AN ESTIMATE OF STERIC INFLUENCE ON NUCLEOPHILIC

SOLVENT ASSISTANCE IN SECONDARY SOLVOLYSIS.

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Nordlander[1] has recently evaluated expression (i) for a number of solvents, where k_{pinOTs} and $k_{2-adOTs}$ are the solvolytic rate constants for pinacolyl tosylate and 2-adamantyl tosylate respectively in those solvents and interpreted the data in terms of ion-pair return in the solvolysis of 2-adamantyl derivatives. This conclusion was based on the assumption that both 2-adamantyl and pinacolyl tosylates undergo idealized k_c reaction.[2,3] Furthermore, it was assumed that in pinacolyl tosylate, methyl migration pre-empted ion-pair return and therefore, that deviations of expression (i) from a value of 1 reflected the degree of ion-pair return in 2-adamantyl tosylate in the particular solvent.

$$\frac{(k_{pinOTs}/k_{2-adOTs})\ \text{solvent}}{(k_{pinOTs}/k_{2-adOTs})\ \text{TFA}} \quad \ldots\ldots\ldots\ldots\ldots \quad (i)$$

Thus it was concluded that ion-pair return increases in the order: trifluoroacetic acid < acetic acid < formic acid < aqueous ethanol.

This interpretation is subject to criticism. Schleyer[4] has recently found that the rate of solvolysis of 1-adamantylmethylcarbinyl tosylate is slightly greater than that of pinacolyl tosylate in trifluoroacetic acid. Since the former compound solvolyses without substantial rearrangement, the greater reactivity of pinacolyl tosylate as compared to isopropyl tosylate was attributed to inductive/hyperconjugative effects rather than differences in ion-pair partitioning. Furthermore, the order of ion-pair return in various solvents, as proposed by Nordlander[1] and justified on the basis of Y values, conflicts with available data. There is considerable evidence that solvent nucleophilicity plays an important part in determining the

degree of ion-pair return. Thus Winstein has found that ion-pair return is large in trifluoro-
acetic and acetic acids, negligible in formic acid and small in ethanol,[5] in almost opposite
order to that suggested by Nordlander.

We believe that the values obtained for expression (i) for different solvents indicate a
small solvent nucleophilic component in the solvolysis of pinacolyl tosylate.

In order to confirm this proposal a similar analysis was performed on 2-butyl and
3-methyl-2-butyl tosylates. The results are expressed in Table 2, together with the data for
pinacolyl and isopropyl tosylates. The rate data for 3-methyl-2-butyl tosylate in aqueous ethanol
and trifluoroacetic acid are presented in Table 1.

Table 1

Rate Constants[a] for 3-Methyl-2-butyl Tosylate

Solvent	Temperature, °C	Rate Constant (sec^{-1})
50% ethanol	50.0	9.2×10^{-4}
	25.0	5.00×10^{-5}
60% ethanol	50.0	4.89×10^{-4}
70% ethanol	50.0	2.20×10^{-4}
80% ethanol	75.0	1.15×10^{-3}
	50.0	1.10×10^{-4}
	25.0[b]	7.10×10^{-6}
trifluoroacetic acid[c]	25.0	1.75×10^{-3}

[a] Rate constants in aqueous ethanol were obtained conductometrically, [b] Extrapolated
from data at higher temperatures. [c] Rate constant obtained spectrophotometrically
using the procedure in Ref. 7.

The values listed in Table 2 for isopropyl tosylate were shown by Schleyer[2c] to indicate
the magnitude of solvent nucleophilic assistance in a number of different solvents. It is readily
seen that successive α-methyl substitution drastically reduces the degree of this nucleophilic
assistance in all solvents and in 80% ethanol a 4400 fold increase in rate due to solvent
nucleophilic assistance is reduced through intermediate values for 2-butyl and 3-methyl-2-butyl

tosylates to a value of 16 for pinacolyl tosylate. This interpretation reveals the high

sensitivity of secondary tosylates to steric hindrance in solvolytic reactions.

Table 2

Estimate of Solvent Nucleophilic Assistance by $\dfrac{(k_{ROTs}/k_{2\text{-}adOTs})}{(k_{ROTs}/k_{2\text{-}adOTs})_{TFA}}$ solvent at 25°C.

Solvent	R =	Pinacolyl[a]	3-Methyl-2-butyl	2-Butyl	2-Propyl[b]
80% EtOH		16	151	980[c]	4400
50% EtOH		7.9	54.4	299[c]	1130
CH_3COOH		7.1	41.7[f]	140[d]	470[d]
HCOOH		4.5	12.6[f]	29[e]	74[e]
TFA		1	1	1[e]	1[e]

[a] Ref. 1. [b] Rate data used to evaluate figures for 2-propyl tosylate from Ref. 2 using revised values for 2-adOTs, in TFA (8.98×10^{-4})[1] and 50% EtOH (4.7×10^{-7})[10]. [c] Values calculated from rate data for 2-butyl brosylate kindly supplied by Professor V.J. Shiner jr. and assuming a OBs/OTs ratio of 5.0 in aqueous EtOH. [d] Rate data from Ref. 6. [e] Rate data from Ref. 7. [f] Data from Ref. 8 assuming a OBs/OTs ratio of 3.0 in CH_3COOH and HCOOH.

Table 3

Grunwald-Winstein m Values for Secondary Tosylates.

R =	Pinacolyl[a]	3-Methyl-2-butyl	2-Butyl[b]	2-Propyl[b]
m value	0.73	0.56	0.47	0.36

[a] Ref. 3(a), value obtained for pinacolyl brosylate. [b] Ref. 9 .

Thus the value of 16 for pinacolyl tosylate reflects the almost limiting behaviour of this sub-

strate compared to isopropyl tosylate. While direct comparison of solvolytic rate constant between

pinacolyl and isopropyl tosylates shows the former to be 10 times _faster_ in 80% ethanol, this

masks the fact that the solvent preferentially assists isopropyl tosylate by a factor of 275 and

that electronic factors associated with the t-butyl group overcompensate for this effect. Only

in the very weakly nucleophilic trifluoroacetic acid is the true influence of the electronic

effects on reaction rate observed by direct comparison of rate constants.

Further support for the contention that there is a dramatic change in the degree of nucleophilic assistance in successively substituted secondary tosylates is found in the fact that the Grunwald-Winstein m values listed in Table 3 show a progressive change toward limiting S_N1 type behaviour in the solvolysis of the more sterically hindered tosylates. Thus the m value of 0.73 obtained for pinacolyl tosylate[3a] is only marginally smaller than values obtained for many standard S_N1 type reactions.[2a]

Finally, an expression of the form of expression (i), using two standard solvents of widely separated nucleophilicities e.g. 80% ethanol and trifluoroacetic acid, may be used to estimate quantitatively the influence of steric factors on nucleophilic solvent assistance, isolated from other reactivity factors.

References

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