

CCA-361

541.124:547.322:546.11.02  
Original Scientific Paper

## Secondary Hydrogen Isotope Effects. VII. Ethanolysis Rates of 1,1-Dimethylallyl-3,3- $d_2$ Chloride and 3,3-Dimethylallyl-1,1- $d_2$ Chloride

V. Belanić-Lipovac, S. Borčić, and D. E. Sunko

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

Received November 27, 1964

Primary and tertiary dimethylallyl chlorides deuterated at either the alpha or gamma position were prepared and subjected to ethanolysis. A kinetic isotope effect ( $k_H/k_D$ ) of 1.20 was observed in the reaction of the primary isomer while the tertiary chloride reacted at the same rate as the undeuterated analog. The absence of an isotope effect in the latter case is explained by the lack of  $sp^3-sp^2$  rehybridization of the carbon-deuterium bonds in the rate determining step.

Compounds having deuterium in the alpha position to the leaving group display in solvolytic reactions a rate retarding kinetic isotope effect of about 10–20 per cent per atom of deuterium<sup>1</sup>. This effect has been ascribed to vibrational changes in the carbon-deuterium bonds occurring during the  $sp^3-sp^2$  rehybridization process. The bending motions of the  $sp^3$  hybridized C—H bond are somewhat hindered by the presence of atoms or groups attached to the respective carbon atom and occur at higher frequencies than the out of the plane vibrations in the trigonal carbon atom. The result of this change in coordination number in going to the trigonal transition state is therefore a loss of energy from the C—H bond with a consequent reduction in zero-point energy differences between the deuterated and undeuterated compounds. Using the carbon-hydrogen bending frequency in an aldehyde group as a model for the carbonium ion a maximum isotope effect of 1.35 was calculated<sup>2</sup>.

According to this »rehybridization theory« the secondary alpha deuterium isotope effect is essentially of stereochemical origin and should be unaffected by the development of a positive charge at the reaction center\*. Therefore, if a carbon-deuterium bond is sterically unaltered in a solvolysis reaction no kinetic isotope effect should result even if a considerable amount of positive charge is displaced to that carbon atom.

The negligible isotope effect observed by Shiner *et al.*<sup>3</sup> in the solvolysis of III is consistent with the above argument.

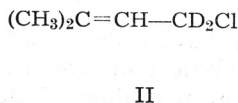
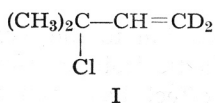
\* Recent, as yet unpublished results from this laboratory, demonstrated the occurrence of a secondary effect of the normal magnitude during the  $sp^3-sp^2$  rehybridization in the Cope rearrangement.



However, the interpretation of this result is not unambiguous because of difficulties in estimating the amount of positive charge displaced to the deuterated carbon atom in the rate determining step of the solvolysis of III (it solvolyzes slightly slower than the corresponding saturated derivative).

On the other hand, 1,1-dimethylallyl chloride solvolyzes  $10^3$  to  $10^5$  times faster than the saturated analog and the solvolysis of the primary 3,3-dimethylallyl chloride is only a few times slower than that of the tertiary isomer. In ethanolysis both compounds give very similar product mixtures consisting of 30 to 40 per cent of the primary ether and 60 to 70 per cent of the tertiary ether<sup>4</sup>. Also, in aqueous ethanol, an internal rearrangement of the tertiary to the primary halide has been observed.

From these data it was concluded that both compounds solvolyze to yield very similar carbonium ion intermediates in which a considerable amount of positive charge resides on the allylic carbon atom. Therefore, in our opinion, the determination of solvolysis rate constants of deuterated dimethylallyl chlorides I and II might better illustrate the electronic influence on secondary alpha deuterium isotope effects.



#### RESULTS

3,3-Dimethylallyl-1,1- $d_2$  alcohol (IV) was prepared by lithium aluminum deuteride reduction of  $\gamma,\gamma$ -dimethylacrylic acid. The reaction of the alcohol with gaseous hydrogen chloride<sup>5</sup> afforded a mixture consisting of 24 per cent of the tertiary chloride (I) and 76 per cent of the primary chloride (II). From this mixture the primary isomer could be obtained through successive v.p.c. separation. The tertiary isomer could not be successfully isolated from this mixture and was, therefore, prepared in a different manner. The reaction of IV with thionyl chloride in di-*n*-butyl ether according to the procedure of Young *et al.*<sup>6</sup> yielded the tertiary chloride I in addition to about 10 per cent of the primary isomer. The composition of the product mixture, as determined by v.p.c. analysis, was checked by infrared spectroscopy (characteristic frequencies, I, 928 and 1115  $\text{cm}^{-1}$ , II, 1252 and 1685  $\text{cm}^{-1}$ ).

Chlorides I and II and their undeuterated analogs were subjected to ethanolysis at various temperatures. The reaction rates were followed by automatic titration of the liberated acid by means of a pH-stat and the rate constant calculated from the titration curves. The rate of the primary isomer was followed up to 80 per cent completion. For the tertiary isomer, only the first 30% of the reaction were taken into account and the calculated rate constant corrected by the method of Brown and Fletcher<sup>7</sup> in order to minimize the error introduced by the presence of a small amount of the slower reacting primary isomer in the starting material. In the calculation

of the average rate constant and uncertainty limits, every individual rate constant calculated from 20 — 30 points on the titration curve, was taken as one measurement. The results, given in Table I and II represent the average of 3- 10 measurements with different samples.

TABLE I  
*Solvolysis Rates of 3,3-Dimethylallyl Chloride and 3,3-Dimethylallyl-1,1-d<sub>2</sub> Chloride in Absolute Ethanol*

t °C	k <sub>H</sub> 10 <sup>5</sup> sec <sup>-1</sup> <sup>a</sup>	k <sub>D</sub> 10 <sup>5</sup> sec <sup>-1</sup> <sup>a</sup>	k <sub>H</sub> /k <sub>D</sub>
35.0	3.05 ± 0.01	2.55 ± 0.05	1.196
44.6	9.02 ± 0.04	7.50 ± 0.02	1.203
54.2	22.60 ± 0.02	18.90 ± 0.01	1.196

$$\Delta H^\ddagger = 21.0 \text{ kcal/mole}^b$$

$$\Delta S^\ddagger = +9.4 \text{ e.u.}^b$$

TABLE II  
*Solvolysis Rates of 1,1-Dimethylallyl Chloride and 1,1-Dimethylallyl-3,3-d<sub>2</sub> Chloride in Absolute Ethanol*

t °C	k <sub>H</sub> 10 <sup>5</sup> sec <sup>-1</sup> <sup>a</sup>	k <sub>D</sub> 10 <sup>5</sup> sec <sup>-1</sup> <sup>a</sup>
24.7	0.218 ± 0.04	
34.6	7.04 ± 0.047	7.08 ± 0.042
44.6	18.28 ± 0.044	18.25 ± 0.032

$$\Delta H^\ddagger = 20.2 \text{ kcal/mole}^b$$

$$\Delta S^\ddagger = +8.9 \text{ e.u.}^b$$

<sup>a</sup> Uncertainties are standard errors.

<sup>b</sup> The calculated standard deviation is 2% of the value.

#### DISCUSSION

From the introductory remarks it is clear that the results obtained are those predicted somewhat naively, on grounds of Streitwieser's »rehybridization theory«. In solvolysis of II, the carbon-deuterium bond changes hybridization and therefore the usual rate retardation is observed. In solvolysis of I, however, the carbon-deuterium bonding orbitals are already *sp*<sup>2</sup> hybridized in the ground state and consequently no isotope effect is observed, although, with respect to the positive charge, the transition state resembles that of an  $\alpha$ -deuterated compound.

Moreover, the C—D bonding orbitals in the latter compound are orthogonal to the  $\pi$ -system in the allyl ion-like transition state. Therefore the usual rate retardation due to lower hyperconjugative electron release of the C—D bond is not observable.

Nevertheless, the lack of any rate effect through  $\gamma$ -deuteration in I is somewhat surprising. From several considerations an inverse isotope effect might have been expected

Firstly, electron withdrawing substituents increase the CH out-of-plane bending frequency in ethylene. On these grounds the electron demand on the double bond in solvolysis of I as expressed by stabilization of the transition state through allylic resonance, should presumably result in stiffening of the C—D bonds and consequently, in rate acceleration.<sup>8</sup>

More important, an inverse isotope effect could be expected because of the larger inductive electron releasing power of deuterium. These inductive deuterium isotope effects have indeed been observed in thermodynamic equilibria and some other reactions<sup>9</sup>. In solvolyses, the importance of the latter factor is less clear. The suggestion has been made that inductive interactions may be responsible for the observation of smaller than calculated  $\alpha$ -deuterium rate effects. A very small rate enhancement ( $1.5\% \pm 1.0\%$ ) has been observed in solvolysis of a bridgehead  $\beta$ -deuterated compound where the hyperconjugative interaction between the isotopic bond and the developing empty  $p$ -orbitals is inhibited<sup>9c</sup>. However, it has been argued by Halevi<sup>10</sup> that this small enhancement is not a fair measure for the importance of the inductive effect as this should, on theoretical grounds, decrease in the order primary > secondary > tertiary deuterium atom.

Small rate accelerations have been observed in solvolyses of  $\gamma$ -deuterated cyclopentyl<sup>11</sup> and cyclopropylcarbinyl<sup>12</sup> sulfonate esters. It has been suggested that there the isotope effect may be inductive in origin. However, enhancements of similar magnitude have also been observed in  $S_N2$  type solvolysis of  $\gamma$ -deuterated  $n$ -propyl bromide<sup>13</sup> where the larger +I effect of deuterium should not have any influence on rate. Therefore, the isotope effects in the former case may also be due to some other cause. This conclusion is also supported by the fact that no rate enhancement was found in solvolysis of III.

#### EXPERIMENTAL

##### 3,3-Dimethylallyl-1,1- $d_2$ Alcohol

$\gamma,\gamma$ -Dimethylacrylic acid (2.1 g., 0.021 mole) in dry ether (10 ml.) was added dropwise to a stirred slurry (0.97 g., 0.023 mole) of lithium aluminum deuteride (Metal Hydrides, Inc.) in ether (250 ml.). The reaction mixture was kept at 0 to 5° during the addition. After stirring for 30 minutes, 10 ml. of water was added with cooling. After working up, the dried ether solution was concentrated by distillation through a Vigreux column, and the product purified by distillation *in vacuo*. Yield 1.3 g. (74%), b.p. 48–52°/22 mm.

##### 3,3-Dimethylallyl-1,1- $d_2$ Chloride

Gaseous dry hydrogen chloride was bubbled at 0° through 1.1 g. of 3,3-dimethylallyl-1,1- $d_2$  alcohol until 0.46 g. was absorbed. The separated water was removed immediately, and the organic layer neutralized with solid anhydrous potassium carbonate. The product consisting of an about 3 to 1 mixture of primary and tertiary chlorides was purified by preparative vapor phase chromatography on an Aerograph A-700 fractometer using a 20 ft. 3/8" silicone column operated between 70 and 115°. Relative retention times and purity were determined by comparison with pure samples of unlabeled chlorides.

##### 1,1-Dimethylallyl-3,3- $d_2$ Chloride

A solution of 3,3-dimethylallyl-1,1- $d_2$  alcohol (1.1 g.) in dry di- $n$ -butyl ether (5 ml.) was slowly added to a stirred mixture of thionyl chloride (1.52 g.) in di- $n$ -butyl ether (20 ml.) which was kept at -10°. The reaction mixture was stirred for one additional hour at 0°. Dry potassium carbonate was cautiously added to neutralize the excess of acid and the solution filtered. The chloride, obtained from the butyl ether solution was purified by repeated distillation on a high vacuum line and contained, as shown by v.p.c. analysis about 10 per cent of the primary isomer.

##### Kinetic Measurements

The solvolysis in absolute ethanol was followed at different temperatures by potentiometric titration of the liberated acid using an automatic recording pH-stat

(Radiometer, Copenhagen, Type TTT-1). Approximately 12 ml. of solvent and 50 mg. samples were used for each determination. The drift in the rate constant observed in the ethanolsis of the tertiary halide became more pronounced if 96 per cent ethanol was used instead of absolute ethanol.

## REFERENCES

1. A. Streitwieser, Jr. *Solvolytic Displacement Reactions*, Mc Graw-Hill Book Co., Inc. New York 1962 p. 172—175 and references therein.
2. A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.* **80** (1958) 2326.
3. V. J. Shiner, Jr., J. W. Wilson, G. Heinemann, and N. Solliday, *J. Am. Chem. Soc.* **84** (1962) 2408.
4. P. B. D. DeLaMare and C. A. Vernon, *J. Chem. Soc.* **1954**, 2504.
5. I. N. Nazarov and I. N. Azerbaev, *Zhur. Obshechi Khim.* **18** (1948) 407.
6. W. G. Young, F. R. Caserio, and D. D. Brandon, *J. Am. Chem. Soc.* **82** (1960) 6163.
7. H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.* **71** (1949) 1845.
8. P. Torkington, *Proc. Roy. Soc.* **206** (1951) 17.
9. a) cf. E. A. Halevi, »Secondary Isotope Effects« in Cohen, Streitwieser, Jr. and Taft, Editors, *Progress in Physical Organic Chemistry*, Vol. 1 (1963), Interscience Publishers New York;  
 b) E. A. Halevi, *Tetrahedron* **1** (1957) 174;  
 c) V. J. Shiner, Jr., *J. Am. Chem. Soc.* **82** (1960) 2655;  
 d) A. J. Kresge and K. N. Rao, *Chemistry and Industry* **1961**, 55;  
 e) H. S. Klein and A. Streitwieser, Jr., *ibid.* **1961**, 180.
10. Ref. 9a, p. 200.
11. S. Borčić, *Croat. Chem. Acta* **35** (1963) 67.
12. S. Borčić, M. Nikoletić, and D. E. Sunko, *J. Am. Chem. Soc.* **84** (1962) 1615.
13. K. T. Leffek, J. A. Lewellyn, and R. E. Robertson, *J. Am. Chem. Soc.* **82** (1960) 6315

## IZVOD

**Sekundarni hidrogenski izotopski efekti. VII. Brzina etanolize  
1,1-dimetilalil-3,3- $d_2$  klorida i 3,3-dimetilalil-1,1- $d_2$  klorida**

V. Belanić-Lipovac, S. Borčić i D. E. Sunko

Pripremljeni su primarni i tercijarni dimetilalil kloridi deuterirani u alfa, odnosno gama položaju i mjerene su njihove brzine etanolize u odnosu na nedeuterirane spojeve. Primarni izomer solvolizirao je za 20% sporije dok kod reakcije tercijarnog izomera nije primijećen nikakav izotopni efekt. Ovi rezultati ukazuju da je alfa deuterijski sekundarni efekt stereokemijskog karaktera i da elektronski faktori u slučaju pomanjkanja  $sp^3$ — $sp^2$  rehibridizacije nemaju utjecaja na reaktivnost.

INSTITUT »RUDER BOŠKOVIĆ«  
ZAGREB

Primljeno 27. studenoga 1964.