assistance is difficult to detect, for instance, for solvolyses of 2-endo-norbornyl sulfonates (structure 4) and derivatives (37–39). Using similar arguments, relative rates for two tertiary substrates in 80% acetone–water and 97% trifluoroethanol have been quoted (94) as evidence for similar mechanisms.

Mixtures of ethanol–water (EW) and acetic acid–formic acid (AF) have also been investigated for the development of mechanistic criteria (81, 95–97). For this work, solvolyses of neophyl tosylate (structure 5, Z = H) were chosen as the reference substrate. Slopes of correlations b_{EW} and b_{AF} were plotted and the patterns of the two lines were categorized as parallel but not dispersed, parallel but dispersed, diverging as Y increases, or converging as Y increases. However, assignment of results to a particular category could not be done merely by considering slopes and $\pm$ errors. Results for 2-adamantyl tosylate ($b_{EW} = 1.56 \pm 0.04$, $b_{AF} = 1.35 \pm 0.04$) were considered from statistical evidence to be parallel, whereas results for pinacolyl brosylate ($b_{EW} = 1.38 \pm 0.02$, $b_{AF} = 1.17 \pm 0.03$) were considered to be divergent. Hence, it is not clear how sensitive these criteria are for weak nucleophilic solvent assistance.

Solvolyses of cyclopentyl and cyclohexyl tosylates showed $b_{EW} = b_{AF}$ (within errors) and the lines were dispersed consistent with nucleophilic solvent assistance (k_s processes). Neopentyl solvolyses also showed $b_{EW} = b_{AF}$ but no dispersion, consistent with the accepted views (98, 99) that methyl participation (bridging) occurs in the rate-determining step in an analogous way to the phenyl participation in neophyl (the reference substrate). A distinction was made between bridging and σ-conjugation (with little motion of the neighboring group), although this may not be clear-cut (98). Diverging lines were explained by the greater "cation solvating power" of water than formic acid, consistent with σ-conjugation leaving the rearside open to solvation (structure 8) compared with bridging (structure 9).

(8)   (9)
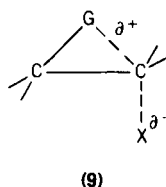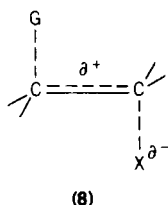
However, this explanation requires that these mechanistic criteria are sufficiently finely tuned to distinguish between cation solvating power and weak nucleophilic solvation. In both cases the solvent interacts with the accessible rearside of a carbon atom on which a positive charge is developing. This problem was considered in detail for solvolyses of *tert*-butyl chloride, and it was concluded that solvents such as water, methanol, and ethanol interact nucleophilically in the transition state rather than by dipole–dipole interactions, because the behavior of benzhydryl chloride (rearside accessible) was similar to that of 1-adamantyl chloride (100).

Another factor that could influence the slopes of ethanol–water and acetic acid–formic acid plots is internal ion pair return, usually greater in ethanol or acetic acid than water or formic acid (34). A series of sterically hindered pinacolyl derivatives was examined (101) and for these solvolyses internal ion pair return is probably absent (55). For these substrates divergent patterns were attributed (101) to a rate-limiting ionization mechanism with "cation solvation."

IV. APPLICATIONS AND LIMITATIONS

Applications of the mechanistic criteria (Section III) include studies of many reactive intermediates in which positive charge is developed on carbon, but there are also studies of nitrenes (102) and substitutions of metal complexes (103). Weakly nucleophilic solvents are usually included in these studies, although investigations of inorganic reaction mechanisms have not yet adopted these solvents. The following examples illustrate the *scope* of recent published work on carbocations. Studies of solvent effects are just one of several pieces of mechanistic evidence used by the various authors to interpret their data, so the original articles should be consulted for discussion of each topic.

Nucleophilic solvent assistance has been observed in the bromination of alkenes (104, 105) and bromination of hexynes has been examined in a range of solvents (106). An m value close to unity has been obtained for bromination of phenol (107). Vinyl cation intermediates have been formed in various solvents by addition (108) and by solvolytic reactions (108, 109).

An extremely active area of recent solvolytic investigations is destabilized secondary and tertiary carbocations, $R_1R_2ZC^+$, where Z is an electron-withdrawing group (110–112); for example, Z = CN (110), CF_3 (76, 77, 113–115), COR (61, 75, 116–118), SO_2CF_3 (119), P(O) $(OEt)_2$ (92, 120), or P(S) $(OEt)_2$ (121). Doubly deactivated carbocations have also been examined, having two CF_3 groups (115) or a CF_3 and a CN group (122). Electron demand is then so different from "typical" solvolyses that m and l values (Equation 9)

(10)
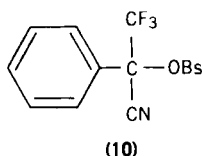
deviate from those predicted in Equation 13; for instance, $m = 0.88$ and $l = 0.49$ for the brosylate (structure **10**) (122). Other applications of Equation 8 include solvolyses of benzhydryl p-nitrobenzoates (123) and tosylates derived from substituted α-phenylethanols (124, 125).

Electronic effects of substituents are solvent-dependent and vice versa (126). Not surprisingly, correlations and interpretations of Y_X plots may be complicated by this interplay. A well-established example is protonation of, or hydrogen bonding to, methoxyl groups by carboxylic acids (79); for instance, in aromatic ethers the tendency for electron donation to the benzene ring is significantly reduced. A similar effect has been proposed (127) for aliphatic ethers in fluorinated alcohols. Rates of solvolyses of the two allylic p-nitrobenzoates (structures **11** and **12**) are very similar in a range of solvents from 96% ethanol to 40% acetone.
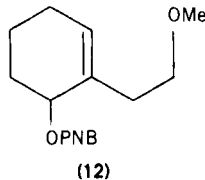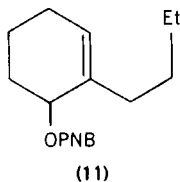

In 97% hexafluoroisopropanol and 97% trifluoroethanol, rates for the ether (structure **12**) are about seven times lower than for the hydrocarbon analog (structure **11**). There are two unexpected features of these results: (1) both fluorinated alcohols deactivate to the same extent, although they differ in acidity by three pK_a units (44); and (2) a plot versus Y_{OTs} is linear for all solvents for the ether (structure **12**) and not, as would be expected, for structure **11**. Although detailed studies of solvolyses of adamantyl p-nitrobenzoates have not yet been made, solvolysis of benzhydryl p-nitrobenzoate in ethanol–water and trifluoroethanol–water gives $m_{OTs} = 0.82$ at 100°C (123) and solvolysis of 1-adamantyl trifluoroacetate gives $m_{OTs} = 0.94$ at 50°C (17).

Hydrogen-bonding to the OH of mustard chlorohydrin (structure **13**) may account for a major part of the "failure of the Raber–Harris probe" –the incorrect prediction of nucleophilic solvent assistance in solvolyses of structure **13** (128).

$$HO(CH_2)_2S(CH_2)_2Cl$$
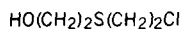
(13)

In the absence of the oxygen atom, the deviation $k_{EW}/k_{97\%_0 CF_3CH_2OH}$ is small (53), although kinetic data for two groups disagree (53, 129), and the substrates are susceptible to salt formation (130, 131). Differences between SMe and SPh substituents (53) may be caused by greater hydrogen bonding to the more basic SCH_3 group. Hydrogen bonding to nitrogen may influence the reactivity of dimethylamino compounds (e.g., structure **14**) (115), which also shows deviations in a Raber–Harris plot versus Y_{OTs} (53).
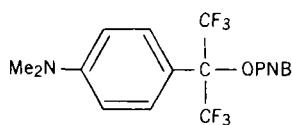
(14)

During the initial work on Y_X scales and on the correlations of solvolysis rates, (15, 34, 35, 39), the presence of extra functional groups was deliberately avoided. Subsequent studies of a wider range of compounds show additional solvation effects; for example, S_N1 solvolyses of carboxylic acid chlorides do not correlate well with Y_{Cl} (46). The possibility of additional specific solvation effects limits the precision of correlations using Y_X scales. For k_Δ processes, it is possible that mY_X plots will be curved because the extent of anchimeric assistance may depend on the solvent ionizing power (132). For nucleophilically assisted processes, steric effects on solvent nucleophilicity may be important (44, 133). Ion pair return is another possible cause of complications.

V. CONCLUSIONS

Data for a wide range of leaving groups are now available to establish "normal" behavior for expected kinetic effects of protic solvents on the heterolytic step of solvolytic reactions. Normally expected effects of solvent nucleophilicity are also established. The Y_X solvent scales will be useful for the correlation and interpretation of new experimental data and for the identification of "anomalous" results. Investigations of "anomalous" results by independent mechanistic probes should then lead to increased understanding of specific solvation effects and/or mechanistic changes.

The empirical parameters (Y_X and N) describe the microscopic events occurring between the initial state and the transition state of solvolytic

reactions. Although their relationship to other empirical parameters is of interest, there is no directly analogous parameter (either empirical or macroscopic). Relationships between Y and Y_X scales for "well-behaved" solvents will be useful for further extending the scope of data available for correlations. For those averse to "proliferation" of empirical scales, we note that Y_{OTs} may be a useful "general-purpose" scale of solvent ionizing power, in cases where data for the most appropriate Y_X scale are not available.

VI. COMPILATIONS

A summary of available data is shown in Table 4. Details are given in Tables 5–9. Because some Y_{OTs} values have been changed from previously recommended values, N_{OTs} values have also been revised (Table 5). There are similarities between Y_{OMs} and Y (Table 6) and between Y_{Cl} and $Y/0.75$ (Table 8), particularly for aqueous alcohol mixtures. Values for Y_X are quoted to a maximum of two decimal places—a difference in Y value of 0.01 corresponds to a rate ratio of 1.023. Most of the original Y values were quoted (3) to three decimal places, corresponding to a precision that is difficult to reproduce, particularly in different batches of the "same" solvent. The uncertainties in relatively slow solvolyses are increased by extrapolations from

TABLE 4
Range of Leaving Groups for Currently Available Y_X Scales of Solvent Ionizing Power

Leaving Group Name, Formula	Y_X scale	Table	Comment
Bromide, Br	Y_{Br}	8	
Brosylate, $SO_2C_7H_7Br$	Y_{OTs}	5	Using OBs/OTs ratios
Chloride, Cl	Y_{Cl}	8	
Dimethylsulfonium, $^+SMe_2$	Y^+	9	
Dinitrophenolate, $OC_6H_3(NO_2)_2$	—[a]	—[b]	
Heptafluorobutyrate, $OCOC_3F_7$	—[a]	7	
Iodide, I	Y_I	8	
Mesylate, SO_2CH_3	Y_{OTs}	5	Using OTs/OMs ratios
	Y_{OMs}	6	
Pentafluorobenzenesulfonate	Y_{PFBS}	6	
Perchlorate, $OClO_3$	Y_{OClO_3}	9	
Picrate, $OC_6H_2(NO_2)_3$	Y_{Pic}	9	
Tosylate, $SO_2C_7H_8$	Y_{OTs}	5	
Tresylate, $SO_2CH_2CF_3$	Y_{OTr}	6	
Triflate, SO_2CF_3	Y_{OTf}	7	
Trifluoroacetate, $OCOCF_3$	—	7	

[a] A specific code has not been assigned to the scale.
[b] Limited data available (145).

TABLE 5

Y_{OTs} Values of Solvent Ionizing Power Defined from Rate Constants for Solvolyses of 1- or 2-Adamantyl Tosylates at 25°C

Solvent[a]	Rate Constants (k, s^{-1})		k_{OTs}/k_{OMs}[c]	Y_{OTs}[d]	N_{OTs}[e]
	2-Ad$(10^5 k)$	1-Ad(k)[b]			
EtOH		0.000044	1.77[f]	−1.96	0.06
90% EtOH		0.000688		−0.77	0.07
80% EtOH	0.0024[g,h]	0.00403[i]	0.97[j]	0.00	0.00
70% EtOH				0.47[k]	−0.05
60% EtOH	0.020[g]	(0.0422)[f]	0.87[l]	0.92	−0.08
50% EtOH	0.047[g]	(0.151)[f]	0.5[l,m]	1.29	−0.09
40% EtOH	0.225[n]			1.97	−0.23
30% EtOH				2.84[k]	−0.35
20% EtOH	5.06[o]		1.32[l]	3.32	−0.34
10% EtOH				3.78[k]	−0.41
H_2O	31.5[p]		2.1[q]	4.1	−0.44
MeOH		0.00048	1.71[j]	−0.92	−0.04
90% MeOH		0.00361	1.72[j]	−0.05	−0.05
80% MeOH				0.47[k]	−0.05
70% MeOH				1.02[k]	−0.08
60% MeOH	0.008[p]		1.35[j]	1.52	−0.13
50% MeOH				2.00[k]	−0.19
40% MeOH	0.64[o]		1.03[j]	2.43	−0.21
30% MeOH				2.97[k]	−0.30
20% MeOH	5.9[o]		1.48[j]	3.39	−0.35
10% MeOH				3.78[k]	−0.41
95% $(CH_3)_2CO$		0.00000448		−2.95	
90% $(CH_3)_2CO$		0.0000416	1.81[r]	−1.99	−0.39
80% $(CH_3)_2CO$		0.000461	0.98[r]	−0.94	−0.42
70% $(CH_3)_2CO$				0.07[k]	−0.42
60% $(CH_3)_2CO$	0.0111[s]		1.26[r]	0.66	−0.41
50% $(CH_3)_2CO$				1.26[k]	−0.39
40% $(CH_3)_2CO$	0.17[t]		1.13[t]	1.85	−0.38
30% $(CH_3)_2CO$				2.50[k]	−0.40
20% $(CH_3)_2CO$	2.7[t]		1.31[t]	3.05	−0.38
10% $(CH_3)_2CO$				3.58[k]	−0.41
90% dioxan		0.0000157		−2.41	−0.51
80% dioxan		0.000201		−1.30	−0.29
Acetonitrile–water mixtures (% w/w) (42)					
50% CH_3CN				1.2	
35% CH_3CN				1.8	
30% CH_3CN				1.9	
25% CH_3CN				2.5	
20% CH_3CN				2.7	
10% CH_3CN				3.6	

TABLE 5 (Continued)

| Solvent[a] | Rate Constants (k, s^{-1}) | | k_{OTs}/k_{OMs}[c] | Y_{OTs}[d] | N_{OTs}[e] |
	2-Ad$(10^5 k)$	1-Ad(k)[b]			
i-PrOH		5.98×10^{-6}		−2.83	0.12
t-BuOH		7.40×10^{-7}		−3.74	
CF$_3$CH$_2$OH–water					
mixtures (% w/w)					
CF$_3$CH$_2$OH	0.142[u]	(0.578)[f]		1.77	−3.07[v]
97% CF$_3$CH$_2$OH	0.164[w,x]		1.06[y]	1.83	−2.79
85% CF$_3$CH$_2$OH	0.200[z]			1.92	−2.01
70% CF$_3$CH$_2$OH	0.243[w,aa]		0.95[y]	2.00	−1.20
50% CF$_3$CH$_2$OH	0.335[z]		0.83[y]	2.14	−0.93
(CF$_3$)$_2$CHOH	15.7[bb]			3.82	
97% (CF$_3$)$_2$CHOH	9.75[w,cc]		0.94[y]	3.61	−4.27
90% HFIP/PDT	2.16[dd]			2.95	−0.64
CH$_3$CO$_2$H	(0.00059)[ee]	0.00053[ff]	0.85[gg]	−0.9	−2.28
75% AF[hh]	0.012			0.70	
50% AF[hh]	0.10			1.62	
25% AF[hh]	0.52			2.34	
HCO$_2$H	2.65[g]		1.00[y]	3.04	−2.35
CF$_3$CO$_2$H	90[ii]		0.44[jj]	4.57	−5.56
CF$_3$CH$_2$OH–EtOH					
mixtures (% v/v)					
80%	0.0218[kk]			0.98	−1.72[ll]
60%	0.00376[kk]			0.21	−1.01[mm]
40%	0.00084[kk]			−0.44	−0.55[mm]
H$_2$SO$_4$ H$_2$O					
mixtures (% w/w)[nn]					
20%			1.8	4.39	−0.71
40%			1.6	4.67	−1.20
60%			1.1	5.29	−2.02
Aprotic and other solvents					
CH$_3$CN[oo]		2.51×10^{-6}		−3.21	
HCONHCH$_3$[pp]		8.03×10^{-5}		−1.70	
CH$_3$CONHCH$_3$[pp]		8.25×10^{-6}		−2.69	
HCON(CH$_3$)$_2$[pp]		2.89×10^{-7}		−4.14	
CH$_3$CON(CH$_3$)$_2$[pp]		4.15×10^{-8}		−4.99	

[a] Solvent compositions refer to % v/v water, before mixing, except where stated otherwise.
[b] Reference 23.
[c] Based on adamantyl solvolyses unless stated otherwise.
[d] All values quoted previously have been retained, unless a significant change (> 0.05) appears to be warranted; newly revised values are underlined; values of rate constants in columns 2 or 3 show the model system chosen.
[e] Calculated from Equation 10; data for solvolyses of methyl tosylate at 50°C from referenc 35.
[f] Data from reference 52.

TABLE 5 (*Continued*)

[a]Reference 34.

[h]Additional result: $k = 2.3 \times 10^{-8} \, \text{s}^{-1}$ (reference 67).

[i]Additional result (interpolated): $k = 4.24 \times 10^{-3} \, \text{s}^{-1}$ (reference 134).

[j]Mesylate data from reference 7.

[k]Interpolated from a plot of log k vs. Y.

[l]Mesylate data from reference 41.

[m]Anomalously low value in comparison with data for cyclohexyl sulfonates (reference 41).

[n]Reference 81.

[o]Reference 7.

[p]Calculated from rate data for the mesylate, assuming the OTs/OMs rate ratio shown.

[q]Based on kinetic data for 2-propyl sulfonates (reference 36).

[r]Additional rate constants for 1-adamantyl mesylate from Table 1 and reference 52.

[s]Reference 33.

[t]Reference 41.

[u]Average (± 0.02) of two independent values (references 39, 67).

[v]Reference 135.

[w]Reference 35.

[x]Additional result: $k = 1.02 \times 10^{-6} \, \text{s}^{-1}$ (reference 58).

[y]Rate constant for 2-adamantyl mesylate from Table 2.

[z]Reference 37.

[aa]Additional result: $k = 2.3 \times 10^{-6} \, \text{s}^{-1}$ (reference 37).

[bb]References 39 and 136.

[cc]Additional values given in Table II of reference 39 and in reference 58.

[dd]Reference 136; PDT is propanedithiol (mole/mole).

[ee]Reference 26.

[ff]Average of four independent measurements (references 8, 22, 24, 25).

[gg]Rate constant for 1-adamantyl mesylate from Table 1; a rate constant for 2-adamantyl mesylate (116) gives OTs/OMs = 0.81.

[hh]Data for acetic acid/formic acid mixtures from reference 81.

[ii]Reference 30.

[jj]Based on kinetic data for 2-propyl sulfonates (116, 137).

[kk]Reference 67.

[ll]Data for methyl tosylate from reference 138.

[mm]Data for methyl tosylate from reference 135.

[nn]Data from reference 43; results for other solvent compositions available; OTs/OMs rate ratios based on 2-propyl.

[oo]Reference 59.

[pp]Reference 60.

<div align="center">

TABLE 6

Y_X Values of Solvent Ionizing Power Defined for Solvolyses of Other Sulfonates at 25°C

</div>

Solvent[a]	Y_{OMs}[b]	Y_{PFBS}[c]	Y_{OTr}[d]	Y[e]
EtOH	−2.22[f]	−1.72	−1.89	−2.03
90% EtOH	−0.82[g]	−0.63	−0.72	−0.75
80% EtOH	0.00	0.00	0.00	0.00
70% EtOH	0.60[g]	0.43	0.49	0.60
60% EtOH	1.13		0.95	1.12
50% EtOH	1.65		1.41	1.66
40% EtOH	2.18			2.20
30% EtOH	2.82[g]			2.72
20% EtOH	3.21			3.05
McOH	−1.17	−1.02	−1.11	−1.09
90% MeOH	−0.30	−0.29	−0.31	−0.30
80% MeOH	0.39	0.33	0.36	0.38
70% MeOH	0.98[g]		0.91	0.96
60% MeOH	1.54		1.42	1.49
50% MeOH	2.05[g]		2.14	1.97
40% MeOH	2.50			2.39
30% MeOH	2.95[g]			2.75
20% MeOH	3.32			3.03
95% (CH₃)₂CO		−2.11	(−2.18)[h]	
90% (CH₃)₂CO	−2.26[f,i]	−1.57	−1.75[f]	−1.86
80% (CH₃)₂CO	−0.95[f,i]	−0.81	−0.93	−0.67
70% (CH₃)₂CO	−0.10[g]	−0.24	−0.24	0.13
60% (CH₃)₂CO	0.66	0.30	0.40	0.80
50% (CH₃)₂CO	1.28[g]		1.02	1.40
40% (CH₃)₂CO	1.94			1.98
30% (CH₃)₂CO	2.53[g]			2.48
20% (CH₃)₂CO	3.08			2.91
95% dioxan		−2.74	(−2.96)[h]	
90% dioxan		−2.00	(−2.09)[h]	−2.03
80% dioxan		−1.13	−1.20	−0.83
70% dioxan		−0.46	−0.46	0.01
60% dioxan			0.25	0.72
50% dioxan			0.95	1.36
CF₃CH₂OH	1.90[f]	1.11	1.71	1.15[k]
97% CF₃CH₂OH[j]	1.92	1.15	1.73	1.15[l]
90% CF₃CH₂OH[j]		1.21	1.79	1.25[l]
80% CF₃CH₂OH[j]		1.30	1.84	1.46[l]
70% CF₃CH₂OH[j]	2.15		1.97	1.66[l]
50% CF₃CH₂OH[j]	2.38		2.16	2.23[l]
97% (CF₃)₂CHOH[j]	3.72		3.40	2.46[m]
90% (CF₃)₂CHOH[j]			2.89	1.99[m]
80% (CF₃)₂CHOH[j]			2.60	1.86[m]

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TABLE 6 (*Continued*)

Solvent[a]	Y_{OMs}[b]	Y_{PFBS}[c]	Y_{OTr}[d]	Y[e]
CH_3CO_2H	−0.83	−1.41	−0.93	−1.67
HCO_2H	3.08		3.00[n]	2.05
CF_3CH_2OH–EtOH				
80%		0.42	0.92	0.41[k]
60%		−0.22	0.16	−0.27[k]
40%		−0.80	−0.57	−0.87[k]
20%		−1.30	−1.24	−1.52[k]

[a]Solvent compositions refer to % v/v water, before mixing, except where stated otherwise.

[b]Based on solvolyses of 1-adamantyl mesylate; data from reference 7 and Table 1, unless stated otherwise.

[c]Based on solvolyses of 2-adamantyl pentafluorobenzenesulfonate (reference 66).

[d]Based on solvolyses of 2-adamantyl tresylate (reference 67); additional values for 1-adamantyl tresylate are available in reference 52.

[e]Reference 3.

[f]Reference 52.

[g]Interpolated from a plot versus Y.

[h]Data at 50°C.

[i]Table 1.

[j]Solvent compositions are % w/w water.

[k]References 135 and 138.

[l]Reference 139.

[m]References 45 and 140.

[n]Reference 52 quotes a value of 2.64.

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TABLE 7
Y_X Values of Solvent Ionizing Power for Perfluoroalkyl Leaving Groups

Solvent[a]	$Y_{7,NbOTf}$[b] (25°C)	Y_{OTf}[c] (25°C)	Y_{OTf}[c] (−20°C)	$\log(k/k_0)_{1\text{-AdOCOCF}_3}$[d] (50°C)	$\log(k/k_0)_{1\text{-AdOCOC}_3F_7}$[e] (50°C)
EtOH	−1.50	−1.66[f]	−1.84[g]		
90% EtOH			−0.65[g]		
80% EtOH	0.00	0.00	0.00	0.00	0.00
70% EtOH			0.53[g]		
60% EtOH	0.88		0.94[g]		
50% EtOH		1.35			
40% EtOH		2.13		2.26[h]	
30% EtOH		2.9			
20% EtOH		3.1			
MeOH		−0.79	−0.88[g]		
90% MeOH			−0.10[g]		
80% MeOH		0.52	0.71[h]	0.63	0.93
70% MeOH			1.26[g]		
60% MeOH		1.53	2.04[g]	1.50	1.62
50% MeOH					
40% MeOH		2.51		2.59	2.59
30% MeOH		2.8			
95% (CH₃)₂CO		−1.15[i]	−0.79[g]		
90% (CH₃)₂CO		−0.64[i]	−0.35[g]		
80% (CH₃)₂CO		0.04	0.24[i]	−0.41	
70% (CH₃)₂CO			0.78[g]		
60% (CH₃)₂CO		1.03	1.30[g]	0.78	0.98
50% (CH₃)₂CO			1.88[g]		

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Solvent					
40% (CH$_3$)$_2$CO	1.78		2.00		
30% (CH$_3$)$_2$CO		2.45	2.5		
i-PrOH			−2.16[f]		
t-BuOH			−2.66[f]		
CF$_3$CH$_2$OH					0.40
97% CF$_3$CH$_2$OH[j]	2.25		0.96	1.23[g]	
90% CF$_3$CH$_2$OH[j]				1.36[g]	
70% CF$_3$CH$_2$OH[j]			1.42	1.61[g]	
50% CF$_3$CH$_2$OH[j]			1.74		
97% (CF$_3$)$_2$CHOH[j]	3.37	3.32	−1.57[f]		−1.78
CH$_3$CO$_2$H			2.51		1.65
HCO$_2$H					1.49
CF$_3$CO$_2$H			1.64		1.76
CF$_3$CH$_2$OH–EtOH mixtures					
80%				0.26[g]	
60%				−0.31[g]	
40%				−1.02[g]	
20%				−1.48[g]	

[a] Solvent compositions refer to % v/v water, before mixing, except where stated otherwise.
[b] Based on solvolyses of 7-norbornyl triflate at 25°C (62).
[c] Based on solvolyses of 2-adamantyl triflate at 25°C; data from reference 65 and Table 3, except where stated otherwise.
[d] Based on solvolyses of 1-adamantyl trifluoroacetate at 50°C (17).
[e] Based on solvolyses of 1-adamantyl heptafluorobutyrate at 50°C (17).
[f] Data from reference 64, using $k_0 = 1.7 \times 10^{-2}$ s^{-1} (65); we have obtained an independent value of 1.79×10^{-2} at 25°C, significantly lower than an extrapolated titrimetric value of 2.13×10^{-2} (64).
[g] Values at −20°C (64).
[h] This work.
[i] Reference 61.
[j] Solvent compositions are % w/w.
[k] Revised value quoted in Table 5 of reference 66.

TABLE 8

Y_χ Values of Solvent Ionizing Power for Solvolyses of Halides at 25°C

Solvent[a]	Y_I^b	Y_{Br}^c	Y_{Cl}^c	$Y/0.75^d$
EtOH	−2.2[r]	−2.4[e]	−2.5[e]	−2.71
90% EtOH	−0.81[e]	−0.84[e]	−0.9[e]	−1.00
80% EtOH	0.00	0.00	0.00	0.00
70% EtOH	0.71[f]	0.68[f]	0.8	0.79
60% EtOH	1.22[f]	1.26	1.38	1.50
50% EtOH	1.79	1.88	2.02	2.21
40% EtOH	2.46[f]	2.62	2.75	2.93
30% EtOH	3.17[f]	3.40	3.53	3.63
20% EtOH	3.68	3.92	4.09	4.07
10% EtOH	3.95[f]	4.17	4.40	4.42
H_2O	4.24	4.44	4.57	4.66
MeOH	−0.84	−1.12[e]	−1.2[e]	−1.45
90% MeOH	0.01[f]	−0.14[e]	−0.2[e]	−0.40
80% MeOH	0.76	0.70[f]	0.67[e]	0.51
70% MeOH	1.46[f]	1.42	1.46	1.28
60% MeOH	1.97	2.04	2.07	1.99
50% MeOH	2.54[f]	2.61	2.70	2.63
40% MeOH	3.02	3.14	3.25	3.19
30% MeOH	3.43[f]	3.61	3.73	3.67
20% MeOH	3.77	3.94	4.10	4.03
10% MeOH	4.01[f]	4.17	4.39	4.37
80% $(CH_3)_2CO$	−0.17	−0.7[e]	−0.8[e]	−0.90
70% $(CH_3)_2CO$	0.58[f]	0.2[e]	0.17[e]	0.17
60% $(CH_3)_2CO$	1.20	1.03	1.00[e]	1.06
50% $(CH_3)_2CO$	1.82[f]	1.74	1.73	1.86
40% $(CH_3)_2CO$	2.43	2.44	2.46	2.64
30% $(CH_3)_2CO$	2.99[f]	3.11	3.21	3.31
20% $(CH_3)_2CO$	3.49	3.66	3.77	3.88
10% $(CH_3)_2CO$	3.79	4.05	4.28	4.31
5% $(CH_3)_2CO$	3.97		4.44	
80% dioxan		−0.60[g]		−1.11
70% dioxan		−0.01[g]		0.02
60% dioxan		0.82[g]		0.95
80% DMSO		0.22[h]		−0.44[i]
70% DMSO		0.82[h]		0.67[i]
60% DMSO		1.71[h]		1.64[i]
50% DMSO		2.46[h]		2.29[i]
CF_3CH_2OH		2.53		1.53
97% CF_3CH_2OH[j]	2.22	2.53	2.83	1.53
80% CF_3CH_2OH[j]		2.67[g]		1.95
70% CF_3CH_2OH[j]	2.61	2.79	2.96	2.21
60% CF_3CH_2OH[j]		2.91[g]		2.53
50% CF_3CH_2OH[j]	2.87	3.04	3.16	2.97
97% $(CF_3)_2CHOH$[j]	3.84	4.51	5.08	3.28
CH_3CO_2H	−2.2	−2.1	−1.6	−2.23
HCO_2H	1.6	2.47	3.20	2.74

TABLE 8 (*Continued*)

Solvent[a]	$Y_I{}^b$	$Y_{Br}{}^c$	$Y_{Cl}{}^c$	$Y/0.75^d$
CF_3CO_2H			4.6	2.45^k
CF_3CH_2OH–EtOH mixtures				
80%		1.62^l		0.55
60%		0.31^l		−0.36
40%		$−0.57^l$		−1.16
20%		$−1.42^l$		−2.03

[a]Solvent compositions refer to % v/v water, before mixing, except where stated otherwise.
[b]Reference 69.
[c]Reference 15.
[d]Y values from Table 6, except where noted otherwise.
[e]Extrapolated from a plot vs. Y.
[f]Interpolated value.
[g]Reference 141.
[h]Reference 142.
[i]Y values from footnote i of Table 2 in reference 141.
[j]Solvent compositions are % w/w.
[k]Reference 143.
[l]Rates at 25°C estimated from rate data (135) at 35°C by assuming that the change in $\Delta H^{\ddagger}$ from 20 to 24 kcal mole^{-1} (for trifluoroethanol to ethanol) occurs in 1-kcal-mol^{-1} steps for each 20% change in solvent composition.

<div align="center">

TABLE 9

</div>

Y_X Values of Solvent Ionizing Power for Perchlorates, Picrates, and Dimethylsulfonium Ions

Solvent[a]	Y_{OClO_3}[b] (0°C)	Y_{Pic}[c] (25°C)	Y^{+}[d] (70.4°C)
EtOH	−1.83	−1.37[e]	−0.02
90% EtOH	−0.70		
80% EtOH	0.00	0.00	0.00
70% EtOH	0.53		
60% EtOH	1.22		0.05
50% EtOH	1.53[c]	0.92	
40% EtOH	2.32[c]	1.28	0.10
30% EtOH	3.07[c]	1.53	
20% EtOH	3.42[c]	1.98	0.20
Water			0.26
MeOH	−0.84	−0.97[e]	0.04
90% MeOH	−0.06		
80% MeOH	0.66[f]	0.05	0.09
70% MeOH	1.30		
60% MeOH	1.74[c]	0.71	0.10
50% MeOH			
40% MeOH	2.73[c]	1.44	0.12
30% MeOH	3.06[c]		
20% MeOH	3.24[c]		0.15
95% $(CH_3)_2CO$	−0.23		0.14
90% $(CH_3)_2CO$	0.16	−0.79[g]	0.14
80% $(CH_3)_2CO$	0.78[j]	−0.29	0.12
70% $(CH_3)_2CO$	1.31	0.06[h]	
60% $(CH_3)_2CO$	1.73[f]	0.44	0.11
50% $(CH_3)_2CO$	2.17		
40% $(CH_3)_2CO$	2.59[c]	1.15	0.13
30% $(CH_3)_2CO$	3.09[c]	1.47	
20% $(CH_3)_2CO$	3.38[c]	1.82	0.18
10% $(CH_3)_2CO$	3.47[c]	2.21	
95% dioxan			−0.24
90% dioxan	(−0.97)[i]		−0.13
80% dioxan	(−0.07)[i]		−0.11
70% dioxan	0.72		−0.04
60% dioxan	1.34		0.00
50% dioxan	2.02		
40% dioxan			0.01
20% dioxan			0.08
i-PrOH	−2.44		−0.13
t-BuOH	−2.68		−0.32
CF_3CH_2OH	(1.21)[i]		0.46
97% CF_3CH_2OH[j]	1.55[c,k]	1.22	0.39
90% CF_3CH_2OH[j]	1.65		0.37
80% CF_3CH_2OH[j]	1.92		
70% CF_3CH_2OH[j]	2.07[f]	1.34	0.34
60% CF_3CH_2OH[j]	2.13		

TABLE 9 (*Continued*)

Solvent[a]	Y_{OClO_3}[b] (0°C)	Y_{Pic}[c] (25°C)	Y^+[d] (70.4°C)
50% CF_3CH_2OH[j]	2.28[f]	1.43	0.29
97% $(CF_3)_2CHOH$[j]	3.7[c]		0.50
90% $(CH_3)_2CHOH$[j]			0.49
70% $(CF_3)_2CHOH$[j]			0.36
50% $(CF_3)_2CHOH$[j]			0.33
CH_3CO_2H	−1.36	−0.90	0.07
HCO_2H			0.04
CF_3CH_2OH-EtOH mixtures			
80%			0.33
60%			0.18
40%			0.12
20%			0.06

[a]Solvent compositions refer to % v/v water, before mixing, except where stated otherwise.
[b]Reference 54.
[c]Reference 65.
[d]Reference 16.
[e]Reference 144.
[f]Average of two independent values (54, 65).
[g]Reference 145.
[h]Interpolated.
[i]Approximate value.
[j]Solvent compositions are % w/w.
[k]Alternative value: 1.30 (54).

data at higher temperatures and/or from data in more polar solvents, although it is possible to minimise such errors by monitoring some reactions for long periods (over a month). Possible sources of systematic error that may be been underestimated are dissolving the substrate (ultrasonics is very useful) and the hygroscopic nature of alcohols (e.g., trifluoroethanol).

Additional results are available for solvolyses of 1-adamantyl nitrate, for which a good correlation with Y_{OTs} has been established (146). Further work on charged sulfonate leaving groups is also in progress (147); because of their hydrophilicity, such leaving groups are particularly useful for highly aqueous media (68, 148).

For the compilations of data (Tables 5–9), we have excluded solvent mixtures that have not been studied extensively and that give anomalous results in Grunwald–Winstein plots or small responses of rates to changes in solvent composition. Rate maxima over a relatively small range of reactivity have been observed for solvolyses in methanol-acetonitrile mixtures of t-butyl halides (149) and of 1-adamantyl halides and tosylate (150)—also for solvolyses of 2-adamantyl perchlorate in methanol-acetone mixtures (151) and for solvolyses of 1-adamantyl picrate (144).

ACKNOWLEDGEMENTS

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