The Magnitude of Secondary β-Deuterium Isotope Effects in Cases of σ-Participation

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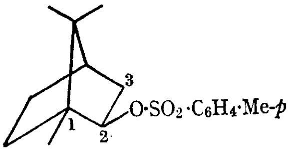
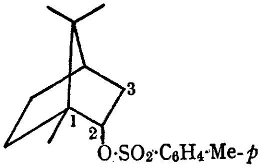
WE report additional evidence on the usefulness of the secondary β-deuterium isotope effect as a probe for neighbouring group participation.

Previous results[1,2] demonstrated a drastically reduced β-effect in the solvolysis of (I; X = $O{\cdot}SO_2{\cdot}C_6H_4{\cdot}Br$-*p*, or Br) and normal behaviour of the corresponding *endo*-norborn-2-yl derivatives (II).

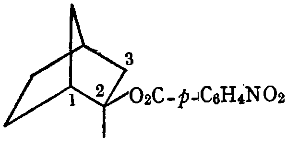
Solvolysis rates of isobornyl, bornyl, and 2-methylnorbornyl derivatives



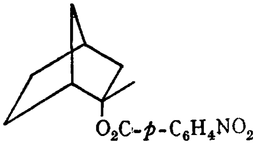
(*exo*-III)



(*endo*-III)



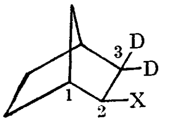
(*exo*-IV)



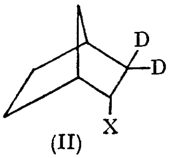
(*endo*-IV)

Compound	Solvent	Temperature	$k \times 10^5$ sec.$^{-1}$ [a]	k_H/k_D [b]
(*exo*-III)	AcOH	20·10	332·6 ± 1·4	1·162 ± 0·007
[3-$^2H_2$](*exo*-III)	AcOH	20·10	286·2 ± 1·6	
(*endo*-III)	AcOH	68·2	9·478 ± 0·094	1·291 ± 0·037
[3-$^2H_2$](*endo*-III)	AcOH	68·2	7·341 ± 0·199	
(*exo*-IV)	70% Me$_2$CO	95·0	20·37 ± 0·26	1·334 ± 0·018
[3-$^2H_2$](*exo*-IV)	70% Me$_2$CO	95·0	15·27 ± 0·07	
(*endo*-IV)	70% Me$_2$CO	120·7	1·079 ± 0·048	1·306 ± 0·060
[3-$^2H_2$](*endo*-IV)	70% Me$_2$CO	120·7	0·826 ± 0·010	

[a] Uncertainties are standard deviations of the mean.
[b] Uncertainties are probable errors.



(I)



(II)

k_H/k_D 1·02—1·04 1·26—1·28

This work has now been extended to the substituted *exo*-norborn-2-yl derivatives (*exo*-III) and (*exo*-IV) and the corresponding 2-*endo*-epimers (*endo*-III) and (*endo*-IV). The results are given in the Table.

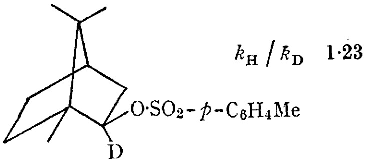
A comparison of these results with those for the unsubstituted norborn-2-yl derivatives shows, as could be predicted, the essentially identical magnitude of the β-effect for all *endo*-derivatives. In the *exo*-series, the rate retardations vary with the degree and site of substitution, with (I) and (*exo*-IV) at the extremes. The same degree of rate retardation observed with (*exo*-IV) as with the three other *endo*-derivatives provides strong evidence that bridging is absent in the transition state of the solvolysis of (*exo*-IV) and that the geometry at the top of the barrier approximates to that of a classical cation.

The result obtained with (*exo*-III) is highly interesting and requires a careful analysis.

In discussing the mechanism of anchimerically assisted reactions one has to consider a number of processes which do not necessarily occur simultaneously. In other words the energy profile of such a reaction involves a number of reaction co-ordinates. There are at least three different processes which in varying degrees contribute to the phenomenon described as neighbouring group participation: (i) ionization of the C–X bond and developing of the positive charge at the reaction centre, (ii) charge delocalization, and (iii) bridging, *i.e.* bond formation between the neighbouring group and the reaction centre.

If our results are analyzed in these terms one also has to take into account the strong conformational dependence of β-isotope effects.[3]

Thus, the absence of a significant effect with (I) indicates that all three processes most probably occur simultaneously. The significant amount of bridging coinciding with charge delocalization reduces almost completely an effective hyperconjugative σ C–D bond overlap with the reacting centre. The normal effect with (*exo*-IV) shows the absence of bridging and a well localized positive charge at tertiary C-2 in the transition state. With (*exo*-III) the effect is about half of its maximum value, suggesting that bridging does not coincide with the weakening of the C–X bond. The transition state for ionization is reached very early with, possibly, an already significant charge delocalization, while bridging has not as yet advanced sufficiently to cause complete elimination of the β-effect. This is further supported by an α-effect of normal magnitude observed in the acetolysis of [2-^{2}H]isobornyl toluene-*p*-sulphonate.[4]



k_H / k_D 1·23

In spite of the fact that we still do not know the exact relationship between bridging, charge delocalization, and the magnitude of the β-effect it appears that in the norbornyl system bridging is a more important factor for the diminution of the β-effect than mere charge delocalization. If this were not so, the β-effect in (*exo*-III) should be of about the same magnitude as with (I) or even smaller. The opposite view, *i.e.* that in the solvolysis of (I; X = Br) charge delocalization precedes bridging, has been argued.[2] We have strong reservations on this conclusion because it also fails to explain the observed effect with [6-^{2}H]-*exo*-norborn-2-yl *p*-bromobenzenesulphonates.[5]

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[1] J. M. Jerkunica, S. Borčić, and D. E. Sunko, *Chem. Comm.*, 1967, 1302.

[2] J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *J. Amer. Chem. Soc.*, 1967, **89**, 6938.

[3] (a) V. J. Shiner, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 2655; (b) V. J. Shiner, jun. and J. S. Humphrey, jun., *J. Amer. Chem. Soc.*, 1963, **85**, 2416.

[4] For a discussion of the α-effects see: R. Eliason, M. Tomić, S. Borčić, and D. E. Sunko, following Communication.

[5] (a) B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Werstiuk, *J. Amer. Chem. Soc.*, 1967, **89**, 1730; (b) J. M. Jerkunica, S. Borčić, and D. E. Sunko, *ibid.*, 1967, **89**, 1732.