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DEUTERIUM ISOTOPE EFFECTS IN THE FORMOLYSIS OF threo-1-METHYL-2-p-TOLYLPROPYL TOLUENE-p-SULPHONATE AND THE QUESTION OF NON-CLASSICAL CARBONIUM ION INTERMEDIATES[1]

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The polarimetric formolysis rate constants for (+)-threo-1-methyl-2-p-tolylpropyl toluene-p-sulphonate $H_3C^3{\cdot}C^2H(C_6H_4CH_3){\cdot}C^1H(CH_3)OTs$ (I), and the deuteriated derivatives $H_3C{\cdot}CH(C_6H_4CH_3){\cdot}CH(CD_3)OTs$ (II), $D_3C{\cdot}CH(C_6H_4CH_3){\cdot}CH(CH_3)OTs$ (III), and $H_3C{\cdot}CH(C_6H_4CD_3){\cdot}CH(CH_3)OTs$ (IV) have been measured at 15.00 °C by a method employed previously[3a] (Table).

TABLE

Polarimetric Rates and Isotope Effects in the Formolysis of threo-1-Methyl-2-p-tolylpropyl Toluene-p-sulphonate.[a,b]

Compound[c]	$k \times 10^2 min^{-1}$ [d]	$(k_H/k_D)^e_{corr.}$
I	2.417 ± 0.007	
II	2.067 ± 0.009	1.177 ± 0.005
III	2.407 ± 0.020	1.006 ± 0.012
IV	2.415 ± 0.020	1.001 ± 0.012

[a] The measurements were made at 15.00 °C.

[b] The solution was 0.061 molar in the ester, and 0.100 molar in HCO_2Na.

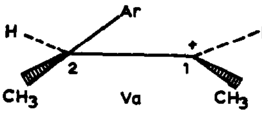
[c] The deuterium content, determined by combustion, was 96% of the theoretical for (II), 74.5% for (III), and 97% for (IV).

[d] Each rate constant represents the average of five to six rate-constant determinations followed from about 13% to 82% reaction.

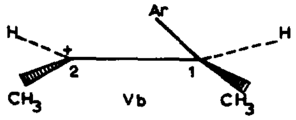
[e] $(k_H/k_D)_{corr.}$ is the k_H/k_D observed corrected to 3.0 atoms of D.

The solvolysis product was the racemic ester of retained configuration, (+)-threo-1-methyl-2-p-tolylpropyl formate — this conforms to the usual criteria for clean non-classical carbonium ion reactions[4] — containing less than 2% of olefinic products associated with the operation of competing reaction pathways.[4] Thus, the reported isotope effects give clearly information about the pathway said to be the non-classical one.

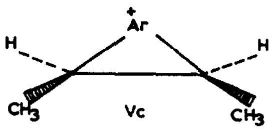
The most interesting feature of the reported isotope effects is the lack of an effect for derivative (IV) — it is only 1.001. This contrasts with an 11% retardation observed in the acetolysis (at 65 °C) of p-tolylmethylcarbinyl chloride on deuteration of the p-methyl group.[5a] These data argue against any substantial contribution by the aryl-electron-deficient structure (Vc) to a resonance hybrid (Va-Vb-Vc)[6] describing an aryl-bridged transition state in our system. This is so provided the usual assumption is made that the magnitude of such secondary isotope effects is a measure of such electron deficiencies.[5]



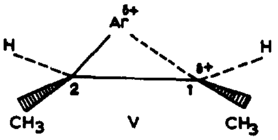
Va



Vb



Vc



V

This is a most significant supplement to the information provided by the essential lack of a retardation for (III) — it is 0.6% — and by its large difference from that for (II) which is 17.7% — a behaviour analogous to that in the 1-methyl-2-phenylpropyl system.[3a] This information is that structure (Vb) contributes little or nothing to the resonance hybrid in contrast to structure (Va). Even though this information suggests an unsymmetrical transition state, as concluded in the study of the 1-methyl-2-phenylpropyl system as well,[3a] it is nevertheless not sufficient evidence to argue for a transition state which deviates greatly in all respects from a symmetrical structure. This is so because formation of the Ar-C_1 bond along the reaction coordinate could possibly run ahead of any rupture of the C_2-Ar bond. This could result in a transition state (V)[6] which even though unsymmetrical, with respect to the relative contributions by structures (Vb) and (Va), could nevertheless enjoy a large contribution by (Vc), thus having progressed considerably toward a symmetrically aryl-bridged structure.

The possibility that the transition state could have the structure discussed in the previous paragraph is negated for the present system by the evidence for the lack of any significant contribution by structure (Vc), as discussed in the third paragraph of this communication.

The present results argue for a very unsymmetrical transition state and thus further support our arguments[3] against the "non-classical model" (direct formation of a single symmetrical intermediate). This is so because in order to render this model compatible with a very unsymmetrical transition state, one would have to accept that the transition state leading from the initial state to the symmetrical intermediate — in this quite endothermic process — would not resemble this intermediate in structure. This is contrary to the usual interpretation for such reactions.[7]

The above mentioned difficulty in interpreting the present and our earlier results[3a,b] in terms of the "non-classical model" is not encountered by our general solvolysis model[3] which, among other features, involves the formation of an unsymmetrical intermediate. An unsymmetrical transition state is certainly quite consistent with the unsymmetrical intermediate of this model. Furthermore, even if a step leading subsequently from this intermediate to a symmetrical one were involved and were rate determining,[3b] the transition state could still be unsymmetrical and deviate greatly from a symmetrical one. This follows from the fact that this transition state would be involved between two states of more or less similar energies — due to these states being both unstable intermediates — unlike the case of the "non-classical model" where the first is a stable initial state and the second is un unstable intermediate. Thus, this transition state could, in principle, resemble either one of them in structure, viz. either the unsymmetrical or the symmetrical one.

Our arguments in this and earlier publications[3] against the "non-classical model" are not affected by the renewed emphasis placed by Schleyer,[7b] Cram[8] and Winstein[9] on the competition between the anchimerically assisted path, k_Δ, and the anchimerically unassisted one, k_s. This emphasis has not modified the model which these authors strongly support and which remains the "non-classical model" (in the anchimerically assisted path). Both this and the "classical model" (rapidly equilibrating classical carbonium ions)[10] had been argued[3] to be inadequate as general models for such reactions.

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