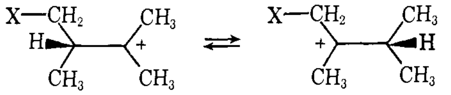
A New Method for Measuring Equilibrium Deuterium Isotope Effects. Isomerization of 3-Deuterio-2,3-dimethylbutyl-2-ium Ion

Sir:

Kinetic deuterium isotope effects are widely used for studying reactions, particularly those involving carbonium ions.[1] Isotope effects measured in solvolysis kinetics are related to energy differences between starting materials and transition states and give no *direct* information about the cations. We wish to report a new and accurate method for the measurement by nmr of *equilibrium* deuterium isotope effects in cations and other systems undergoing rapid degenerate rearrangements. The dimethylisopropylcarbonium ion[2] undergoes a rapid degenerate hydride shift leading to the equilibrium $I_H \rightleftarrows II_H$ where I_H and II_H are identical ($I_H/II_H = 1$). In SbF_5–SO_2ClF its nmr spectrum displays a *single* doublet at τ 7.07 ppm for the six protons of the methyl groups attached to C^+ averaged with the six protons of the methyl groups of the isopropyl group. Substitution by deuterium of one hydrogen of a methyl group yields *different* ions I_D and II_D. If the γ-deuterium isotope effect on the stability of the carbonium ion in I_D is different from the β-deuterium isotope effect in II_D, a ratio $I_D/II_D \neq 1$ is expected; consequently *two* doublets should be observed for the methyl groups in the nmr spectrum of $I_D \rightleftarrows II_D$.



I_H, X = H $\quad$ II_H

I_D, X = D $\quad$ II_D

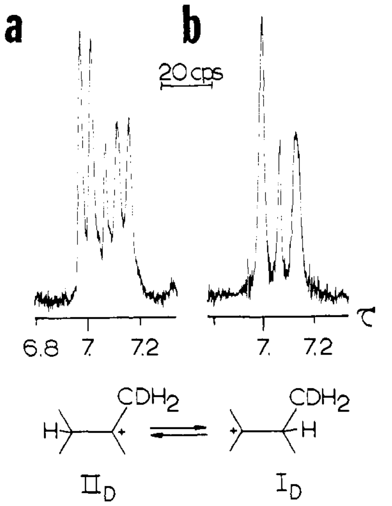


Figure 1. Nmr spectrum of $I_D \rightleftarrows II_D$ and A in SbF_5–SO_2ClF at −56°.

The 3-deuterio-2,3-dimethylbutyl-2-ium ion (A) was prepared by distilling *in vacuo* 2-chloro-2,3-dimethylbutane-*3-d* (prepared by DCl addition to the dimethylbutene) into a solution of SbF_5 in SO_2ClF cooled at −100°. The nmr spectrum[3] of A is a single peak (unresolved deuterium coupling) at τ 7.07 ppm. The rearrangement[2] of A into deuteriodimethylpropyl (B) and deuteriodiethylmethyl (C) carbonium ions was followed by nmr at −40°. Besides the expected peaks for B and C[2] two new doublets attributed to $I_D \rightleftarrows II_D$ appeared in the region of τ 7 surrounding the single peak of A (see Figure 1a). The lower field doublet is due to the averaging of the six protons of the methyls attached to C^+ of I_D with the six protons of the methyls attached to the methylene group of II_D; the higher field doublet is due to the averaging of the five protons of the methyls attached to CH of I_D with the five protons of the methyls on C^+ of II_D. The six-proton doublet being located at lower field than the five-proton doublet shows that the carbonium ion prefers to be substituted by unlabeled methyl group, as in I_D; β-deuterium destabilizes the cationic center more than γ-deuterium. By irradiating the methylene proton of $I_D \rightleftarrows II_D$ at τ 5.4 ppm decoupling was obtained simultaneously for the two doublets as shown in Figure 1b. The ratio I_D/II_D is obtained from the nmr spectrum using the relation $K = I_D/II_D = (\Delta\omega + D)/(\Delta\omega - D)$ where $\Delta\omega$ is the chemical-shift difference between the different methyl groups in a "frozen" equilibrium $I_D \rightleftarrows II_D$, and D is the chemical-shift difference between the two observed doublets (see Figure 1a).

The hydride shift that interconverts I_D and II_D is very fast even at low temperature;[2,4] thus $\Delta\omega$ cannot be measured. However a good approximation to it is obtained from the observed chemical-shift difference in *tert*-amyl cation.[5] Using $\Delta\omega = 210$ Hz and $D = 13 \pm 0.5$ Hz[6] measured at $-56 \pm 2°$, $K = 1.132 \pm 0.007$ is calculated. The temperature dependence[8] of K was easily measured in our case: the observed D value is temperature dependent. Between −92 and −44° an enthalpy difference $H_{II_D} - H_{I_D} = 54 \pm 3$ cal/mol was found using a simple exponential expression for the temperature dependence. Our $H_{II_D} - H_{I_D}$ value is strikingly similar to the values obtained ($\Delta\Delta F^{\ddagger}$ per deuterium atom = 55–59 cal/mol) for the β secondary deuterium isotope effect on reaction rate in the solvolysis of *tert*-butyl chloride[9] and other alkyl systems going through classical carbonium ion intermediates.[10] Our value also agrees with theoretically calculated values for ionization–equilibrium isotope effect in *tert*-butyl and

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(1) (a) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963); G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964); J. W. Timberlake, J. A. Thompson, and R. W. Taft, *ibid.*, **93**, 274 (1971); (b) P. Laszlo and Z. Welvart, *Bull. Soc. Chim. Fr.*, 2412 (1966).

(2) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 4739 (1967); G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Brides, *ibid.*, **93**, 459 (1971); D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 210 (1968); D. M. Brouwer and J. A. van Doorn, *ibid.*, **89**, 88 (1970).

(3) Spectra were taken with a Varian HA 100 spectrometer; external TMS was used as lock signal and reference.

(4) H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **88**, 1305 (1969).

(5) M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, **90**, 6882 (1968).

(6) The relatively large error estimated for D considers the deuterium shift on protons of the CH_2–D group[1b,7] enlarging the high-field peak (see Figures 1a and 1b).

(7) M. Saunders, J. Plostnieks, P. S. Wharton, and H. H. Wasserman, *J. Chem. Phys.*, **32**, 317 (1960); E. O. Bishop, *Annu. Rept. Progr. Chem.*, **58**, 70 (1961).

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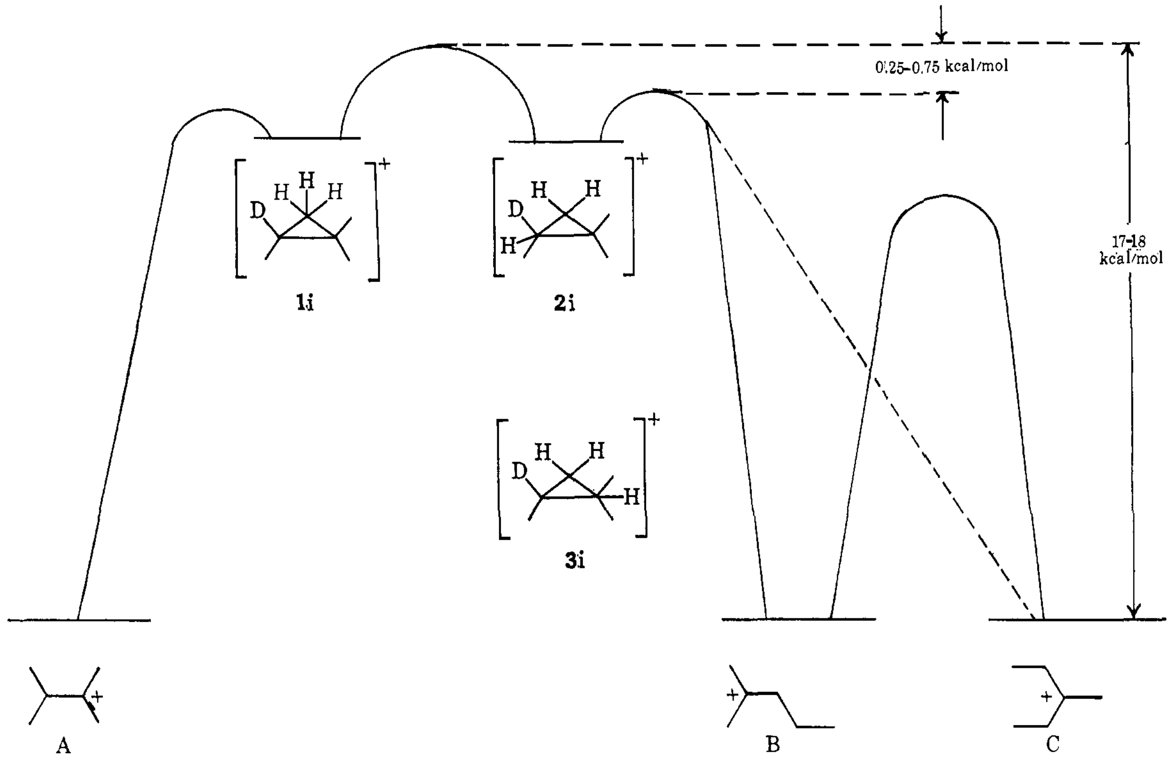
(9) G. J. Frisone and E. R. Thornton, *J. Amer. Chem. Soc.*, **90**, 1211 (1968); K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *Can. J. Chem.*, **38**, 2171 (1960).

(10) M. Nikoletik, S. Borcic, and D. E. Sunko, *Tetrahedron*, **23**, 649 (1967); K. L. Servis, S. Borcic, and D. E. Sunko, *ibid.*, **24**, 1247 (1968).

Scheme I



tert-butyl-d_9 chlorides[11] and for equilibruim β-deuterium isotope effect in cations.[12] The agreement is improved by assuming a small γ-deuterium isotope effect on the cationic center as reported for several solvolysis experiments.[13]

The kinetics of the rearrangement of 3-deuterio-2,3-dimethyl-butyl-2-ium ion (A) gave new information about the energy surface involving the three *tert*-hexyl ions A, B, and C.[2,4] It is postulated[14] that the reaction A $\rightleftarrows$ B and C proceeds through a corner- or edge-protonated cyclopropane intermediate in which protons migrate from corner to corner yielding the transition states or intermediates **1i**, **2i**, and **3i** (see Scheme I). Strong evidence for the involvement of similar intermediates is gathered from *tert*-amyl,[16] methylcyclopentyl,[17] *sec*-butyl,[5] isopropyl, and *tert*-butyl[18] cations.

At −40° we found the rate of rearrangement of A into B and C to be three–ten times faster than the rate of deuterium–hydrogen scrambling in A yielding $I_D \rightleftarrows II_D$. Therefore the energy barrier for the process **2i** (or **3i**) $\rightleftarrows$ **1i** $\rightleftarrows$ A is 0.25–0.75 kcal/mol higher than the energy barrier for the ring opening of **2i** (or **3i**) giving B and C.

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(14) The energy barrier (~15 kcal/mol) for the methide migration interconverting ions B and C is lower than that of the rearrangement of A into B and C.[15]

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(18) E. L. Hagen, Ph.D. Thesis, Yale University, 1969.

(19) Fellow of the Alfred P. Sloan Foundation.

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Equilibrium Deuterium Isotope Effects in Systems Undergoing Rapid Rearrangements. Dimethyl-*tert*-butylcarbonium Ion and Cyclopentyl Cation

Sir:

In previous communications[1,2] we have shown that deuterium substitution in molecules undergoing rapid degenerate rearrangements can lift the degeneracy giving rise to nonstatistical equilibrium constants between the isomers and leading to additional splitting in the spectra. This occurs when the processes occurring *do not* rapidly mix all equivalent groups. If a group of hydrogens and deuteriums was *completely* scrambled by a rapid process (*i.e.*, all possible isomers rapidly achieved), then each proton would experience *the same* average environment and therefore all protons would have an identical chemical shift and yield only a single averaged peak. However, in spite of the fact that no additional splitting is expected, deuterium–hydrogen isotope effects can disturb the statistical probability of protons residing in the chemically different environments and thus produce a net chemical shift. In order to observe such a shift accurately, it is desirable to include, in the same sample, some of the undeuterated

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(1) M. Saunders, M. H. Jaffe, and P. Vogel, *J. Amer. Chem. Soc.*, **93**, 2558 (1971).

(2) M. Saunders and P. Vogel, *ibid.*, **93**, 2561 (1971).