n- and π-Participation and Secondary Deuterium Isotope Effects

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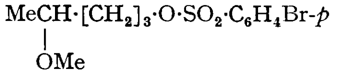
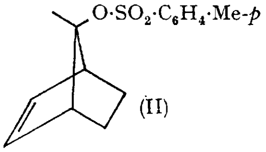
SOME years ago, Streitweiser[1] pointed out that the magnitude of secondary α-deuterium isotope effects could be used as a measure for changes in the geometry of the transition state. The discussion of this type of "steric hindrance effect" has been centred around the phenonium-ion problem with the underlying reasoning that "participation of a neighbouring group should also count as an entering group which should lower an α-deuterium isotope effect". Experimental evidence confirming this view is very scarce, and in 1965 we expressed doubts about the validity of this approach.[2] Systems showing undoubtedly enhanced solvolytic reactivities ascribed to neighbouring-group participation gave rise to α-effects of normal magnitude (*e.g.* [1-$^2H_2$]cyclopropylmethyl methanesulphonate,[3a] [1-$^2H_2$]cyclopropylmethyl chloride[3b]) while some other systems indicated a lowering of the α-effect to about 50% of its "normal" value.[4] All of the compounds investigated involved σ- and π-participating systems, which were, and to a certain extent still are, a subject of controversy. Unfortunately no data could be found for n-participating systems, where bond formation with the internal nucleophile in the transition state has never been challenged.

We report measurements on secondary α-deuterium isotope effects in unambiguous cases of n- and π-participation.

Compounds (I) and (II) were chosen as the most convenient models, and the results of kinetic measurements are presented in the Table.



$\underset{\text{OMe}}{\text{MeCH}}\cdot[CH_2]_3\cdot O\cdot SO_2\cdot C_6H_4Br\text{-}p$ (I)



(II)

The MeO-5 participation in solvolysis has been thoroughly investigated by Allred and Winstein.[5] For 4-methoxy-1-pentyl *p*-bromobenzenesulphonate they found that the ratio k_Δ/k_s which measures the competition between assisted and unassisted solvolysis is $1{\cdot}22 \times 10^{-4}$ for acetolysis and 106 for ethanolysis. Thus, in the latter case, only about 1% of (I) reacts by the unassisted route. The complete absence of an α-effect in the ethanolysis of (I) can be attributed to steric

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Secondary deuterium isotope effects for n- and π-participation

Compound	Solvent	$T°$	10^4k(sec.$^{-1}$)[a]	k_H/k_D[b]
(I)	96% EtOH	40	3·36 ± 0·05	1·01 ± 0·02
[1-$^2H_2$] (I)	96% EtOH	40	3·32 ± 0·03	
(II)	AcOH	30	8·67 ± 0·05	1·13 ± 0·02
[7-^{2}H](II)	AcOH	30	7·65 ± 0·10	

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

hindrance due to bond formation between the methoxy-oxygen atom and C-1. The geometry of the transition state in this case resembles the trigonal bipyramid encountered in direct displacement reactions, without a net change in the force field at the reacting centre.

In the case of n-participation, the electron pair required for the new bond formation is freely available, and no synchronous breakage of a σ- or π-bond has to take place. This is probably also one of the factors influencing the ease of approach of the neighbouring group and a consequently sterically crowded transition state.

The 7-*anti*-norbornyl toluene-*p*-sulphonate showed only a slightly reduced α-effect indicating the virtual absence of any steric hindrance at C-7 due to the participation of the double bond. In this rigid system the interaction apparently occurs at a greater distance so that changes in the bonding frequencies are not affected by the participating π-system. This is in full accord with the opinion[6] that in anchimerically assisted reactions ionization and charge delocalization do not necessarily occur simultaneously with the new bond formation. It appears that α-effects are less sensitive to changes in the geometry of the transition state than the β-effects. Extensions of this work to other systems are imperative before definite conclusions can be drawn regarding the usefulness of α-secondary isotope effects in the investigation of π and σ participation.

(*Received, July 22nd,* 1968; *Com.* 992.)

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