Further Unusual Deuterium Isotope Effects—β *versus* α—on the Polarimetric Rate of Solvolysis of *threo*-1-Methyl-2-phenylpropyl Toluene-*p*-sulphonate and the Question of Non-classical Carbonium Ion Intermediates†

By SPYRO L LOUKAS, MARGARET R VELKOU, and GEORGE A GREGORIOU*

(*Chemistry Department, N R C "Democritos," Greek Atomic Energy Commission, Athens, Greece*)

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 1 104 *versus* 1 094, 1·142 *versus* 1 040, and 1 133 *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, but are claimed to be understandable in terms of a third model previously suggested by one of us

THE polarimetric acetolysis, formolysis, and trifluoroacetolysis rate constants for (+)-*threo*-1-methyl-2-phenylpropyl toluene-*p*-sulphonate H_3C^3 C^2HPh $C^1H(CH_3)OTs$ (I), and the deuteriated derivatives H_3C $CHPh$ $CD(CH_3)OTs$ (II) and H_3C $CDPh$ $CH(CH_3)OTs$ (III) have been measured by the method employed previously to obtain the isotope effects in the solvolysis of the deuteriated derivatives H_3C $CHPh$ - $CH(CD_3)OTs$ (IV) and D_3C $CHPh$ $CH(CH_3)OTs$ (V)[1] (Table)

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

Compound	Solvent[a]	Temp (°)	$(k_H/k_D)^b corr$
(II)	AcOH	75 10	1 104 ± 0 006
(III)			1 094 ± 0 012
(II)	HCO_2H	25 02	1 142 ± 0 010
(III)			1 040 ± 0 010
(II)	CF_3CO_2H	−7 9	1 133 ± 0 014
(III)			1 009 ± 0 015

[a] Compositions similar to those given in ref 1a

[b] Corrected to 1 0 atoms of D Based on rate constants obtained as the average of 2—5 rate constant determinations

These isotope effects provide further insight into the question of the structure of the intermediate—non-classical (direct formation of a single symmetrical intermediate),[2] classical (rapidly equilibrating classical carbonium ions),[3] or the general model suggested by us [1 4]

According to the classical model, the isotope effects for (II) and (III) should be fairly similar since they should resemble the usual α- and β-isotope effects respectively *i e* 12—15% retardation for the former[5a] and 8—15% for the latter [5b]

According to the non-classical model, the most reasonable behaviour should again result in similar isotope effects for (II) and (III) if the transition state involved does not deviate greatly from a symmetrical structure The magnitude of this effect for (II) should be reduced relative to the usual α-effects due to the participation by the neighbouring group [5]‡

The data of the Table indicate that the retardations for (II) and (III) are similar in acetolysis, 10 4 as compared to 9 4%—a feature that suits either model—although the slightly lower than usual α-isotope effect for the former may favour the non-classical model In conjunction with the acetolysis isotope effects for (IV) and (V), 1·073 and 1 065 respectively, and their interpretation,[1] the present acetolysis results argue in favour of the non-classical model

In formic and trifluoroacetic acid, the respective retardations for (II) are in the usual range of α-effects, being 14 2 and 13 3% The retardations for (III), however, differ considerably from those for (II), being 4 and 0 9% respectively in the two solvents These latter values correspond neither to a normal β effect[5b] nor to a normal α effect [5a] Thus, the behaviour in formic and, particularly, trifluoroacetic acid argues against the classical model It also militates against a non-classical transition state approaching a symmetrical structure Very limited bridging in the transition state could account for the isotope effects observed for (III), as the dihedral angle between the β-carbon–hydrogen bond axis and the carbon-leaving group axis would be unfavourable for orbital overlap [6]

A trend of the above mentioned features toward increasing non-classical carbonium ion behaviour is observed in going from trifluoroacetic to acetic acid, the difference being most pronounced in acetic acid § This trend is the reverse of that generally observed and justified [1]

The isotope effects observed for (II) and (III) are consistent with the interpretation given previously[1] for those of the derivatives (IV) and (V) This further enhances our long held position [1,4] that neither model [2,3] provides the answer to the classical *versus* non-classical carbonium ion controversy A satisfactory answer can be provided, as argued,[1,4] by an alternative general model, a very brief outline of which is as follows (i) The first-formed intermediate is not the "symmetrical" non-classical species but instead an "unsymmetrical" one, either classical or fractionally bridged, (ii) it is not a carbonium ion but involves extensive covalencies with the leaving group and with the incoming solvent, (iii) A symmetrical intermediate may be formed along the rearrangement path but not as a first intermediate, (iv) One of the various steps may be rate determining or the rates may be competitive, (v) Different products may be preferred from the different intermediates involved along the rearrangement and the substitution-reaction co-ordinates

Lack of recognition of (ii) and (iii) has been argued[4] to be among the basic flaws in the arguments of either school of thought on the classical *versus* the non-classical carbonium

---

† Part of a paper presented at the Symposium on Isotope Effects York July 1969

‡ The answer may not be as simple as that particularly if the suggested covalent bonding between the solvent and the rear of C α in the usual so called limiting solvolyses (ref 4) is accepted In this case participations by a neighbouring group would be taking the place otherwise held by solvent and would not alter drastically the picture at the rear of C-α

§ The significance of the acetolysis isotope effects could possibly be obscured by the complicated nature of the reaction (ref 2a) ion problem (*e.g.* windshield-wiper effect, weak rate accelerations,[3] or the direct formation of a symmetrical intermediate[2]), as well as in the conventional approach to reaction mechanisms in general.

We thank Professor G. J. Karabatsos for helpful discussions.

(*Received, December 23rd,* 1969; *Com.* 1937.)

---

[1] (a) S. L. Loukas, M. R. Velkou, and G. A. Gregoriou, *Chem. Comm.*, 1969, 1199; (b) Paper presented at the Conference on Carbonium Ions, Cleveland, Ohio, October 1968. A detailed discussion appeared in: (c) "The Concept of Non-Classical Carbonium Ions in the Light of the Unified Theory. II. Deuterium Isotope Effects—β *versus* γ—on the Polarimetric Rate of Solvolysis of *threo*-3-Phenyl-2-butyl tosylate," Greek Atomic Energy Commission, *DEMO*, 1969, **69**/4.

[2] (a) D. J. Cram, *J. Amer. Chem. Soc.*, 1949, **71**, 3863 and 3875; 1952, **74**, 2137; 1964, **86**, 3767; 1969, **91**, 1778; (b) P. von R. Schleyer and C. J. Lancelet, *ibid.*, 1969, **91**, 4297, (c) A. F. Diaz and S. Winstein, *ibid.*, 1969, **91**, 4300.

[3] (a) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, 1965, **87**, 2137; (b) C. J. Kim and H. C. Brown, *ibid.*, 1969, **91**, 4287 and 4289.

[4] (a) Ref. 7 in ref. 1a; (b) G. A. Gregoriou, "The Concept of Carbonium Ions in Solution in the Light of the Unified Theory," Greek Atomic Energy Commission, *DEMO*, 1963, **68**/2; *Atomindex*, 1969, **11**, No. 5, 1487; (c) G. A. Gregoriou, S. L. Loukas, and M. R. Velkou, "The Concept of Non-Classical Carbonium Ions in the Light of the Unified Theory. III. Deuterium Isotope Effects—α, β and γ—as possible Probes of the Structure of the Intermediate System in the Solvolysis of 3-Phenyl-2-butyl Tosylate," Greek Atomic Energy Commission, *DEMO*, 1969, **69**/5.

[5] (a) A. Streitwieser, jun., "Solvolytic Displacement Reactions," McGraw-Hill, New York, 1962, pp. 172—175; (b) ref. 3 in ref. 1a.

[6] V. J. Shiner, jun. and J. S. Humphrey, *J. Amer. Chem. Soc.*, 1963, **85**, 2413; W. H. Saunders, jun., and R. Glaser, *ibid.*, 1960, **82**, 3586.

Printed by W Heffer & Sons Ltd Cambridge England