Tetrahedron, 1959, Vol. 5, pp. 116-117. Pergamon Press Ltd. Printed in Great Britain.

SECONDARY HYDROGEN ISOTOPE EFFECT IN A GAS-PHASE EQUILIBRIUM*

PETER LOVE, ROBERT W. TAFT, JR. and THOMAS WARTIK

College of Chemistry and Physics, Pennsylvania State University

THE following is a preliminary report of a study of the secondary isotope effect on a gas-phase equilibrium.

The substitution of β deuterium for hydrogen atoms in reactions in which the transition states possess considerable carbonium ion character leads to a reduction in the reaction rate.[1,2] Considerable evidence indicates that this isotope effect is associated with hyperconjugation stabilization of the carbonium ion-like transition states.†

Since the proposed relation between hyperconjugation and the secondary isotope effect has been investigated only for reaction rates in solution, an important test of the scope of the theory is provided by an investigation of the secondary isotope effect on the position of equilibrium in an appropriate gas phase reaction.

In carrying out such an investigation we have selected as a model for a hyperconjugated system the Lewis acid, $B(CH_3)_3$. An appropriate equilibrium is the Lewis acid–base reaction of the class investigated so extensively by H. C. Brown and his students:[3]

$$B(CH_3)_{3(g)} + :N(CH_3)_{3(g)} \rightleftharpoons (CH_3)_3B:N(CH_3)_{3(g)} \qquad (1)$$

According to hyperconjugation theory,[4] hyperconjugation stabilization of $B(CH_3)_3$ is expected to be appreciably greater than that for the addition compound, $(CH_3)_3B:N(CH_3)_3$, since the open orbital on boron in the former compound is involved in bond formation with nitrogen in the latter. Consequently, the theory of the secondary isotope effect anticipates that substitution of the β-hydrogen atoms of $B(CH_3)_3$ by deuterium (which is expected to reduce hyperconjugation preferentially in the reactant molecule of the above reaction) should shift the equilibrium (1) towards the addition compound. In other words the equilibrium constant for the following reaction (designated as K_D/K_H) should be greater than unity:

$$B(CD_3)_{3(g)} + (CH_3)_3B:N(CH_3)_{3(g)} \rightleftharpoons B(CH_3)_{3(g)} + (CD_3)_3B:N(CH_3)_{3(g)} \qquad (2)$$

---

* This work was supported in part by the office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

† For reviews of this subject see papers of E. S. Lewis on page 143 and V. J. Shiner, Jr., elsewhere in this volume.

[1] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **75**, 2925 (1953); *Ibid.* **76**, 1603 (1954).

[2] E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.* **76**, 791 (1954).

[3] H. C. Brown, D. H. McDaniel and O. Häfliger, *Determination of Organic Structures by Physical Methods* (Edited by E. A. Braude and F. C. Nachod) pp. 634–643. Academic Press, New York (1955).

[4] R. A. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941); J. W. Baker, *Hyperconjugation*. Oxford University Press (1952); C. A. Coulson and V. A. Crawford, *J. Chem. Soc.* 2052 (1953); Y. I'Haya, *J. Chem. Phys.* **23**, 1165, 1171 (1955); M. M. Kreevoy and H. Eyring, *J. Amer. Chem. Soc.* **79**, 5121 (1957).

Using a slightly modified procedure described by Brown *et al.*,[3,5] we have determined the equilibrium constants for reaction (1) over the temperature interval 65–95° with both $B(CH_3)_3$ and $B(CD_3)_3$, the sample of the latter compound containing no more than one per cent hydrogen. The values obtained for the former compound are in satisfactory agreement with those reported by Brown *et al.*[5] and those obtained with the latter compound give $K_D/K_H = 1{\cdot}25 \pm 0{\cdot}03$.

These results are thus in accord with the prediction of the hyperconjugation theory of the secondary isotope effect. Whatever the cause of the favorable formation of the *heavy* addition compound, $(CD_3)_3B{:}N(CH_3)_3$, the effect is actually larger than is apparent in the above value of K_D/K_H. The mass effect contribution of the translational entropy change to the equilibrium constant of reaction (2) is:

$$\left[\frac{M_{B(CH_3)_3}M_{(CD_3)_3BN(CH_3)_3}}{M_{B(CD_3)_3}M_{(CH_3)_3BN(CH_3)_3}}\right]^{3/2} = 0{\cdot}89$$

That is, the mass effect on the translational entropy favors the *light* addition compound by 11 per cent. It is probable that the mass effect on the rotational entropy change also favors the *light* addition compound, though by not as large a factor. The proposed greater inductive electron-releasing ability of deuterium than hydrogen,[6] if significant, would also favor the *light* addition compound. Thus there is an effect (or effects) favoring the *heavy* addition compound by at least 36 per cent in the equilibrium constant (or $>$ 200 cal/mole in $-\Delta F°$). We hope to be able to identify these effects upon completion of an examination of the spectra of the compounds involved in reaction (2).

---

[5] H. C. Brown, H. Bartholomay, Jr. and M. D. Taylor, *J. Amer. Chem. Soc.* **66**, 435 (1944).

[6] E. A. Halevi and M. Nussim, *Bull. Res. Council Israel* A5, 263 (1956); *Ibid.* **6**, 167 (1957); E. A. Halevi, *Tetrahedron* **1**, 174 (1957); G. V. D. Tiers, *J. Amer. Chem. Soc.* **79**, 5585 (1957).