Some Unusual Deuterium Isotope Effects—β *versus* γ—on the Polarimetric Rate of Solvolysis of *threo*-1-Methyl-2-phenylpropyl Toluene-*p*-sulphonate†

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Summary Acetolysis, formolysis, and trifluoroacetolysis of (+)-*threo*-1-methyl-2-phenylpropyl toluene-*p*-sulphonate (I), and the deuteriated derivatives (II) and (III) gave isotope effects, k_I/k_{II} *versus* k_I/k_{III}, of 1·073 *versus* 1·065, 1·160 *versus* 1·015, and 1·170 *versus* 1·009, respectively, which are not satisfactorily interpreted in terms of either a non-classical symmetrical phenonium ion or two rapidly equilibrating classical carbonium ions.

THE polarimetric acetolysis, formolysis, and trifluoroacetolysis rate constants for (+)-*threo*-1-methyl-2-phenylpropyl toluene-*p*-sulphonate (I), and the deuteriated derivatives (II) and (III) have been measured by following the change in the optical rotation of their respective solutions placed in the thermostatted polarimeter tube of a photoelectric polarimeter (Table).

$H_3C^3{\cdot}C^2HPh{\cdot}C^1H(CH_3)OTs$ (I)

$H_3C{\cdot}CHPh{\cdot}CH(CD_3)OTs$ (II)

$D_3C{\cdot}CHPh{\cdot}CH(CH_3)OTs$ (III)

TABLE

Polarimetric rates and isotope effects (β and γ) in the solvolysis of threo-1-*methyl*-2-*phenylpropyl toluene*-p-*sulphonate*

Compound[a]	Solvent	Temp. (°c)	$k \times 10^2$ min.$^{-1}$ [b]	$(k_H/k_D)^c_{corr.}$
(I)	AcOH[d]	75·10	1·285 ± 0·008	
(II)			1·207 ± 0·008	1·073 ± 0·009
(III)			1·217 ± 0·008	1·065 ± 0·009
(I)	HCO_2H[e]	25·02	1·646 ± 0·011	
(II)			1·439 ± 0·009	1·160 ± 0·009
(III)			1·624 ± 0·003	1·015 ± 0·007
(I)	CF_3CO_2H[f]	−7·9°	2·299 ± 0·025	
(II)			1·992 ± 0·040	1·170 ± 0·026
(III)			2·281 ± 0·026	1·009 ± 0·019

[a] The deuterium content, determined by combustion, was 91% of the theoretical for (II), and 87% for (III).

[b] Each rate constant represents the average of four to six rate-constant determinations followed from about 14% to 80% reaction.

[c] $(k_H/k_D)_{corr}$ is the k_H/k_D observed corrected to 3·0 atoms of D. The uncertainties in $(k_H/k_D)_{corr}$ are based on those of k_H and k_D and are not adjusted for the uncertainty in the deuterium content.

[d] 0·17 M in NaOAc, 2% (W/V) in Ac_2O, 0·135M in the toluene-*p*-sulphonate.

[e] 0·10M in HCO_2Na, 0·077 M in the toluene-*p*-sulphonate.

[f] 0·10 M in CF_3CO_2Na, 1·4% (W/V) in $(CF_3CO)_2O$, 0·068 M in the toluene-*p*-sulphonate.

The non-classical carbonium ion school has argued that this system solvolyses *via* a phenonium ion intermediate,[1] whereas the classical carbonium ion school has presented a detailed model consisting of two rapidly equilibrating perfectly classical carbonium ions,[2] thus rendering the system a very controversial one.

The comparison of isotope effects for pairs of deuteriated derivatives such as the above should be one of the most subtle ways to check the importance of bridging in the rate-determining transition state and thus, perhaps, in the succeeding intermediate. Thus, according to the classical model, the isotope effects for (II) and (III) should resemble the usual β- and γ-isotope effects respectively; namely, 8—15% retardation per deuterium atom for the former[3] and possibly a very slight acceleration of about 1% for the latter,[4] although little can be said about γ-effects.‡ According to the non-classical model, the most reasonable behaviour would be a decrease in the magnitude of the β-effect,[3a,5] and an increase in that of the γ-effect due to charge delocalization into C-2.

The data of the Table have some significant features. The isotope effects for the two deuteriated species are similar in acetolysis, 7·3 as compared with 6·5%—a feature that suits the non-classical model—but differ greatly in the other solvents, 16 as against 1·5% in formolysis and 17 as compared with 1% in trifluoroacetolysis. The behaviour in the latter solvents agrees with the classical model or with a non-classical transition state that involves only limited bridging.

The difference of these isotope effects from the usual β- and γ-effects leads to the following conclusions: the small β-isotope effect, only 2% per deuterium atom, for the acetolysis of (II) is consonant with the non-classical model. The substantial γ-isotope effect in acetolysis, 6—7%, also agrees with the non-classical model. On the other hand, the very small, only 1—2%, γ-effect in the other solvents agrees better with the classical model.

In addition to the above features, one can also observe a considerable and unusual difference between the results in acetic acid and those in the other two solvents.§ All usual criteria for non-classical carbonium ion behaviour suggest, as generally interpeted,[6] that in formolysis and even more so in trifluoroacetolysis, as compared to acetolysis, there should be greater participation by the neighbouring group, *i.e.* increased non-classical behaviour. Our experimental results, however, suggest the opposite.

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‡ We are currently investigating β- and γ-isotope effects in suitable model systems.

§ The possibility that there might be an unusual temperature effect on these isotope effects or on the mechanism of the reaction is under investigation.

Looking at these isotope effects as a whole and taking them at face value one can argue that neither model, particularly the classical one, provides a satisfactory interpretation for them. An interpretation of these and other relevant results in terms of an alternative model suggested by one of us,[7] which requires the involvement of successive intermediates including fractionally bridged ones, will appear elsewhere.

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