Secondary Kinetic Deuterium Isotope Effects in Vinyl Cations

By ROBERT J. HARGROVE, THOMAS E. DUEBER, and PETER J. STANG*
(*Department of Chemistry, University of Utah, Salt Lake City, Utah* 84112)

Summary The β-deuterium isotope effect in the solvolysis of β-styryl trifluoromethanesulphonate (1), $k_H/k_D = 1{\cdot}42$, is much larger than in normal carbonium ions.

ALTHOUGH secondary deuterium isotope effects have been extensively employed in solvolysis rate studies of carbonium ions[1] they have not been examined in the generation of vinyl cations despite a growing interest in such species.[2] We report the secondary β-deuterium isotope effect in a vinyl cation, generated by solvolysis from β-styryl trifluoromethanesulphonate.

Addition of trifluoromethanesulphonic acid to phenylacetylene according to the method of Stang and Summerville[3] afforded, upon distillation, β-styryl trifluoromethanesulphonate (1a) (35—65%), b.p. 44—45° (0·3 mm Hg), n.m.r. (CCl_4) δ 5·30 (d, *J* 3·8 Hz, 1H), 5·46 (d, *J* 3·8 Hz, 1H), and 7·30 (m, 5H). The same product was obtained from acetophenone according to the method of Dueber *et al.*[4] The deuteriated analogue (1b) was prepared in a similar manner from trideuterioacetophenone.† The rates and products of solvolyses of vinyl trifluoromethanesulphonate (1) are summarized in Tables 1 and 2, respectively.

As seen from Table 1, the secondary β-deuterium isotope effect in the solvolysis of β-styryl trifluoromethanesulphonate to a vinyl cation is $k_H/k(\beta\text{-}D_2) = 1{\cdot}42 \pm 0{\cdot}03$ at 25·0°. However, before the significance of the isotope effect can be discussed two alternative mechanisms; addition—elimination,[5] and concerted elimination,[3,6] must be ruled out.

The addition–elimination sequence is ruled out by the

---

† Trideuterioacetophenone was obtained from acetophenone by repeated exchange with D_2O in the presence of catalytic amounts of NaOD. N.m.r. analysis of compound (1b) indicated 98 ± 3% deuteriation.

following considerations: (1) the observation of some phenylacetylene as product; (2) the mild solvolysis conditions in near neutral media, since addition–elimination requires more acidic conditions[5,7] and or much higher temperatures; and finally (3) it is rendered improbable by the fact that the observed solvent isotope effects for carbon protonation are generally significantly larger[8] $k_{80H}/k_{80D} = 1{\cdot}2$—$3{\cdot}1$, than found in this study; $k_{80H}/k_{80D} = 1{\cdot}04 \pm 0{\cdot}05$.

TABLE 1. *Rates of reactions of vinyl trifluoromethanesulphonates* (1a) *and* (1b)

Compd.	Temp	Solvent	k, (s^{-1})	ΔH, kcal/mole	ΔS e.u.
(1a)	25·0°	80% EtOH	$(1{\cdot}12 \pm 0{\cdot}006) \times 10^{-4}$	22·4	−1·5
(1a)	50·0°	80% EtOH	$(2{\cdot}26 \pm 0{\cdot}044) \times 10^{-3}$		
(1a)	50·0°	80% EtOD, 20% D_2O	$(2{\cdot}18 \pm 0{\cdot}055) \times 10^{-3}$		
(1b)	25·0°	80% EtOH	$(7{\cdot}92 \pm 0{\cdot}037) \times 10^{-5}$	22·3	−2·3
(1b)	50·0°	80% EtOH	$(1{\cdot}59 \pm 0{\cdot}048) \times 10^{-3}$		
(1b)	50·0°	70% EtOH	$(3{\cdot}46 \pm 0{\cdot}11) \times 10^{-3}$		

Concerted elimination, with the solvent acting as base[3,6] is ruled out by the product studies and in particular the inveriance of products in the presence of added bases. As the data in Table 2 indicate the products are, within experimental error, identical in the presence and absence of added base such as Et_3N and even a strong base such as NaOH. Whereas, if concerted elimination were important the amount of phenylacetylene should be greatly increased in the presence of base. The small difference in products, in the presence and absence of base, in aqueous ethanol are undoubtedly due to media effects on the product-determining step.

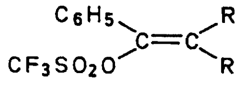
The observed solvent m value, $m = 0{\cdot}57$, is consistent with a vinyl cation intermediate and in good accord with solvent effects observed in other systems involving disubstituted carbonium ions.[3,9]

It is instructive to compare the β-deuterium isotope effect observed in the generation of a vinyl cation with that observed in the generation of the analogous saturated (trisubstituted) carbonium ion. The β-deuterium isotope effect observed by Shiner and his co-workers[1e] in the solvolysis of 1-phenylethyl bromide in 80% ethanol at 25° was $k_H/k(\beta\text{-}D_3) = 1{\cdot}220$ or an average change in free energy of activation per deuterium of $\Delta\Delta F^{\ddagger} \simeq 40$ cal/mole. Clearly the effect of β-deuterium substitution is much larger in the generation of a vinyl cation ($\Delta\Delta F^{\ddagger} \simeq 100$ cal/mole) than in the generation of a carbonium ion.

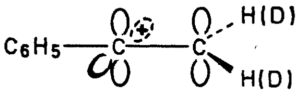
Two reasons may be offered for the enhanced β-deuterium isotope effect in vinyl cations as compared with carbonium ions. (i) As pointed out by Noyce and Schiavelli[8a] in the transition state of a vinyl cation the isotopically substituted C–H bond is ideally suited for overlap with the developing, vacant p-orbital, as shown in structure (2). This hypothesis is in good agreement with the work of Shiner and his co-workers[10] who have demonstrated that the magnitude of the β-deuterium isotope effect is strongly dependent upon the dihedral angle. (ii) In a vinyl cation the C–C bond distance is that of a C(sp)–C(sp^2) and the β-C–H distance that of a C(sp^2)–H, as compared with C(sp^2)–C(sp^3) and C(sp^3)–H in a normal carbonium ion, hence shorter and closer to the developing vacant p-orbital.

TABLE 2. *Products of solvolyses of β-styryl trifluoromethanesulphonate* (1a) *at* 50·0°

Solvent	%$C_6H_5C{\equiv}CH$	%$C_6H_5COCH_3$
80% EtOH	$35{\cdot}1 \pm 0{\cdot}4$	$64{\cdot}8 \pm 0{\cdot}4$
80% EtOH + 1 equiv. Et_3N	$38{\cdot}2 \pm 0{\cdot}4$	$61{\cdot}8 \pm 0{\cdot}4$
70% CH_3COCH_3	$33{\cdot}1 \pm 0{\cdot}2$	$67{\cdot}0 \pm 0{\cdot}2$
70% CH_3COCH_3 + 2 equiv. Et_3N	$34{\cdot}0 \pm 0{\cdot}3$	$66{\cdot}2 \pm 0{\cdot}3$
70% CH_3COCH_3 + 1·5 equiv. NaOH	$33{\cdot}0 \pm 0{\cdot}4$	$67{\cdot}1 \pm 0{\cdot}4$



(1a) R = H
(1b) R = D



(2)

Financial support by the Petroleum Research Fund administered by the American Chemical Society, the Research Corporation, and the University of Utah Research Committee are gratefully acknowledged.

We are indebted to Dr. R. L. Hansen of the Minnesota Mining and Manufacturing Co. for samples of trifluoromethanesulphonic acid. We also thank Professor W. M. Jones for a preprint of related[9] work prior to publication.

(*Received, October 5th,* 1970; *Com.* 1703.)

---

[1] (a) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, 1960; (b) F. W. Westheimer, *Chem. Rev.*, 1961, **61**, 265; (c) A. Streitwieser, jun., "Solvolytic Displacement Reactions," McGraw-Hill, New York, 1962; (d) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1963, **1**, 109; (e) V. J. Shiner, jun., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 1968, **90**, 418.

[2] For a review, see M. Hanack, *Accounts Chem. Res.*, 1970, **3**, 209.

[3] P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, 1969, **91**, 4600.

[4] T. E. Dueber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. Imhoff, P. von R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *Angew. Chem.*, 1970, **82**, 517.

[5] P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, 1968, **90**, 6515; W. M. Schubert and G. W. Barfknecht, *ibid.*, 1970, **92**, 207; Z. Rappoport, T. Bassler, and M. Hanack, *ibid.*, p. 4985.

[6] P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, 1969, **91**, 6194.

[7] D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, 1968, **90**, 1020.

[8] (a) D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, 1968, **90**, 1023; (b) D. S. Noyce and R. M. Pollack, *ibid.*, 1969, **91**, 120; (c) V. Gold and M. A. Kessick, *J. Chem. Soc.*, 1965, 6718.

[9] Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, 1969, **91**, 5246; M. D. Schiavelli, S. C. Hixon, and H. W. Moran, *ibid.*, 1970, **92**, 1082; W. M. Jones and D. D. Maness, *ibid.*, p. 5457.

[10] V. J. Shiner, jun., B. L. Murr, and G. Henemann, *J. Amer. Chem. Soc.*, 1963, **85**, 2413; V. J. Shiner, jun., and J. S. Humphrey, jun., *ibid.*, p. 2416; V. J. Shiner, jun., and J. G. Jewett, *ibid.*, 1964, **86**, 945.