observed by Modena and coworkers[25] in the solvolysis of various β-arylthiovinylsulfonates.

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[25] *Inter alia:* G. Modena, *et al., Chem. Commun.*, 1363, 1676 (1968); *Tetrahedron Lett.*, 4039 (1968); *J. Chem. Soc. C*, 2617, 2621, 2625 (1970); *J. Chem. Soc. B*, 374, 381, 1569, 1700 (1971); *Chem. Commun.*, 1520 (1969); 1325 (1971); *J. Chem. Soc., Chem. Commun.*, 8 (1972).

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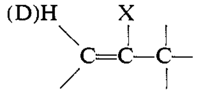
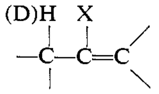
Secondary Kinetic Deuterium Isotope Effects in the Solvolysis of Vinyl Triflates. Further Evidence for a Vinylidene Phenonium Ion[1]

Sir:

Deuterium isotope effects have been extensively employed in organic mechanistic studies,[2] particularly in the area of solvolytic displacement reactions. Similar to the deuterium isotope effects observed in normal carbonium ions, there may be several kinds of secondary deuterium isotope effects, α and β, in the solvolytic generation of vinyl cations. Observation of an α-deuterium isotope effect in a vinyl cation would require the formation of a highly energetic "primary" vinyl cation that has so far not been possible. On the other hand β-deuterium isotope effects should be readily observable. Indeed, in vinyl cations, there may be two different kinds of β-deuterium isotope effects: one where the isotopic substitution is β to the leaving group on an unsaturated carbon **1a**, and one where it is β but on an adjacent saturated carbon as in **1b**.[3] A number of examples of the former have recently been reported,[4,5] but to date no examples of the latter have been observed. In this communication we wish to report a β-deuterium isotope effect of the second kind as well as the first example of a kinetic γ-deuterium isotope effect in a vinyl cation.

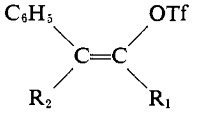


1a

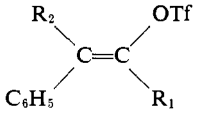


1b

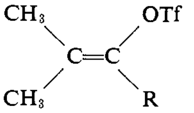
The systems investigated are the *cis-* and *trans*-3-phenyl-2-buten-2-yl triflates **2** and **3** and the 3-methyl-2-buten-2-yl triflate **4**. Substrates **2** and **3** were prepared and isolated as described in the preceding communication,[1a] and **4** was prepared in a similar manner from 3-methyl-2-butanone. Rates were measured in 60% aqueous ethanol buffered with pyridine and are averages of three–six determinations. The results are summarized in Table I.



2a, $R_1 = R_2 = CH_3$
b, $R_1 = CD_3$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = CD_3$



3a, $R_1 = R_2 = CH_3$
b, $R_1 = CD_3$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = CD_3$



4a, $R = CH_3$
b, $R = CD_3$

Table I. Rates and Isotope Effects in the Solvolysis of Vinyl Triflates **2**, **3**, and **4**

Compd	Temp, °C	k, sec^{-1} [a]	k_H/k_D [b]
2a	99.81	$(9.30 \pm 0.24) \times 10^{-5}$	
2b	99.81	$(6.35 \pm 0.09) \times 10^{-5}$	1.47 ± 0.06
2c	99.81	$(1.03 \pm 0.02) \times 10^{-4}$	0.90 ± 0.04
3a	99.86	$(1.58 \pm 0.01) \times 10^{-3}$	
3b	99.86	$(1.37 \pm 0.01) \times 10^{-3}$	1.16 ± 0.02
3c	99.86	$(1.52 \pm 0.02) \times 10^{-3}$	1.04 ± 0.02
4a	74.96	$(1.30 \pm 0.02) \times 10^{-4}$	
4b	74.96	$(9.12 \pm 0.04) \times 10^{-5}$	1.46 ± 0.04 [c]

[a] Determined conductometrically, 0.6 µl/10 ml. [b] Uncorrected for small amounts of residual H's (4–9%) and for the scrambling observed in the trans substrates.[1] [c] Corrected for 8% H.

Two salient features emerge from the data in Table I. The β-deuterium isotope effect (α-CD$_3$ group) in the cis isomer **2b** is very much larger, $k_H/k_D = 1.47$, than for the corresponding trans isomer **3b** with $k_H/k_D = 1.16$. Control experiments[6] indicate that this difference is real and that the higher value in the case of the cis isomer is not due to a contribution from a primary isotope effect due to allene formation in the rate-determining step. The larger magnitude of k_H/k_D in **2b** is consistent with the cis isomer **2** ionizing to an essentially open linear vinyl cation, or ion pair,[1a] **5a**, and a greater charge concentration in the α position of the cis isomer in the transition state leading to **5a**. In contrast, there is considerable charge delocalization into the phenyl ring (with a concomitant reduction in the α position) and hence a lower isotope effect in the trans isomer **3** due to bridging in **5b**. Secondly, in the cis isomer **2c** the γ-deuterium isotope effect (β-CD$_3$ group) is inverse. Since deuterium is known to be electron donating relative to hydrogen, γ-deuterium isotope effects in normal trisubstituted carbonium ions are inverse[2] although

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[1] (a) Paper VIII in a series on the preparation and solvolysis of vinyl triflates. Paper VII: P. J. Stang and T. E. Dueber, *J. Amer. Chem. Soc.*, **95**, 2683 (1973). (b) Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972.

[2] For reviews see: C. J. Collins and N. S. Bowman, Ed., "Isotope Effects in Chemical Reactions," Van Nostrand Reinhold Co., New York, N. Y., 1970; P. Laszlo and Z. Welvart, *Bull. Soc. Chim. Fr.*, 2412 (1966); E. R. Thornton, *Annu. Rev. Phys. Chem.*, **17**, 349 (1966); E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963); A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; F. W. Westheimer, *Chem. Rev.*, **61**, 265 (1961); L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960; K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

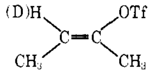
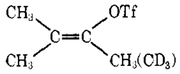
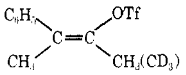
[3] (a) This distinction may be extended to γ- as well as δ-deuterium isotope effects as in (D)HCC=C(X)C– and >C=C(X)CCH(D). (b) In the former case, *i.e.*, **1a**, a further distinction can be made on the basis of stereochemistry, depending on whether the deuterium is cis or trans to the leaving group.

[4] (a) D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, **90**, 1023 (1968); (b) P. J. Stang and R. Summerville, *ibid.*, **91**, 4600 (1969); (c) W. M. Jones and D. D. Maness, *ibid.*, **92**, 5457 (1970); (d) R. J. Hargrove, T. E. Dueber, and P. J. Stang, *Chem. Commun.*, 1614 (1970).

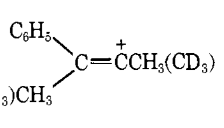
[5] P. J. Stang, *Progr. Phys. Org. Chem.*, **10**, 276 (1973).

[6] Vinyl triflate **2a** was found to be stable, with no trace of allene formation, in decane and in THF in the presence of pyridine or triethylamine at 100 and 130°, making the incursion of an E2 elimination along with the rate-determining formation of the intermediate vinyl cation unlikely.

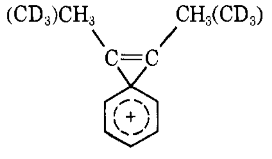
Table II. Summary of β-Deuterium Kinetic Isotope Effects in Vinyl Cations

Substrate	Reactn condn	k_H/k_D	$\Delta\Delta F^{\ddagger a}$	Ref
	60% EtOH, 75°	1.23	143	4b
	60% EtOH, 75°	1.46	87	This work
	60% EtOH, 100°	1.47	95	This work

[a] Average reduction in free energy of activation per deuterium in calories/mole.



5a



5b

usually of considerably smaller magnitude than observed for vinyl cations in this study. Presumably the π system in a vinyl cation transmits the electronic effects more efficiently than a saturated C–C bond in a normal carbonium ion. Hence, such an inverse γ-isotope effect is once again consistent with ionization to an open vinyl cation **5a** for the cis isomer **2**. On the other hand, in the trans isomer **3** the γ-deuterium isotope effect, although small, is positive indicating some charge delocalization into the β carbon in the transition state leading to the intermediate bridged ion **5b**. The fact that the β- and γ-isotope effects in **3** are not equal indicates that the transition state leading to the intermediate ion **5b** occurs early in the reaction coordinate diagram and must be unsymmetrical. In that case the experimentally observed k_H/k_D of 1.04 for **3c** must be a combination of a β and γ effect operating in opposite directions.[4a] Assuming that the γ effect in **3c** would be the same as the observed γ effect of 0.90 in **2c**, one can calculate[4a] a β-secondary isotope effect of 1.15 (1.04/0.90) for **3c** which is within experimental error identical with the observed β effect of 1.16 for **3b**. The unequal isotope effects and the postulated unsymmetrical transition state in the vinylidene phenonium ion are consistent with similar observations in the analogous saturated phenonium ions.[7]

Finally, the available data allow a comparison between secondary kinetic deuterium isotope effects observed in vinyl cations resulting from solvolysis of vinyl substrates of type **1a** and **1b**. The relevant data are shown in Table II. If it is assumed that the *cis*-2-buten-2-yl triflates as well as the 2-methyl-2-buten-2-yl and *cis*-3-phenyl-2-buten-2-yl triflates go to a similar open linear vinyl cation, $RCH_3C{=}C^+CH_3$, then the average reduction in free energy of activation per deuterium ($\Delta\Delta F^{\ddagger}$) is about 50–60% higher for a β-isotopic substitution on the double bond, such as in **1a**, than for β-isotopic substitution on an adjacent saturated β carbon such as **1b**. This observation is in accord with Shiner's hypothesis[8] that the magnitude of β-deuterium isotope effect is strongly dependent upon the dihedral angle between the empty p orbital and the β C–H bond. In the vinyl cation, resulting from **1a**, the β hydrogens on the double bond are rigidly held in the same plane as the empty p orbital allowing for greater hyperconjugative overlap than in the ion resulting from **1b**. Furthermore, overlap is probably better across the shorter C=C double bond in **1a** than across the C—C single bond in **1b**.

Acknowledgment. We thank Mr. R. J. Hargrove for some computer assistance in the calculation of rate data. Financial support by the University of Utah Research Committee, the Research Corporation, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(7) W. H. Saunders, Jr., S. Asperger, and D. H. Edison, *J. Amer. Chem. Soc.*, **80**, 2421 (1958); S. L. Loukas, M. R. Velkou, and G. A. Gregoriou, *Chem. Commun.*, 1199 (1969); S. L. Loukas, F. S. Varveri, M. R. Velkou, and G. A. Gregoriou, *Tetrahedron Lett.*, 1803 (1971).

(8) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Amer. Chem. Soc.*, **85**, 2413 (1963); V. J. Shiner, Jr., and J. S. Humphrey, Jr., *ibid.*, **85**, 2416 (1963); V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **86**, 945 (1964).

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A Reactive New d^8 Metal Center for Oxidative Addition Reactions

Sir:

Herein we report oxidative addition[1] reactions of $Rh(DO)(DOH)pn^2$ (**1a**) and its BF_2 derivative **1b**. The structure and reactivity patterns of **1a,b** are strikingly similar to those of anionic "supernucleophilic" cobalt(I) and rhodium(I) complexes with dinegative tetradentate ligands.[3] The novel features of **1a,b** are the highest reactivity yet reported for an isolated, neutral d^8 complex, the steric constraints afforded by the DOH ligand, and competing chemistry of the oxime bridge.

Coordinatively unsaturated **1a** forms deep blue 1:1 phosphine (Ph_3P, PEt_3) complexes similar to Co(DO)-

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(1) (a) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, 7, 54 (1968); (b) J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970).

(2) The synthesis of **1a** is similar to that described for **1b** using basic ethanol as a reducing agent. The molecular structure depicted for **1a** has been confirmed by a complete X-ray crystallographic study. The only surprising feature of this structure is that the intracrystalline arrangement does not afford linear chains of Rh atoms. The closest Rh–Rh distance is 6.7 Å: J. P. Collman, E. B. Fleischer, D. Y. Jester, and D. W. Murphy, unpublished results.

(3) G. N. Schrauzer and E. Deutsch, *J. Amer. Chem. Soc.*, **91**, 3341 (1969).