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Temperature Dependence of the Rate Constants of H and D-Atom Additions to C_2H_4, C_2H_3D, C_2D_4, C_2H_2, and C_2D_2

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The high pressure limiting rate constants of H and D-atom additions to C_2H_4, C_2H_3D, C_2D_4, C_2H_2, and C_2D_2 have been measured in the temperature range from 206 to 461 K by means of the pulse radiolysis-resonance absorption method. Practically no isotope effects due to the deuteration of ethylene and acetylene could be observed. The rate constants were compared with those calculated by the activated complex theory using the potential energy surfaces provided by the *ab initio* calculations. Concerning the isotope effects, very poor agreement was obtained between theory and experiment. This seems to suggest that the assumptions on which the activated complex theory is based have to be reconsidered when it is applied to such reactions as $H+C_2H_4 \rightarrow C_2H_5$ and $H+C_2H_2 \rightarrow C_2H_3$.

The reaction of H-atoms with ethylene has been extensively studied for the last 50 years.[1] The following reaction mechanism is now established:

$$H + C_2H_4 \rightleftharpoons C_2H_5^* \xrightarrow{+M} C_2H_5. \tag{1}$$

Here M stands for the third body for the deactivation of the energized ethyl radicals, $C_2H_5^*$. When H_2 is used as the third body, 200 Torr (1 Torr=133.3 Pa) is probably high enough to suppress the decomposition of $C_2H_5^*$.[2] The reaction of H-atoms with acetylene has also been studied for many years and a similar reaction mechanism has been proposed:

$$H + C_2H_2 \rightleftharpoons C_2H_3^* \xrightarrow{+M} C_2H_3. \tag{2}$$

Recently, we studied the unimolecular decomposition of $C_2H_3^*$[3] and showed that 500 Torr of He is high enough to suppress the decomposition of $C_2H_3^*$. If H_2 is used, 300 Torr may be high enough. In the present paper, we report the high pressure limiting rate constants of these addition reactions in the temperature range 206—461 K. Such measurements were made by Lee *et al.* on the reaction $H+C_2H_4 \rightarrow C_2H_5$[4] and by Payne and Stief on the reaction $H+C_2H_2 \rightarrow C_2H_3$.[5]

Since these addition reactions are relatively simple, the *ab initio* calculations have been carried out for drawing the potential energy surfaces.[6-9] Nagase and Kern predicted the structure of the activated complex for the $H+C_2H_2$ reaction[6] and Nagase *et al.* for the $H+C_2H_4$ reaction.[9] Using this calculated potential energy surface, Nagase *et al.* predicted the kinetic isotope effects in the $H+C_2H_4$ reaction on the basis of the activated complex theory (ACT). We therefore extended our measurement to the reactions with D-atoms and to those with isotopic ethylenes and acetylene, C_2H_3D, C_2D_4, and C_2D_2. A short communication on the $H+C_2H_4$ reaction has already been published.[10]

The kinetic isotope effect is one of the key points when the rate theory of chemical reactions is discussed. The potential energy surfaces calculated for any reactions are not accurate enough to estimate the absolute rate constants;[11] an error of 0.1 kcal/mol (1 kcal=4.184 kJ) introduces a crucial effect on the estimation of the rate constant. For the discussion on the isotope effect, however, such an accurate potential energy surface is not considered necessary.

Experimental

The details of the apparatus and experimental procedures were given in previous papers.[2,12]

The main modification of the apparatus is that the temperature of the reaction system can be controlled in the range from 200 to 500 K. The temperatures lower than room temperature were obtained by letting chilled nitrogen gas flow in a box made of Styroform which surrounds the cell. Higher temperatures were attained by winding the cell with flexible insulated heating tapes. The gas temperature was measured with an accuracy of ±2 K with a copper-constantan thermocouple at the center of the cell prior to each pulse irradiation. Because of the small capacity of the reaction cell and of the simple technique of temperature control, some temperature deviation during a series of measurements (2—3 h) could not be avoided; however, since the rate measurement is finished within 0.1 s, the temperature fluctuation during each measurement may be ignored.

The H_2, D_2 (Takachiho Shoji Co.), and He (Nihon Helium Co.) were used after having been passed through traps filled with molecular sive 4A at 77 K. The C_2H_4, C_2H_2 (Takachiho Shoji Co.), C_2H_3D, C_2D_4, and C_2D_2 (Merck Sharp and Dohme, Canada Ltd.) were used as received. The nominal purities of the last three compounds are 98, 99, and 99%, respectively; these values have been confirmed by gas chromatographic and mass spectrometric analyses.

Results

With a system containing only H_2 or D_2, a very slow decay of H or D-atoms was observed at every temperature. The decay rate increased from 2 to 10 s^{-1} with increasing temperature. This decay may be attributable to the diffusion of the atoms from the optical path. In the presence of a small amount of ethylene or acetylene, the decay of H or D-atoms was far more rapid (10^2—10^4 s^{-1}). A typical oscillogram is shown in Fig. 1. The mixture of 0.212 Torr[†] C_2D_2 and 595 Torr D_2 was irradiated at 273 K. The lower figure is the first order decay plot of the optical density at 121.6 nm against the reaction time. From this first order decay plot, we can calculate a bimolecular rate constant. All data thus obtained for the reaction of $D+C_2D_2$ are listed in Table 1. When the average of rate constants in each group of measurements is estimated, the deviation due to a small difference of temperature is corrected by using the following formula:

[†] 1 Torr ≈ 133.322 Pa.

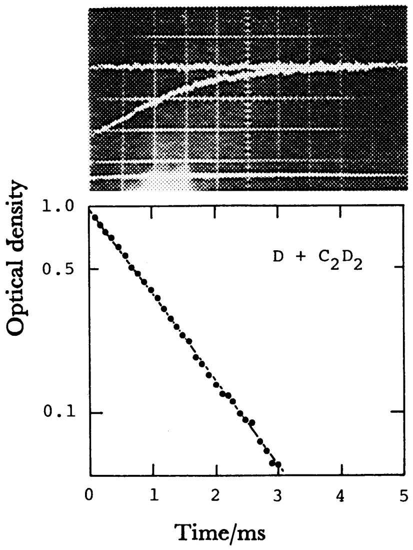

Fig. 1. The oscillogram for the decay of D-atoms in the system of 0.212 Torr C_2D_2 and 595 Torr D_2 at 273 K.

$$k(T+\Delta T) = k(T)[1+(E/R)(\Delta T/T^2)].$$

Here, $k(T)$ is the rate constant at temperature T, E is the activation energy, and R is the gas constant. For the reaction with ethylene, E was assumed to be 2.2

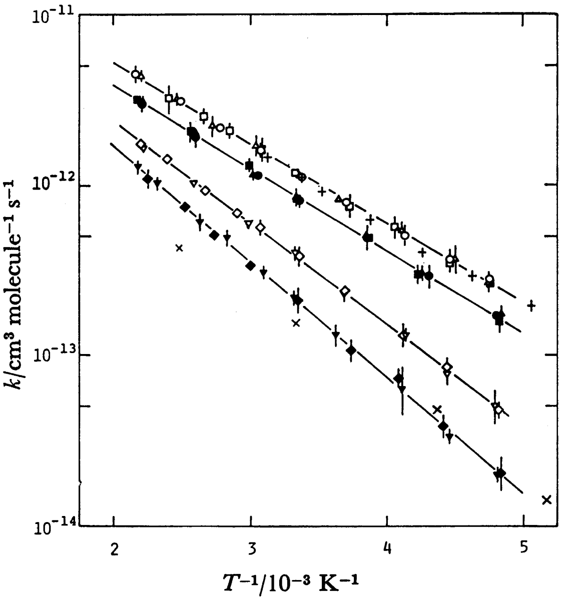

Fig. 2. The Arrhenius plots for the reactions: (○), $H+C_2H_4$; (△), $H+C_2H_3D$; (□), $H+C_2D_4$; (●), $D+C_2H_4$; (▲), $D+C_2H_3D$; (■), $D+C_2D_4$; (◇), $H+C_2H_2$; (▽), $H+C_2D_2$; (◆), $D+C_2H_2$; (▼), $D+C_2D_2$; (+), the results of Lee *et al.* for $H+C_2H_4$; (×), the results of Payne and Stief for $H+C_2H_2$.

TABLE 1. RATE MEASUREMENTS ON THE REACTION OF D ATOMS WITH C_2D_2
Uncertainties are 2σ.

$\frac{C_2D_2}{mTorr}$	D_2/Torr	T/K	$\frac{k_{dr}}{10^3\,s^{-1}}$	$\frac{k}{10^{-13}\,cm\,s^{-1}}$
55	607	452	1.48	12.6
138	616	450	3.83	12.9
359	615	452	8.80	11.5
775	615	452	20.9	12.6
		av. 452		12.5±1.4[a)]
46	595	427	1.11	10.7
89	600	427	2.02	10.1
279	605	425	5.95	9.38
691	606	427	14.9	9.54
		av. 427		9.97±1.11
48	570	379	0.825	6.76
102	580	375	1.46	5.55
454	570	375	7.02	6.00
		av. 376		6.07±0.93
68	568	352	0.920	4.95
107	563	352	1.27	4.32
189	566	352	2.66	5.13
293	562	352	3.58	4.46
515	563	350	6.84	4.82
		av. 352		4.76±0.70
92	541	322	0.830	3.01
118	537	318	1.04	2.89
293	538	322	2.56	2.91
591	540	322	5.66	3.20
859	540	322	8.02	3.11
		av. 321		3.01±0.22
201	520	298	1.33	2.04
234	650	294	1.66	2.17
237	758	294	1.64	2.11
470	532	298	3.07	2.02
476	521	298	3.09	2.01
616	528	298	4.55	2.28
899	597	299	5.98	2.06
		av. 297		2.10±0.27
43	593	272	2.22	1.45
212	595	273	9.97	1.33
512	469	275	22.5	1.24
833	545	273	32.3	1.26
		av. 273		1.32±0.25
39	550	243	1.15	0.740
190	732	237	4.09	0.528
498	780	243	10.1	0.509
792	545	243	19.4	0.616
		av. 242		0.603±0.184
36	507	223	0.486	0.311
97	505	222	1.31	0.310
194	786	225	2.93	0.352
481	494	223	7.07	0.340
775	510	220	9.77	0.287
1083	510	223	15.2	0.323
		av. 223		0.323±0.022
35	500	210	0.338	0.210
109	490	207	0.940	0.185
295	485	205	2.56	0.184
778	480	207	7.10	0.196
		av. 207		0.192±0.012

a) Before averaging, the correction for temperature is made. See the text for the details.

TABLE 2. RATE CONSTANTS OF H OR D-ATOMS WITH C_2H_4, C_2H_3D, C_2D_4, C_2H_2, OR C_2D_2
Uncertainties are 2σ.

Reaction	T/K	$k/10^{-13}$ cm^3 molecule^{-1} s^{-1}
$H+C_2H_4$	461	44.2±5.2
	401	31.2±1.8
	360	21.9±1.3
	325	16.4±1.6
	297	11.4±0.9
	270	7.94±0.68
	242	5.06±0.54
	224	3.66±0.56
	211	2.84±0.54
$H+C_2H_3D$	451	43.0±5.0
	411	31.3±3.1
	368	22.3±3.7
	329	17.4±3.1
	297	11.6±1.0
	275	8.27±0.49
	243	5.48±0.85
	221	3.59±0.77
	210	2.71±0.46
$H+C_2D_4$	455	43.7±1.7
	411	31.3±7.4
	373	24.3±2.9
	348	20.3±1.9
	321	16.0±2.6
	298	11.4±0.9
	269	7.39±1.01
	245	5.54±0.98
	223	3.40±0.15
	209	2.59±0.11
$D+C_2H_4$	453	30.2±3.2
	384	19.4±2.7
	327	11.5±0.9
	298	8.19±0.74
	260	4.91±0.95
	232	2.96±0.50
	208	1.70±0.10
$D+C_2H_3D$	449	30.6±3.0
	382	20.3±1.4
	331	12.0±1.4
	299	8.62±1.12
	259	5.06±0.32
	234	3.14±0.46
	206	1.73±0.24
$D+C_2D_4$	457	30.8±2.6
	392	20.5±3.2
	333	12.8±1.0
	298	8.18±0.47
	257	4.81±0.37
	235	2.97±0.47
	206	1.55±0.22
$H+C_2H_2$	451	17.9±0.6
	415	14.5±1.2
	374	9.58±1.29
	343	6.85±0.84
	326	5.63±0.62
	297	3.79±0.37
	270	2.40±0.14
	242	1.28±0.20
	225	0.846±0.127
	207	0.477±0.045
$H+C_2D_2$	448	16.2±0.4
	385	10.2±0.6
	331	5.86±0.35
	298	3.82±0.49
	270	2.25±0.28
	241	1.28±0.09
	224	0.759±0.129
	208	0.485±0.117
$D+C_2H_2$	443	10.9±1.3
	394	7.58±0.50
	364	5.10±0.24
	327	3.35±0.23
	297	2.07±0.46
	267	1.08±0.22
	244	0.774±0.099
	226	0.384±0.059
	206	0.202±0.402

kcal/mol, and for acetylene, 3.0 kcal/mol was used.

For the other nine reactions, similar measurements and calculations were carried out. The rate constants thus obtained are summarized in Table 2 and in Fig. 2 in the form of an Arrhenius plot, together with the results of Lee *et al.* and Payne and Stief. The results of Lee *et al.* are in good agreement with the present ones, while those of Payne and Stief on the $H+C_2H_2$ reaction are in serious disagreement with ours. This discrepancy will be discussed later.

At high temperatures, the total pressure used might not be high enough to obtain the high pressure limiting rate constant. Figure 3 shows the result of this check.

Table 3 summarizes the Arrhenius parameters calculated from Fig. 2 by the least-squares method, in which the weights resulting both from the experimental errors and from the calculation of the logarithms of

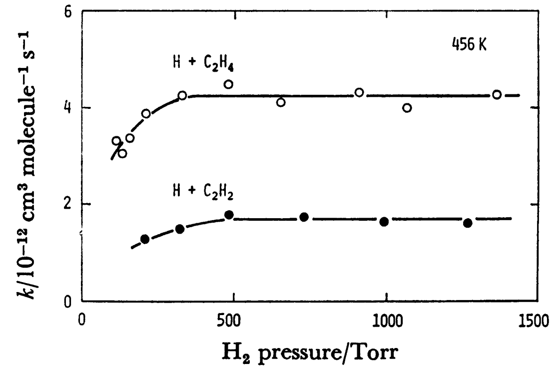

Fig. 3. The pressure dependence of the rate constants for the reactions, $H+C_2H_4$ and $H+C_2H_2$, at 456 K.

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

	H-Atom addition		D-Atom addition	
	A	E	A	E
C_2H_4	4.70±0.49	2178±58	3.36±0.15	2186±23
C_2H_3D	4.43±0.76	2153±100	3.57±0.34	2193±56
C_2D_4	4.57±0.49	2160±51	3.55±0.43	2216±71
C_2H_2	3.80±0.20	2731±35	3.44±0.61	3023±117
C_2D_2	3.17±0.20	2643±47	4.39±0.31	3184±36

rate constants are included. This calculating method was recently discussed by Cvetanovic *et al.*[13] In the previous communication,[10] we did not use this procedure. The Arrhenius parameters reported in the previous communication should be read as those shown in Table 3 of this paper, although the discrepancy is not substantial. It should be noted in this table that practically no isotope effects due to the deuteration of ethylene and acetylene could be observed.

Discussion

Effect of Product Radicals on the Decay of Atoms. One of the most difficult problems in the present experiment is whether or not the produced ethyl or vinyl radicals affect the measurement of the decay of the reacting atoms. It is established that, if the concentration of hydrogen atoms is higher than or comparable to that of the reactant, ethylene or acetylene, the produced ethyl or vinyl radicals participate into the decay of the reacting atoms, and the decay rate of the atoms is thus overestimated.

As Fig. 2 shows, the temperature dependence of the rate constant of the $H+C_2H_4$ reaction obtained is in good agreement with that obtained by Lee *et al.*, but in the case of the $H+C_2H_2$ reaction, the agreement between the present measurement and that by Payne and Stief is very poor; our data is twice as large as theirs at low temperatures and three times larger at high temperatures. This discrepancy has been discussed in a previous paper;[3] its final conclusion was retained because, when the resonance absorption method is used, the concentration of atoms cannot be reduced to lower than 10^{11} cm^{-3}. In the measurement of the rate constant of the $H+C_2H_4$ reaction, Lee *et al.* used the resonance fluorescence method, by which the atomic concentration can be reduced to 10^{10} cm^{-3}. In fact they obtained the rate constants shown in Fig. 2 by using this low concentration of H-atoms.

When we discussed the participation of vinyl radicals in the $H+C_2H_2$ system, the Runge-Kutta integration method was used to estimate the concentration of vinyl radicals. It was concluded that the participation of this radical in the decay of hydrogen atoms is negligibly small at room temperature; however, since the rate constant $k(H+C_2H_2)$ at room temperature is about 3 times slower than $k(H+C_2H_4)$ at room temperature, there remains a small suspicion about the calculation. As is shown in Fig. 2, $k(H+C_2H_2)$ at 400 K is almost in the same order as $k(H+C_2H_4)$ at room temperature; therefore, if the value for k $(H+C_2H_4)$ at room temperature is reliable, the same thing may be said to that for k $(H+C_2H_2)$ at 400 K. On the other hand, all Arrhenius plots obtained in the present experiments are nicely linear. Consequently, we believe that the rate constants obtained here do not suffer from any disturbance due to the participation of product radicals, although we have no proper explanation for the discrepancy between our results and those of Payne and Stief.

The ACT Calculations. In order to calculate the absolute rate constant of an elementary reaction by the ACT, we need the geometrical structure and the normal mode frequencies of the activated complex. For the reactions of $H+C_2H_4$ and $H+C_2H_2$, we have two sets of data for each reaction. The one is that somewhat arbitrarily constructed for the discussion of the uni-

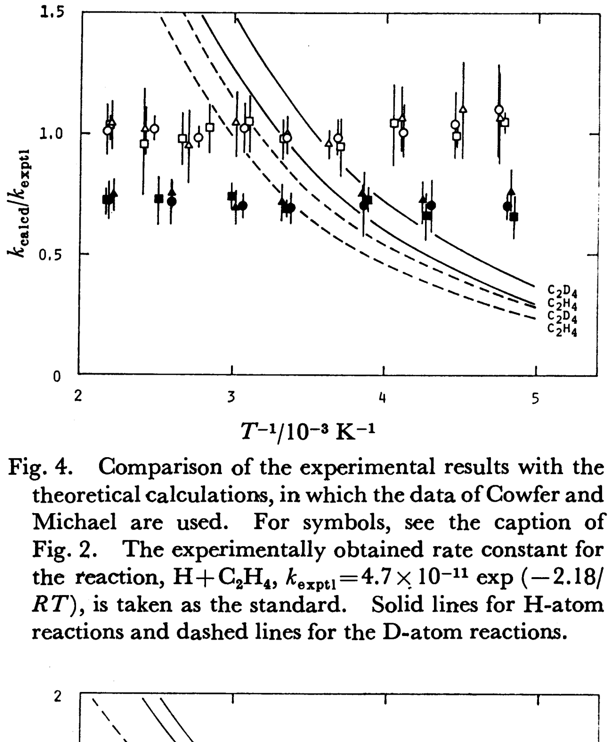

Fig. 4. Comparison of the experimental results with the theoretical calculations, in which the data of Cowfer and Michael are used. For symbols, see the caption of Fig. 2. The experimentally obtained rate constant for the reaction, $H+C_2H_4$, $k_{exptl}=4.7\times10^{-11}\exp(-2.18/RT)$, is taken as the standard. Solid lines for H-atom reactions and dashed lines for the D-atom reactions.

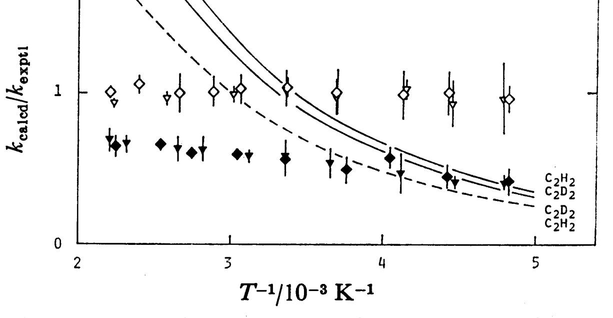

Fig. 5. Comparison of the experimental results with the theoretical calculations, in which the data of Keil *et al.* are used. For symbols, see the caption of Fig. 2. The experimentally obtained rate constant for reaction, $H+C_2H_2$, $k_{exptl}=3.8\times10^{-11}\exp(-2.73/RT)$, is taken as the standard. Solid lines for the H-atom reactions and dashed lines for the D-atom reactions.

molecular decomposition of energized ethyl[14] and vinyl radicals,[15] and the other is the results of the *ab initio* calculations.[6,9]

Figures 4 and 5 compare the experimental results with those calculated by using the parameters estimated for the discussion of the unimolecular decomposition of energized radicals. Here, the experimental rate constants for the $H+C_2H_4$ and $H+C_2H_2$ reactions, $k_{\text{exptl}}=4.7\times10^{-11}\exp(-2.18/RT)$ and $k_{\text{exptl}}=3.8\times10^{-11}\exp(-2.73/RT)$ respectively, are taken as the standard for each group of reactions, and the $k_{\text{calcd}}/k_{\text{exptl}}$ ratios are plotted as a function of $1/T$. In these calculations, the barrier heights for the two groups of reactions are adjusted so as to fit the room temperature rate constants for the $H+C_2H_4$ and $H+C_2H_2$ reactions to the experimental ones.

For the convenience of the following discussions, we give the formula used for the calculation of the rate constant:

$$k_{\text{calcd}} = \kappa \frac{kT}{\text{h}} \frac{F^{\ddagger}_{\text{tr}}}{F_{\text{atom}}F^{\text{i}}_{\text{tr}}} \frac{f^{\ddagger}_{\text{rot}}}{f^{\text{i}}_{\text{rot}}} \frac{f^{\ddagger}_{\text{vib}}}{f^{\text{i}}_{\text{vib}}} \exp(-E/RT) \tag{3}$$

$$E = V + \frac{1}{2}\Sigma h\nu_{\ddagger} - \frac{1}{2}\Sigma h\nu_{\text{i}}. \tag{4}$$

Here V is the barrier height and the other symbols are the same as those appearing in a textbook of reaction kinetics.[16]

In the calculation of the theoretical curves shown in Figs. 4 and 5, the V values are adjusted and found to be 2.83 kcal/mol for the $H+C_2H_4$ reaction and 3.56 kcal/mol for the $H+C_2H_2$ reaction. The transmission coefficient κ is assumed to be unity. As both figures show, the agreement between calculation and experiment is very poor, especially for the temperature dependence.

In the treatment of the unimolecular decomposition of ethyl and vinyl radicals, the activated complexes were assumed to be loose, in order to explain the fall-off pressure.[14,15] In the "loose activated complex," most of the normal mode frequencies are very close to those in the reactants, except for the vibrations newly formed in the activated complex, and their frequencies are considered to be small compared with those in stable compounds. In fact, Cowfer and Michael estimated 120 cm^{-1} for the frequency of the two newly formed vibrations in the activated complex of the $H+C_2H_4$ reaction. The substitution of this value into the vibrational partition function, $f^{\dagger}_{\text{vib}}=(1-e^{-h\nu/kT})^{-1}$, gives 2.29 at 300 K. Small vibrational frequencies thus increase the preexponential factor and result in the increase of the adjustable barrier height. This seems to be the main reason for the disagreement between calculation and experiment in Figs. 4 and 5. If the frequencies of the newly formed vibrations in the activated complex could be estimated to be more than 400 cm^{-1} with no effect on the other vibrations, the agreement between calculation and experiment would be much improved.

On the other hand, the recent *ab initio* calculations have suggested that the activated complexes for the reactions of $H+C_2H_4$ and $H+C_2H_2$ have more "tight" structures than those discussed above. The structure and the normal mode frequencies calculated have already been published in previous papers;[3,10] therefore it will not be necessary to restate them. According to these data, the frequencies of the newly formed vibrations in the activated complexes are larger than 400 cm^{-1}, but, along with this increase, other vibrational frequencies are changed and the isotope effects strongly appear. Figures 6 and 7 show the calculated results. In these calculations, the transmission coefficients are estimated by using Wigner's approximation:

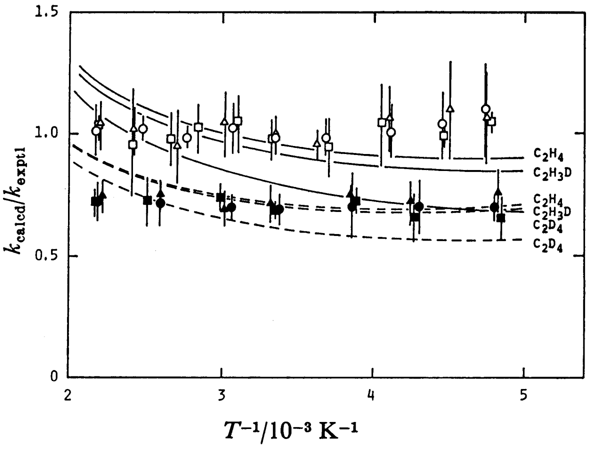

Fig. 6. Comparison of the experimental results with the theoretical calculations, in which the results of the *ab initio* calculations by Nagase *et al.* are used. For the details, see the caption of Fig. 4.

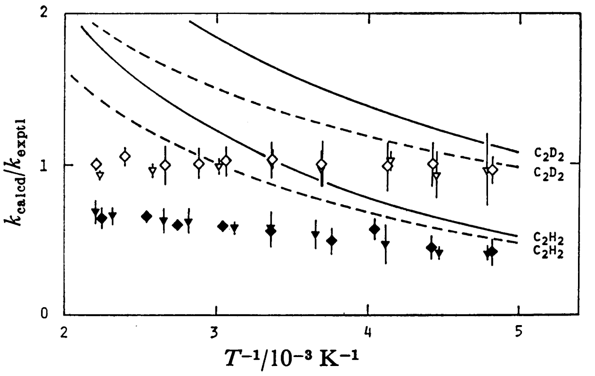

Fig. 7. Comparison of the experimental results with the theoretical calculations, in which the results of the *ab initio* calculations by Nagase and Kern are used. For the details, see the caption of Fig. 5.

$$\kappa = 1 + \frac{1}{24}(h|\nu|/kT)^2. \tag{5}$$

Here, ν is the imaginary frequency along the reaction coordinate at the top of the barrier. The adjustable V values used in the calculation of the theoretical curves in Figs. 6 and 7 are 2.43 and 2.46 kcal/mol, respectively.

Comparing these figures with Figs. 4 and 5, we can say that the agreement for the temperature dependence between calculation and experiment in Figs. 6 and 7 is better than that in Figs. 4 and 5; however, concerning the isotope effects due to the deuteration of the reactants, C_2H_4 and C_2H_2, the agreement seems to get worse. Another method for the estimation of the transmission coefficient using an inverted parabola[17] does not improve the situation.

Recently Kupperman and Truhlar developed the generalized transition state theory, in which they stressed that the real activated complex is not necessarily situated on the top of the barrier of the reaction coordinate.[18] This concept was discussed by Horiuchi years ago.[19] This treatment might improve the agreement between the theoretical calculation and experiment; however, as Figs. 6 and 7 show, the isotope effects between C_2H_4 and C_2D_4, and between C_2H_2 and C_2D_2 are so remarkable that filling the gap would be a difficult task.

In 1938, Wigner classified the assumptions on which the ACT is based into three categories:[20] 1) adiabatic condition, 2) quantum effects, and 3) return at the saddle point. The second and third categories have been discussed by many investigators. The transmission coefficient discussed above belongs to the second category. The problem in the third category has been discussed in connection with the trajectory calculation on the atom-diatomic molecule reaction.[21] In the present case, the overshoot of the theoretical curves at high temperatures may be explained by this effect.

Our present impression is that any corrections belonging to the second and third categories cannot improve the agreement between calculation and experiment, especially for the isotope effects due to the deuteration of reactants, and that the first category—adiabatic condition—has to be reconsidered when the ACT is applied to such reactions as $H+C_2H_4$ and $H+C_2H_2$.

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