BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (4), 984—986 (1979)

The H/D Isotope Effect in the Reaction of Hydrogen Atoms with Olefins

Yo-ichi ISHIKAWA and Shin SATO*

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received August 14, 1978)

The absolute rate constants of reaction of deuterium atoms with seven simple olefins at room temperature have been measured by using the pulse-radiolysis technique. The comparison with the rate constants of reaction of hydrogen atoms previously obtained shows that the ratios of k(D+olefin)/k(H+olefin) are in the range of 0.7—0.8. This isotope effect is theoretically discussed.

The H/D isotope effect has widely been used for the elucidation of the reaction mechanism of a complex reaction;[1)] however, reliable absolute rate constants which can be utilized for the analysis of the isotope effect in an elementary reaction are not abundant. In 1975, Mihelcic *et al.* measured the absolute rate constants of the reactions between H or D atoms and C_2H_4, C_2D_4, or C_3H_6 and discussed the kinetic isotope effects.[2)]

In a previous paper,[3)] we obtained the absolute rate constants of reaction of hydrogen atoms with seven simple olefins by using a pulse-radiolysis technique and found that the relative rate constants obtained are in good agreement with those reported as reliable values in the literature. Since the method we used can easily be extended to the reactions of deuterium atoms, we have attempted to measure the absolute rate constants of reaction of deuterium atoms with the same seven olefins and to discuss the H/D isotope effect.

Experimental

The technique used in this study consists of that of pulse radiolysis coupled with the time resolved detection of the resonance absorption of deuterium atoms. The apparatus and procedure used are similar to those previously described for the reaction of hydrogen atoms,[3)] except for the detection system. A photomultiplier tube for the vacuum ultraviolet region (Hamamatsu TV Co., R976) was mounted for the detection of Lyman-α line of D atoms. The signal/noise ratio was improved to about 20. The photomultiplier output was amplified by an operational amplifier (Harris HA-2625) and monitored by a Tektronix 475 oscilloscope.

The deuterium gas, whose nominal purity was 99.5% (Showa Denko Co.), was used after having been passed through a molecular sieve 4A at the temperature of liquid nitrogen. The research grade olefins supplied by the Takachiho Shoji Co. were used after thorough degassing.

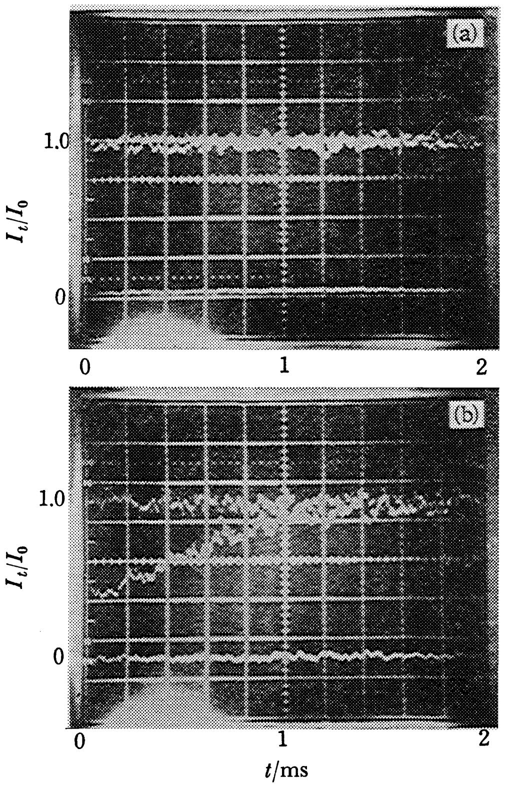

Fig. 1. a) The pulse-irradiated H_2 gas at 500 Torr was detected by the Lyman-α of D atoms. No absorption can be observed. b) Under the same condition of the lamp, the D_2 gas at 500 Torr containing 74 mTorr trans-2-butene was pulse-irradiated.

In order to ascertain the separation of Lyman-α's of H and D atoms, 500 Torr H_2 gas was pulse-irradiated and the absorption of the product at the wavelength of Lyman-α was pursued

TABLE 1. THE ABSOLUTE RATE CONSTANTS OF REACTION OF HYDROGEN AND DEUTERIUM ATOMS WITH SIMPLE OLEFINS AT ROOM TEMPERATURE

Olefin	Mihelcic *et al.*[2)]		k_D/k_H	Present authors		k_D/k_H
	k_H	k_D		k_H[3)]	k_D	
	10^{-12} cm^3 molecule^{-1} s^{-1}			10^{-12} cm^3 molecule^{-1} s^{-1}		
Ethylene	1.25±0.03	0.87±0.03	0.70	1.1±0.1	0.8±0.1	0.73
Ethylene-d_4	1.15±0.03	0.85±0.03	0.74			
Propylene	1.68±0.05	1.14±0.02	0.68	1.7±0.1	1.3±0.2	0.76
1-Butene				2.0±0.5	1.6±0.1	0.80
trans-2-Butene				1.1±0.1	0.8±0.1	0.73
cis-2-Butene				1.0±0.1	0.8±0.1	0.80
2-Methylpropene				5.2±0.6	3.8±0.3	0.73
2-Methyl-2-butene				2.4±0.3	2.0±0.3	0.83

by using a lamp in which D_2 gas was made to flow. As Fig. 1a shows, pratically no absorption could be observed. On the other hand, when the reactant was replaced by D_2 gas under the same condition of the lamp, a strong absorption could be observed. Figure 1b shows the decay of deuterium atoms obtained with 500 Torr D_2 and 74 mTorr *trans*-2-butene.

Results

Figure 2 shows the decay rates of deuterium atoms as functions of the concentration of olefins. From the slopes of the linear relations, the rate constants of reaction of deuterium atoms with olefins can be calculated. The results are summarized in Table 1, together with the rate constants previously obtained for hydrogen atoms and with the results obtained by Mihelcic *et al.*[2] All of the ratios $k(\text{D}+\text{olefin})/k(\text{H}+\text{olefin})$ are in the range of 0.7—0.8. The experimental errors prevent us from determining whether the ratios are dependent upon the kind of olefins.

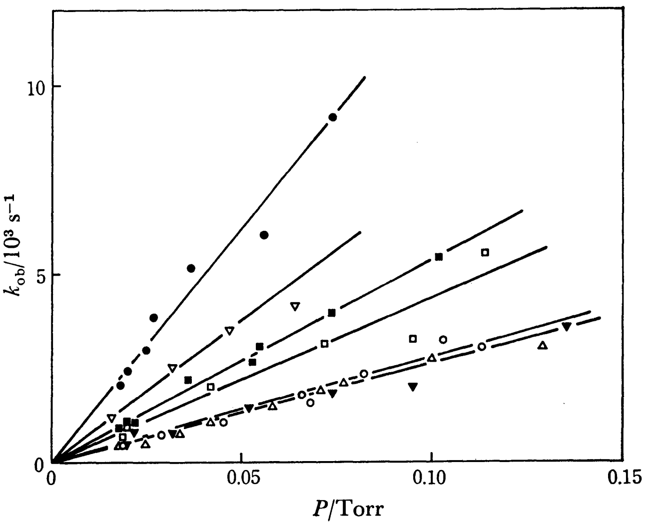

Fig. 2. Plots of the decay rates of D atoms against the olefin pressures. The deuterium pressure is around 500 Torr. ○: Ethylene, □: propylene, ■: 1-butene, △: *trans*-2-butene, ▼: *cis*-2-butene, ●: 2-methylpropene, ▽: 2-methyl-2-butene.

Discussion

Correlations between the Rate Constants and the Reaction Index Calculated by the Semi-empirical MO Method for Olefins. When Jennings and Cvetanović measured the relative rate constants of reaction of hydrogen atoms with several olefins,[4] they correlated their data with the reaction index calculated by the simple Hückel method including hyperconjugation and found a linear relationship between the logarithm of the relative rate constants and the atom localization energies of olefins.[5] Since symmetric olefins such as ethylene and *cis*- and *trans*-2-butenes have two reactive sites for the addition reaction of a hydrogen atom, the rate constants might have to be divided by two when such a correlation is examined; however, the division by two does not lead to the linear relationship.

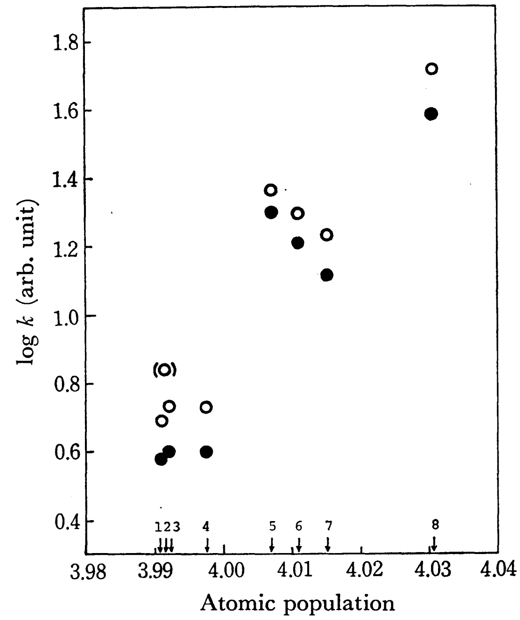

Fig. 3. The logarithm of the rate constants against the atomic populations calculated by the INDO method. 1: *cis*-2-Butene, 2: 2,3-dimethyl-2-butene (estimated from the data in Ref. 4), 3: *trans*-2-butene, 4: ethylene, 5: 2-methyl-2-butene, 6: 1-butene, 7: propylene, 8: 2-methylpropene. ○: For hydrogen atoms and ●: for deuterium atoms.

Recently Koda *et al.* showed a linear relationship between the logarithm of the relative rate constants of reaction of hydrogen atoms with simple olefins and the atomic population on the less substituted of the doubly bonded carbon atoms calculated by the CNDO/2 method.[6] In this case, they divided the relative rate constants for symmetric olefins by two. In their plots, however, 2-methyl-2-butene was not included. We, therefore, have calculated the atomic populations using the INDO method. As Fig. 3 shows, we could not find a linear relationship between the logarithm of the rate constants we obtained and the atomic population calculated.

A Simple Interpretation of the H/D Kinetic Isotope Effect. According to the recent *ab initio* calculation using STO 3G basis set for the reaction path of the addition of a hydrogen atom to ethylene, a hydrogen atom approaches one of the doubly bonded carbon atom perpendicularly to the plane of the ethylene molecule and there is no energy barrier on the reaction path.[7]

In the present experiment, however, we have found that $k(\text{H}+\text{2-methylpropene})/k(\text{H}+\text{ethylene})=4.7$ at room temperature. This large ratio cannot easily be explained by the difference in the preexponential factor of the Arrhenius equation. Moreover, recent measurements suggest that the apparent activation energy for the reaction between hydrogen atoms and ethylene is in the range of 1—3 kcal mol^{-1}.[8—10]

In the present treatment, we tentatively assume that there is a small energy barrier, E_0, on the reaction path for the approach of a hydrogen atom to ethylene and also that this type of addition reaction may be treated as a bimolecular association between an atom (H or D) and a radical (A). Then the activated complex theory predicts the rate constant of reaction between H and A as follows:[11)]

$$k_{\mathrm{H}} = \kappa\frac{kT}{h}\frac{\dfrac{[2\pi(m_{\mathrm{H}}+m_{\mathrm{A}})kT]^{3/2}}{h^3}}{\dfrac{(2\pi m_{\mathrm{H}}kT)^{3/2}}{h^3}\;\dfrac{(2\pi m_{\mathrm{A}}kT)^{3/2}}{h^3}}\frac{8\pi^2 I_{\mathrm{HA}}kT}{\sigma h^2}e^{-E_0/RT} \quad (1)$$

Here, m_{H} and m_{A} stand for the atomic weight of hydrogen and the molecular weight of ethylene, respectively, and I_{HA} for the moment of inertia of the activated complex. Using this equation, we can easily calculate the isotope effect for $k_{\mathrm{D}}/k_{\mathrm{H}}$.

$$\begin{aligned}\frac{k_{\mathrm{D}}}{k_{\mathrm{H}}} &= \left[\frac{m_{\mathrm{H}}}{m_{\mathrm{D}}}\right]^{3/2}\left[\frac{m_{\mathrm{D}}+m_{\mathrm{A}}}{m_{\mathrm{H}}+m_{\mathrm{A}}}\right]^{3/2}\left[\frac{I_{\mathrm{DA}}}{I_{\mathrm{HA}}}\right] \\ &= \left[\frac{m_{\mathrm{H}}}{m_{\mathrm{D}}}\,\frac{m_{\mathrm{D}}+m_{\mathrm{A}}}{m_{\mathrm{H}}+m_{\mathrm{A}}}\right]^{1/2} \\ &= 0.72 \qquad (2)\end{aligned}$$

Almost the same value can be obtained for $k_{\mathrm{D}}/k_{\mathrm{H}}$ for other olefins. As Table 1 shows, all of the values of $k_{\mathrm{D}}/k_{\mathrm{H}}$ obtained in these experiments are a little larger than the calculated one. This is probably due to the simplification made for the calculation. However, in order to make a more detailed analysis, we have to wait for the detailed calculation of the potential energy surface.

The authors wish to express their thanks to Dr. Kazuo Shimokoshi of this Institute for the use of the program of INDO calculation.

References

1) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York (1960).

2) D. Mihelcic, V. Schubert, F. Hölfer, and P. Potzinger, *Ber. Bunsen Phys. Chem.*, **79**, 1230 (1975).

3) Y. Ishikawa, M. Yamabe, A. Noda, and S. Sato, *Bull. Chem. Soc. Jpn.*, **51**, 2488 (1978).

4) K. R. Jennings and R. J. Cvetanović, *J. Chem. Phys.*, **35**, 1233 (1961).

5) S. Sato and R. J. Cvetanović, *J. Am. Chem. Soc.*, **81**, 3223 (1959).

6) S. Koda, K. Nakamura, T. Hoshino, and T. Hikita, *Bull. Chem. Soc. Jpn.*, **51**, 957 (1978).

7) C. S. Sloane and W. L. Hase, *Faraday Discuss. Chem. Soc.*, **62**, 210 (1977).

8) J. H. Knox and D. G. Dalgleish, *Int. J. Chem. Kinet.*, **1**, 69 (1969).

9) R. D. Penzhorn and B. deB. Darwent, *J. Chem. Phys.*, **55**, 1508 (1971).

10) J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, *J. Chem. Phys.*, **68**, 1817 (1978).

11) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co. Inc., New York (1941).