Bull. Chem. Soc. Jpn., **55**, 3720—3723 (1982) [Vol. 55, No. 12

Kinetic Isotope Effects in the H+ $C_3H_6 \rightarrow C_3H_7$ Reaction

Toshifumi Watanabe, Takeshi Kyogoku, Shigeru Tsunashima,
Shin Sato,*,† and Shigeru Nagase††
Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152
†*Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152*
††*Chemistry Division, Faculty of Education, Yokohama National University, Hodogaya-ku, Yokohama 240*
(Received April 27, 1982)

The absolute rate constants of the addition of H and D atoms to propylene-d_0 and -d_6 have been measured by means of the pulse radiolysis-resonance absorption technique over the temperature range of 200—500 K. The rate constants obtained were well expressed by these Arrhenius equations: $k(\mathrm{H}+\mathrm{C_3H_6})=(3.00\pm0.38)\exp[-(1612\pm66)/RT]$, $k(\mathrm{H}+\mathrm{C_3D_6})=(2.55\pm0.57)\exp[-(1509\pm128)/RT]$, $k(\mathrm{D}+\mathrm{C_3H_6})=(1.99\pm0.05)\exp[-(1550\pm15)/RT]$, and $k(\mathrm{D}+\mathrm{C_3D_6})=(2.20\pm0.27)\exp[-(1587\pm67)/RT]$ in units of 10^{-11} cm^3 molecule^{-1} s^{-1}. The unit of activation energy is cal mol^{-1}. Practically no isotope effects attributable to the difference between C_3H_6 and C_3D_6 could be observed. This is similar to the kinetic isotope effects previously observed in the rate constants of the addition of H and D atoms to isotopic ethylenes. The theoretical rate constants of the above reactions have been calculated by the conventional activated complex theory using the potential energy surface drawn by the *ab initio* method; however, no agreement with regard to the isotope effects could be obtained between experiment and theory because of the difference between C_3H_6 and C_3D_6. This also is similar to the isotope effects found in the $\mathrm{H}+\mathrm{C_2H_4}\rightarrow\mathrm{C_2H_5}$ reaction.

In previous papers,1,2) we reported the absolute rate constants of the addition of H and D atoms to C_2H_4, C_2H_3D, C_2D_4, C_2H_2, and C_2D_2 obtained by the pulse radiolysis-resonance absorption technique over the temperature range of 200—500 K, and discussed the kinetic isotope effects on the basis of the activated complex theory, since the potential energy surfaces obtained by the *ab initio* calculations were available for both reactions, $\mathrm{H}+\mathrm{C_2H_4}\rightarrow\mathrm{C_2H_5}$3) and $\mathrm{H}+\mathrm{C_2H_2}\rightarrow\mathrm{C_2H_3}$.4) Experimentally, no differences among three isotopic ethylenes, C_2H_4, C_2H_3D, and C_2D_4, as well as between two acetylenes, C_2H_2 and C_2D_2 could be found in the rate constants of the H- and D-atom-addition reactions, while, theoretically, these differences clearly appeared, mainly because of the zero-point energy differences between the reactants and the activated complexes.

It is well known that the present status of the *ab initio* calculations is not reliable enough to discuss the absolute value of the barrier height for a reaction involving polyatomic molecules. Therefore, we parametrized the barrier heights so as to fit the theoretical rate constants for the $\mathrm{H}+\mathrm{C_2H_4}\rightarrow\mathrm{C_2H_5}$ and $\mathrm{H}+\mathrm{C_2H_2}\rightarrow\mathrm{C_2H_3}$ reactions at room temperature to the experiment, and then investigated the isotope effects; however, no agreement could be obtained between experiment and theory.

The present paper is a simple extension of the previous one. Experimentally, however, more accurate measurements of the reactant pressure and the temperature were required because the rate constant of the $\mathrm{H}+\mathrm{C_3H_6}\rightarrow\mathrm{C_3H_7}$ reaction was larger than that of $\mathrm{H}+\mathrm{C_2H_4}\rightarrow\mathrm{C_2H_5}$. In the theoretical calculation, about twice as much time was consumed.

Experimental and Calculational Procedures

The experimental procedure was the same as that described previously.2) Hydrogen or deuterium gas (≈500 Torr; 1 Torr≈133.322 Pa) containing a small amount of propylene (0.01—0.1 Torr) was pulse-irradiated with high-energy electrons from Febetron 706 (Hewlett Packard Co.), and the decay of the concentration of H or D atoms was observed by the use of Lyman-α's. From this first-order decay curve, the rate constant was estimated.

The propylene used was purchased from the Takachiho Shoji Co. The propylene-d_6 was the product of Merck, Sharp, and Dohme, Canada, Ltd., the nominal purity being 99%; this purity was confirmed gaschromatographically.

The *ab initio* calculation method used is the same as that used for drawing the potential energy surface for the $\mathrm{H}+\mathrm{C_2H_4}\rightarrow\mathrm{C_2H_5}$ reaction.3) The details of the calculated results will be published elsewhere; in the present paper, only the data necessary for the estimation of the rate constants are presented.

Results

Table 1 summarizes the rate constants obtained. Four to five different pressures of propylenes were used to measure the rate constants at each temperature. The fluctuation of the temperature (±2 °C) in each measurement was corrected in the same manner as that previously described in detail.2) In Fig. 1, all the rate constants obtained are plotted in the form of Arrhenius plots. The Arrhenius parameters thus determined are summarized

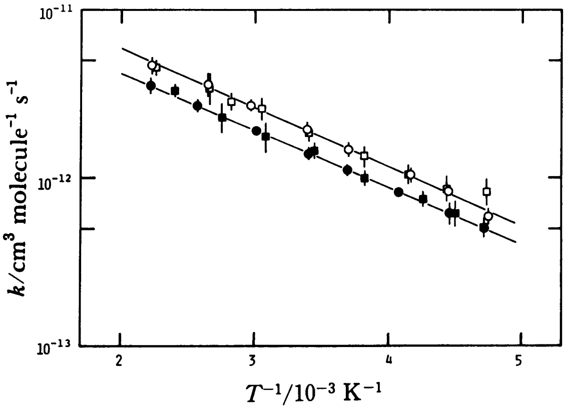

Fig. 1. The Arrhenius plots for the reactions: (○), $\mathrm{H}+\mathrm{C_3H_6}$; (□), $\mathrm{H}+\mathrm{C_3D_6}$; (●), $\mathrm{D}+\mathrm{C_3H_6}$; (■), $\mathrm{D}+\mathrm{C_3D_6}$.

Table 1. The high pressure limiting rate constants of the addition of H and D atoms to propylene-d_0 and -d_6

Reaction	$\frac{T}{K}$	$\frac{k}{10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}}$
$H+C_3H_6$	448	46.9 ±5.5
	378	36.3 ±5.5
	337	27.3 ±2.1
	295	19.4 ±2.1
	270	14.7 ±1.4
	240	10.4 ±1.1
	225	8.31±0.55
	211	5.93±0.61
$D+C_3H_6$	451	35.6 ±3.8
	389	27.0 ±2.4
	332	18.9 ±1.1
	295	13.9 ±1.1
	271	11.2 ±0.6
	245	8.25±0.43
	224	6.18±0.89
	212	5.04±0.42
$H+C_3D_6$	423	45.4 ±4.8
	376	34.5 ±7.2
	355	28.6 ±3.3
	328	25.9 ±3.9
	294	18.4 ±1.9
	262	13.4 ±1.9
	241	10.6 ±1.3
	225	8.72±1.46
	211	8.33±1.48
$D+C_3D_6$	417	33.1 ±2.8
	364	23.0 ±4.7
	325	17.6 ±3.6
	291	14.4 ±1.5
	262	9.93±1.00
	235	7.46±0.78
	222	6.19±1.08
	212	5.18±0.75

Table 2. Arrhenius parameters obtained $A/10^{-11}$ cm^3 molecule^{-1} s^{-1} and E/cal mol^{-1}; uncertainties are 2σ.

	H-atom addition		D-atom addition	
	A	E	A	E
C_3H_6	3.00±0.38	1612± 66	1.99±0.05	1550±15
C_3D_6	2.55±0.57	1509±128	2.20±0.27	1587±67

in Table 2. The uncertainties are 2σ. The method of calculating these uncertainties has been described previously.[2)] It is noticeable that no kinetic isotope effects due to the difference between C_3H_6 and C_3D_6 could be observed.

Figure 2 shows the structures of propylene and the activated complex calculated by the *ab initio* unrestricted Hartree-Fock method with the 4-31 split-basis set. These geometries were fully optimized with the energy-gradient method. The force-constant matrices for propylene and the activated complex were then constructed by the numerical differentiation of the energy gradients.

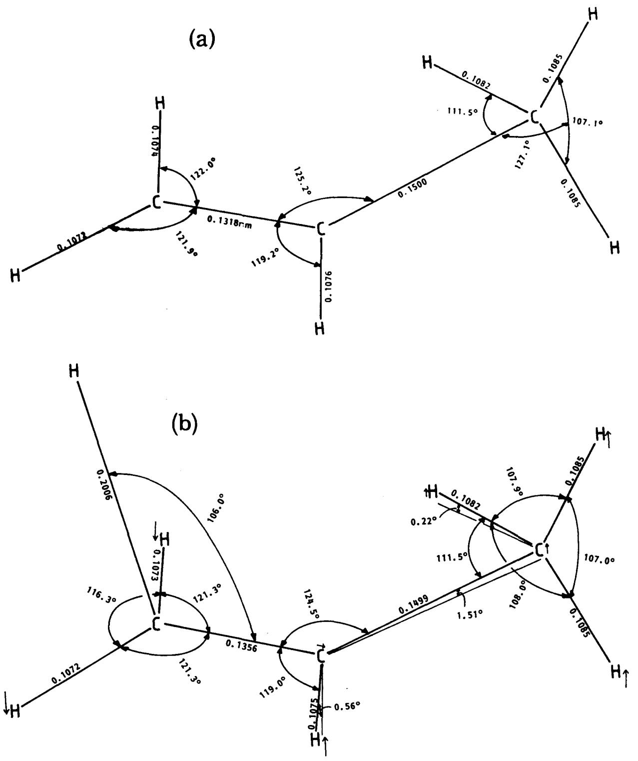

Fig. 2. The Geometries of C_3H_6 (a) and the activated complex for the reaction, $H+C_3H_6$, (b). Arrows indicate the direction of the displacement of the equilibrium position from the reactant.

Table 3 summarizes the resultant normal-mode frequencies, moments of inertia, and zero-point energies. Although the calculated normal-mode frequencies for propylene did not agree exactly with those experimentally obtained,[5)] we did not ascertain the correction factor since the discrepancy between experiment and calculation was not systematic and prevented us for estimating a simple correction factor.

The barrier height calculated for the $H+CH_3CH{=}{-}CH_2 \rightarrow CH_3CH{-}CH_3$ reaction was 2.41 kcal/mol (1 kcal=4.184 kJ), a value which was obviously too high compared with the experimentally obtained activation energies. Therefore, we had to parametrize this value in the calculations of the rate constants, as will be shown later. It is well known that hydrogen atoms mainly add to the double bond of propylene at the terminal carbon atom.[6)] The *ab initio* calculation is consistent with this observation: the barrier height for $H+CH_3CH{=}CH_2 \rightarrow CH_3CH_2CH_2$ addition reaction was calculated to be 4.24 kcal/mol.

Discussion

Propylene is known to be more reactive than ethylene to hydrogen atoms at room temperature.[7)] The present experiments clearly showed that this difference comes from the activation energies. The Arrhenius equation for the $H+C_2H_4 \rightarrow C_2H_5$ reaction previously obtained is $k_{exp}=(4.70\pm0.49)\times10^{-11}\exp[-(2178\pm58)/RT]$ cm^3 molecule^{-1} s^{-1}.[2)] Since the pre-exponential factor for the reaction of propylene is about 2/3 of that for the

TABLE 3. NORMAL MODE FREQUENCIES, MOMENTS OF INERTIA, AND ZERO-POINT ENERGIES

		Species					
		C_3H_6	$C_3H_7{}^\dagger$	$C_3H_6D^\dagger$	C_3D_6	$C_3D_6H^\dagger$	$C_3D_7{}^\dagger$
Vibrational frequencies ν/cm^{-1}		3398	3402	3402	2528	2534	2534
		3321	3315	3315	2471	2441	2441
		3306	3298	3298	2414	2414	2414
		3245	3262	3262	2404	2405	2405
		3218	3214	3214	2380	2376	2376
		3167	3166	3166	2279	2278	2278
		1879	1689	1687	1787	1545	1539
		1656	1657	1657	1287	1274	1274
		1647	1645	1645	1202	1199	1199
		1612	1588	1587	1195	1193	1193
		1580	1572	1572	1189	1187	1187
		1471	1383	1380	1155	1132	1131
		1324	1308	1307	1047	1031	1030
		1218	1180	1180	1020	959	957
		1154	1065	1065	886	834	826
		1116	1053	1028	845	826	799
		1074	1028	1021	825	789	789
		980	954	949	797	751	745
		678	719	708	507	558	540
		478	465	463	394	412	381
		229	429	347	168	379	323
			286	220		273	212
			194	191		143	141
			624i	472i		617i	470i
Moments of inertia $I/10^{-47}$ kg m^2	I_a	89.55	101.37	107.79	116.35	129.06	137.48
	I_b	102.03	109.96	119.71	135.78	143.63	151.64
	I_c	17.58	24.33	29.88	29.61	36.55	42.32
Zero-point energy/kcal mol^{-1}		53.97	54.14	53.84	41.14	41.36	41.05

reaction of ethylene, if the Arrhenius equations can be extrapolated to higher temperatures, the rate constants of these two reactions will coincide with each other at around 360 °C.

According to the conventional activated complex theory, the rate constant of the $H+C_3H_6\rightarrow C_3H_7$ reaction is expressed as follows:

$$\kappa = \kappa L^\dagger \frac{kT}{h} \frac{F^\dagger}{F_H F_P} \frac{f_{rot}{}^\dagger}{f_{rot}} \frac{f_{vib}{}^\dagger}{f_{vib}} \exp(-V/RT). \quad (1)$$

Here, κ is the transmission coefficient, which may be calculated by Wigner's approximation:

$$\kappa = 1 + (1/24)(h|\nu_i|/kT)^2. \quad (2)$$

The values of ν_i are listed in Table 3. $L^\dagger$ is the path degeneracy. F_H, F_P, and $F^\dagger$ are the translational partition functions for hydrogen atoms, propylene molecules, and an activated complex respectively. f_{rot} and $f_{rot}{}^\dagger$ are the rotational partition functions without a symmetry number. f_{vib} and $f_{vib}{}^\dagger$ are the vibrational partition functions including the contribution of zero-point energies. V is the barrier height.

Since the calculated barrier height was too high, we adjusted this value so as to fit the theoretical rate constant of the $H+C_3H_6\rightarrow C_3H_7$ reaction at room temperature to the experimental result. The adjusted barrier height was 1.63 kcal/mol. This value is common to three other reactions also; $D+C_3H_6$, $H+C_3D_6$, and $D+C_3D_6$.

Figure 3 compares the rate constants thus calculated with those obtained in the present experiments. Here, the experimentally obtained Arrhenius equation for the $H+C_3H_6\rightarrow C_3H_7$ reaction, $k_{exptl}=3.00\times 10^{-11}$ exp $(-1612/RT)$ cm^3 molecule^{-1} s^{-1}, is taken as the standard. Obviously the agreement between experiment and theory is poor for the isotope effects because of the difference between C_3H_6 and C_3D_6, while the isotope

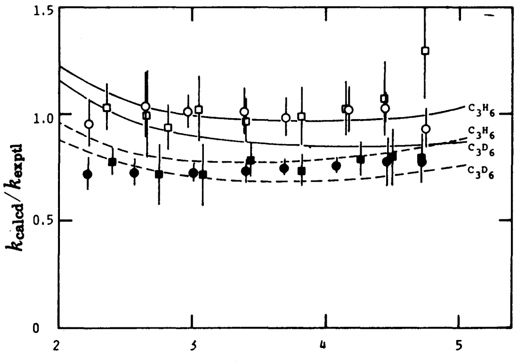

Fig. 3. Comparison of the experimental results with the theoretical calculations. For symbols, see the caption of Fig. 1. The experimentally obtained rate constant for the reaction, $H+C_3H_6$, $k_{exptl}=3.00\times 10^{-11}$ exp $(-1612/RT)$ cm^3 molecule^{-1} s^{-1}, is taken as the standard. Solid lines are for the H-atom reactions and dashed lines for the D-atom reactions.

effects due to the difference between H and D atoms are well explained. This is exactly the same as was found previously in the reactions of H and D atoms with isotopic ethylenes.[1,2]

At present, we have no proper interpretations for this disagreement. One possible reason might be fundamental assumption on which the activated complex theory is based. In the formulation of the activated complex theory, the equilibrium between a reactant and the activated complex is postulated; however, in such exothermic fast reactions as $H+C_3H_6 \rightarrow C_3H_7$, some normal modes of vibration in the activated complex might not be able to reach the equilibrium before the reaction system crosses over the saddle point. Consequently, some normal modes of vibration in the reactant remain as they are and cannot contribute to the change of the state density, *i.e.*, to the rate constant. It is well known that the kinetic isotope effect results from the difference in zero-point energy between reactant and activated complex. The critical energy defined by the following equation is a crucial factor in determining the isotope effects:

$$E_0 = V + \Delta E_{\mathrm{vib}},$$

$$\Delta E_{\mathrm{vib}} = \frac{1}{2}\sum h\nu^{\dagger} - \frac{1}{2}\sum h\nu.$$

Here, $\nu^{\dagger}$ and ν are the normal-mode frequencies in the activated complex and the reactant. If ΔE_{vib} is reduced by the reasoning above stated, the isotope effects in the rate constants will also be reduced. A rigorous formulation of this will be the subject of our further investigations.

References

1) K. Sugawara, K. Okazaki, and S. Sato, *Chem. Phys. Lett.*, **78**, 259 (1981).

2) K. Sugawara, K. Okazaki, and S. Sato, *Bull. Chem. Soc. Jpn.*, **54**, 2872 (1981).

3) S. Nagase, T. Fueno, and K. Morokuma, *J. Am. Chem. Soc.*, **101**, 5849 (1979).

4) S. Nagase and C. W. Kern, *J. Am. Chem. Soc.*, **101**, 2544 (1979).

5) G. Herzberg, "Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules," D. van Nostrand, New York (1945).

6) W. E. Falconer, B. S. Rabinovitch, and R. J. Cvetanović, *J. Chem. Phys.*, **39**, 40 (1963).

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