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The Absolute Rate Constants of Reaction of Hydrogen Atoms with Several Olefins

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Using the techniques of pulse-radiolysis and of the absorption of Lyman-α radiation by hydrogen atoms, the absolute rate constants of reaction of hydrogen atoms with several olefins have been measured at room temperature.

Olefin	$k/10^{-12}$ cm^3 molecule^{-1} s^{-1}
Ethylene	1.1 ± 0.1
Propylene	1.7 ± 0.1
1-Butene	2.0 ± 0.5
trans-2-Butene	1.1 ± 0.2
cis-2-Butene	1.0 ± 0.1
2-Methyl-1-propene	5.2 ± 0.6
2-Methyl-2-butene	2.4 ± 0.3

These rate constants were invariant over hydrogen pressures ranging from 200 to 1200 Torr.

When hydrogen gas at one atmosphere is irradiated with high energy electrons, many different active species are produced and react with each other as well as with hydrogen molecules; however, in a very short time ($\approx$ 10 μs) after the irradiation, active species other than hydrogen atoms disappear in the reaction system. Since the recombination of hydrogen atoms and the diffusion to the wall of the reaction vessel are slow processes, the concentration of hydrogen atoms actually remains constant for a while. If a small amount of an olefin is present in this system, the decrease in the concentration of hydrogen atoms results from the reaction of hydrogen atoms with the olefin. The change of the concentration of hydrogen atoms can be pursued by the absorption of Lyman-α radiation. Hikida *et al.* used this technique for the measurement of the rate constants of reaction of hydrogen atoms with oxygen, carbon monoxide, nitric oxide, and ethylene.¹⁾ Mihelcic *et al.* extended this technique to the reactions of H and D atoms with C_2H_4, C_2D_4, and C_3H_6.²⁾

On the other hand, the relative rates of reaction of hydrogen atoms with various olefins have been measured by many investigators. Among them, Cvetanović and coworkers used three different photochemical techniques: the mercury-photosensitized decompositions of butane³⁾ and of hydrogen⁴⁾ and the photolysis of hydrogen sulfide,⁵⁾ as sources of hydrogen atoms, and measured the relative rates. These relative rate constants are one of the important sets for the reactions of hydrogen atoms.

Recently, we have constructed an apparatus similar to that used by Mihelcic *et al.* and measured the absolute rate constants of reaction of hydrogen atoms with several olefins.

Experimental

A schematic diagram of the set-up of instruments is shown in Fig. 1. As the source of Lyman-α, a water-cooled capillary discharge lamp with a flow of a gas mixture of 5% hydrogen and 95% helium was used. The highest ratio of signal/noise, about 10, was obtained at 600 V and 0.6 A. We could not find any strong lines other than Lyman-α between 104 and 200 nm.

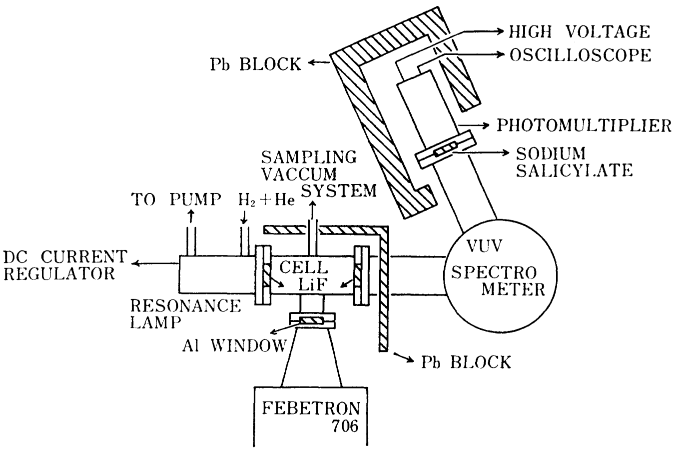

Fig. 1. The schematic diagram of the pulse radiolysis-resonance absorption apparatus.

The reaction vessel was made of stainless steel, 11 cm long and 5 cm in diameter. A pair of LiF windows was attached to the vessel perpendicularly to the path of the electron beam. At the entrance of the electron beam was framed another window covered with an aluminium foil, 80 μm in thickness. The LiF plates used were supplied by the Harshow Chem. Co., 2 mm thick, and can transmit over 70% of Lyman-α radiation.

The Lyman-α was isolated with the VUV monochromator (Shimadzu, Model SGV-50). The light signal was detected with a photomultiplier (Hamamatsu TV Co., R268) through the wave-shifter of sodium salicylate. The output of the photomultiplier was amplified and monitored with an oscilloscope (Tektronix 475). The risetime of the detection system was about 3 μs. The negative high voltage power sypply (Hamamatsu TV Co., Model HTV-C448) for the photomultiplier was operated at 700 V and the bleeder current was about 1 mA, which was about 10^3 times the signal current.

The pulsed electron beam— a few ns of the pulse-width and 600 keV of the upper-limit energy—was generated by a Febetron 706 (Hewlett Packard Co.). The total output energy was nominally 12 J pulse^{-1}. Only a small fraction of it was absorbed by the hydrogen gas because of the low electron density. The dose absorbed by hydrogen at 760 Torr in the reaction vessel was estimated to be 10^{16} eV pulse^{-1} by using the dinitrogen oxide dosimeter. The *G*-value of nitrogen was assumed to be 12.4.[6)]

The pressure of the gases introduced into the reaction vessel was measured with a Wallace and Tiernan type aneroid manometer (Nagano Keiki Co., Model GP 15-201). The high-purity dried hydrogen (Showa Denko Co.) was passed through a trap filled with molecular sieve 4A at the temperature of liquid nitrogen. The research grade olefins: ethylene, propylene, 1-butene, *cis*- and *trans*-2-butene, 2-methyl-1-propene, and 2-methyl-2-butene, were supplied by the Takachiho Shoji Co., and were used after thorough degassing.

Results

Pure Hydrogen. Figures 2a and 2b show the oscillograms for the time-dependence of hydrogen atom-concentration obtained with pure hydrogen at 1200 Torr. As Fig. 2a shows, the formation of hydrogen atoms is completed within 20 μs after the pulse irradiation. The signal shown before 20 μs does not correspond to the true change of the concentration of hydrogen atoms, because the recovery of the detection system from the large noise induced by the electron pulse is slow.

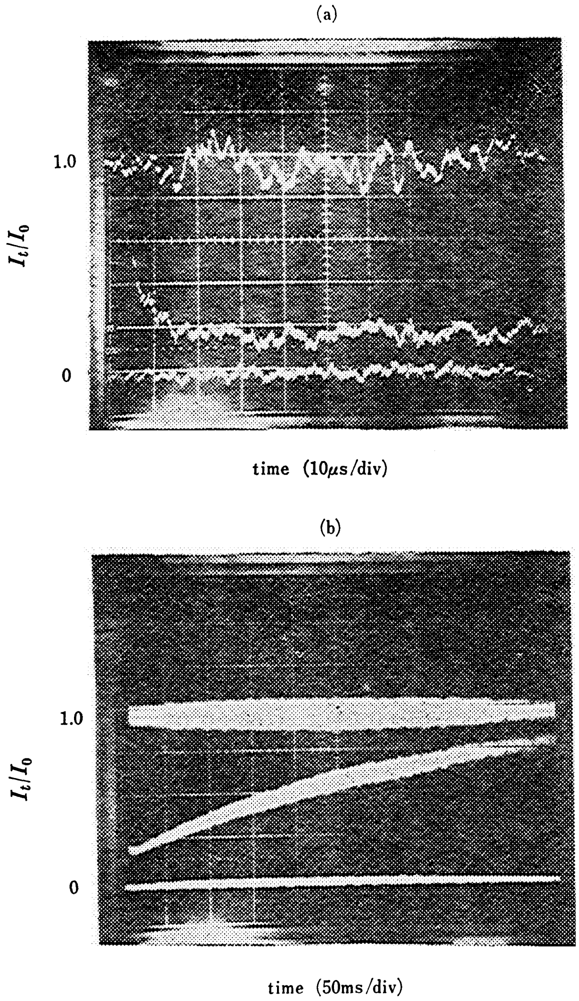

Fig. 2. Transmission of Lyman-α in the pulse irradiated pure hydrogen at 1200 Torr.

Figure 2b shows the gradual decrease of the concentration of hydrogen atoms. Most of the curves obtained with pure hydrogen at various pressures obeyed the first-order decay; for example, the lifetime obtained at 760 Torr was 0.18 s. As is shown later, this decay rate is two orders of magnitude slower than the slowest decay rate obtained in the presence of an olefin. The decrease in the concentration of hydrogen atoms observed with pure hydrogen is probably due to the diffusion of hydrogen atoms to the wall of the reaction vessel; however, the reaction with impurities eventually introduced cannot be ignored. Consequently, no further analysis has been attempted in the present experiment.

For the measurement of the concentration of hydrogen atoms, the present experiment uses the optical density for the Lyman-α radiation from the discharge lamp. However, since the profile of the Lyman-α cannot be the same as that of the absorption line of hydrogen atoms produced in the reaction vessel, the linearity between the concentration of hydrogen atoms and the optical density may not always hold.

Figure 3 shows the maximum optical density obtained with pure hydrogen after the pulse irradiation as a function of the hydrogen pressure. At low pressures, the energy transferred from high energy electrons to hydrogen gas may be regarded as proportional to the pressure; that is, the concentration of hydrogen atoms produced may be proportional to the pressure of hydrogen. As Fig. 3 shows, if the absorbance is lower than 60%, the linearity between the hydrogen atom-concentration and the optical density for Lyman-α may be used in the present experiment.

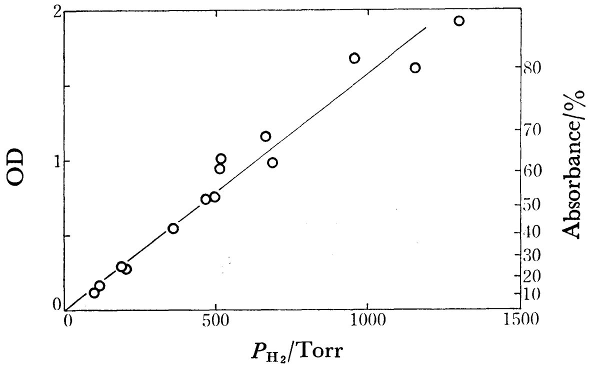

Fig. 3. The highest optical density after pulse irradiation as a function of the hydrogen pressure.

In the Presence of Olefin. Because of the high absorption coefficient of olefins at 121.6 nm, the pressure of olefins could not be raised above 0.15 Torr, which corresponds to 8.4×10^{-9} mol cm^{-3}.

One of the oscillograms for the decay of hydrogen atoms obtained in the presence of ethylene is shown in Fig. 4. From this oscillogram, we plotted the logarithm of the optical density as a function of time, as is shown in Fig. 5. The slope of this plot corresponds to the decay rate of hydrogen atoms. The rate constant of the reaction between hydrogen atoms and ethylene can be calculated by dividing this decay rate by the concentration of ethylene.

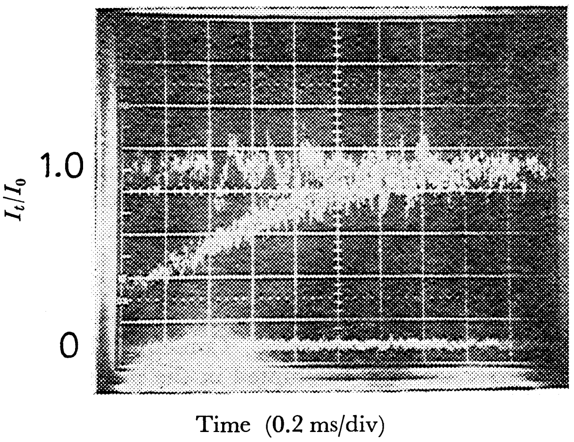

Fig. 4. Transmission of Lyman-α in the pulse irradiated hydrogen at 750 Torr containing 50 mTorr ethylene.

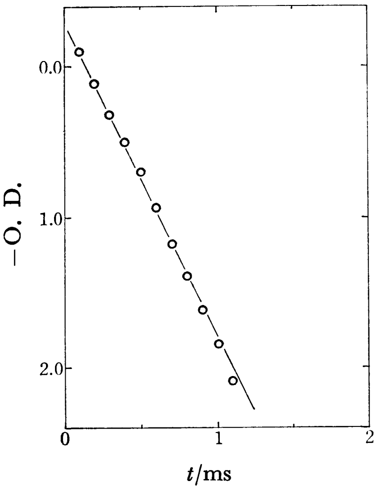

Fig. 5. The first order decay plot for the reaction of hydrogen atoms with ethylene.

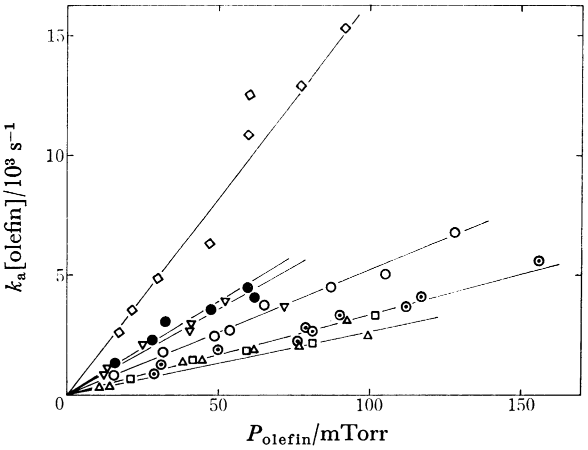

Fig. 6. Plots of the decay rates against the olefin pressures. The hydrogen pressure is around 750 Torr. ⊙: Ethylene, ○: propylene, ▽: 1-butene, □: *trans*-2-butene, △: *cis*-2-butene, ◇: 2-methyl-1-propene, ●: 2-methyl-2-butene.

All of the rate constants thus calculated are summarized in the last column of Table 1. The hydrogen pressure ranges from 200 to 1200 Torr and the olefin pressure from 0.02 to 0.15 Torr. The rate constant obtained with an olefin is independent of both the hydrogen and olefin pressures within the experimental errors. Figure 6 shows the decay rates obtained at around 750 Torr of hydrogen as functions of the pressures of olefins examined.

Discussion

The Initial Concentration of Hydrogen Atoms. Since no stable products can be obtained, the radiolysis of hydrogen has not been investigated except for that of the mixture of hydrogen and deuterium. For this mixture system, the famous chain reaction:

TABLE 1. ABSOLUTE RATE CONSTANTS OF REACTION OF HYDROGEN ATOMS WITH OLEFINS AT ROOM TEMPERATURE

Author[a]	DLT	KD	DNW	BL	KPB	MSHP	This work
Method[b]	FD/MS	FD/CA	FD/MS	FP/RF	FP/RF	PR/RA	PR/RA
Pressure/Torr	2—25(∞)[c]	≃2	0.4—2.8	5—75(∞)[c]	5—500(∞)[c]	800—1650	200—1200
Third body	He	Ar	He	He, N_2	He	H_2	H_2
$[Olefin]_0/[H]_0$	1—100	≃3	0.01	>100	>100	>1000	>100
			$k_a/10^{-12}$ cm^3 molecule^{-1} s^{-1}				
Ethylene	2.0±0.7	0.18		1.00±0.15	1.36±0.19	1.25±0.09	1.1±0.1
Propylene	1.3±0.4		(0.76±0.04)[d]		1.61±0.04	1.68±0.04	1.7±0.1
1-Butene	1.5±0.45		1.38±0.08				2.0±0.5
trans-2-Butene			0.89±0.07	1.00±0.15			1.1±0.1
cis-2-Butene			0.79±0.06				1.0±0.1
2-Methyl-1-propene		5.3	(0.7)[d]	3.8±0.6			5.2±0.6
2-Methyl-2-butene			1.51±0.16				2.4±0.3

a) DLT: Dodonov, Lavrovskaya, and Tal'roze, Ref. 15; KD: Knox and Dalgleish, Ref. 16; DNW: Daby, Niki, and Weinstock, Ref. 17; BL: Braun and Lenzi, Ref. 18; KPB: Kurylo, Peterson, and Braun, Refs. 11 and 19; MSHP: Mihelcic, Schubert, Höfler, and Potzinger, Ref. 2. b) FD, flow discharge; MS, mass spectrometry; CA, calorimetry; FP, flash photolysis; RF, resonance fluorescence; PR, pulse radiolysis; RA, resonance absorption. c) The value in this column is the one extrapolated at infinite pressure. d) The values in parentheses are less reliable.

$$H_2^+ + H_2 \rightarrow H_3^+ + H,$$

$$H_3^+ + H_2 \rightarrow H_2 + H_3^+,$$

has been studied.[7] However, the G-value of hydrogen atoms has not been measured.

According to the theoretical calculation,[8] the G-values of initial active species in the radiolysis of hydrogen are as follows: $G(H_2^*$, excited state$)=1.92$, $G(H^*$, hot atoms$)=0.94$, $G(H)=2.49$, $G(H^+)=0.40$, and $G(H_2^+)=2.43$. With these values, we can estimate the upper limit of the G-value of hydrogen atoms.

$$\begin{aligned} G(H) &= 1.92 \times 2 + 0.94 + 2.49 + 0.40 + 2.43 \times 2 \\ &= 12.53 \end{aligned}$$

Using the absorbed dose of 10^{16} eV pulse^{-1}, the initial concentration of hydrogen atoms in the reaction system can be estimated to be 10^{-11} mol cm^{-3}.

An independent estimation can be made as follows. In the study of the reaction of hydrogen atoms, Michael and Weston measured the relationship between the optical density for Lyman-α and the concentration of hydrogen atoms.[9] The optical density of 0.5 was obtained at the hydrogen atom-concentration of 13.3×10^{12} atoms cm^{-3} with the optical path of 3.5 cm. Since their procedure is similar to the method in the present experiment, let us assume that the relation obtained by Michael and Weston holds for the present measurement, in which the optical path is 11 cm. Then, the concentration of hydrogen atoms at the optical density of 0.5 can be calculated to be 0.7×10^{-11} mol cm^{-3}.

The lowest olefin pressure used in the present experiment was 0.02 Torr, which corresponds to 1.0×10^{-9} mol cm^{-3}. The concentration ratio [H]/[olefin], therefore, is always smaller than 10^{-2}.

Active Species other than Hydrogen Atoms. The thermalization times of high energy electrons in various gases have been measured by Warman and Sauer.[10] In hydrogen gas, the product of the thermalization time and pressure, $\tau_{th}\times p$, was estimated to be 1.5×10^{-6} s Torr; *i.e.*, the thermalization time in hydrogen at 760 Torr is about 2 ns. Since the species heavier than electrons are thermalized more rapidly than electrons, all of the active species produced in hydrogen must be thermalized in a few ns after the electron pulse.

The neutralization time is one of the problems in radiation chemistry. In the study of the emission from the helium–mercury system irradiated by high energy electrons, we have recently measured the time-dependence of the emission and found that the slowest emission resulted from the neutralization reaction between mercury ions and thermalized electrons in helium at 760 Torr, which was completed within 10 μs.[11] Consequently, we can conclude that, at 20 μs after the pulse irradiation, no active species other than hydrogen atoms are present in the reaction system and that all hydrogen atoms are thermalized.

The Contribution of the Reaction of Alkyl Radicals. It is now well known that the reaction between hydrogen atoms and olefins is mainly the addition reaction forming alkyl radicals, and that the abstraction reactions of a hydrogen atom from an olefin make up less than 10% of the total reaction.[4]

$$\left.\begin{aligned} H + \text{Olefin} &\rightarrow R & (1)\\ &\rightarrow H_2 + R' & (1') \end{aligned}\right\} k_a$$

If the pressure in the reaction system is low, the radical produced in Reaction 1 may decompose before the thermalization. In the case of ethylene, this decomposition leads to the reformation of hydrogen atoms, so that the apparent decay rate of hydrogen atoms may be decreased with the decrease in the total pressure. However, as stated in the Results section, no such pressure dependence could be observed under the present experimental condition. Probably such a decomposition would occur at pressures lower than 200 Torr. In the present experiment, we could not make any measurements at pressures lower than 200 Torr, because the concentration of hydrogen atoms produced was too low for the measurement of decay rate.

The successive reactions of the radicals produced in Reaction 1 may be written as follows:

$$\left.\begin{aligned} R + R &\rightarrow R_2 & (2)\\ &\rightarrow RH + \text{Olefin} & (2') \end{aligned}\right\} k_b$$

$$\left.\begin{aligned} R + H &\rightarrow RH & (3)\\ &\rightarrow H_2 + \text{Olefin} & (3') \end{aligned}\right\} k_c$$

If Reactions 3 and 3′ are the only process for the disappearance of alkyl radicals, the decay rate of hydrogen atoms would become twice the value of k_a, the sum of the rate constants of Reactions 1 and 1′. However, Reactions 2 and 2′ are also fast processes and contribute to the disappearance of alkyl radicals. If the concentration ratio [H]/[olefin] is infinitely small, the apparent decay rate of hydrogen atoms is exactly equal to the sum of the rate of Reactions 1 and 1′.

In order to estimate the contribution of Reactions 3 and 3′, we defined the following correction factor:

$$\gamma = \frac{-\mathrm{d}\ln[H]/\mathrm{d}t}{k_a[\text{Olefin}]_0}.$$

Here $[\text{olefin}]_0$ stands for the initial concentration of olefins. On the basis of the reaction mechanism from (1) to (3′), we can construct simultaneous differential equations for [H], [olefin], and [R]. Using the Runge-Kutta numerical integration procedure, we calculated the value of γ as functions of the ratio of $[\text{olefin}]_0$ to $[H]_0$ and of the ratio of k_a/k_c. In this calculation, the following values were assumed: $k_b=9.0\times 10^{-12}$ cm^3 mol-

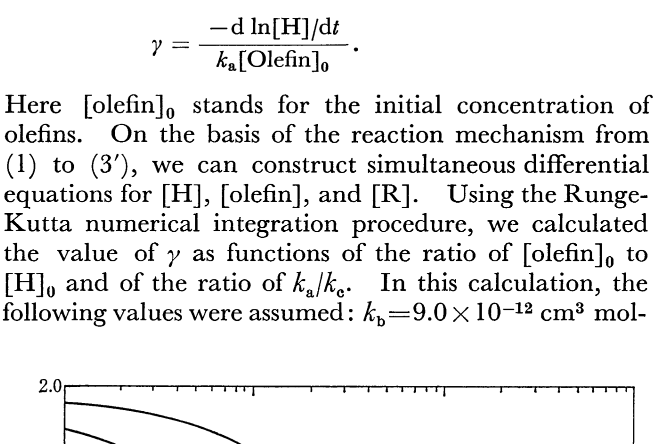

Fig. 7. The correction factor, γ, as functions of the ratios, $[\text{olefin}]_0/[H]_0$ and k_a/k_c.

TABLE 2. RELATIVE RATE CONSTANTS OF REACTION OF HYDROGEN ATOMS WITH OLEFINS AT ROOM TEMPERATURE

Author[a)]	JC	WC	CD	CKMY	This work
Method[b)]	Hg/PRA	PH/PRA	Hg/PRA	Hg/RA	PR/RA
Pressure/Torr	$\simeq$435	10—760	600—700	10—15	200—1200
Third body	n-C_4H_{10}	CO_2	H_2	He	H_2
$[\text{Olefin}]_0/[\text{H}]_0$	$\gg 1$	>100	$\gg 1$	>100	>100
	Relative rate constant				
Ethylene	(0.53)	0.62	0.60	0.41	0.63
Propylene	1.00	1.00	1.00	1.00	1.00
1-Butene	1.12	1.00		1.42	1.17
trans-2-Butene	0.63			0.57	0.63
cis-2-Butene	0.48			0.43	0.57
2-Methyl-1-propene	2.41	2.44	2.46	3.58	3.01
2-Methyl-2-butene			1.07		1.36

a) JC: Jennings and Cvetanović, Ref. 3; WC: Woolley and Cvetanović, Ref. 5; CD: Cvetanović and Doyle, Ref. 4; CKMY: Cowfer, Keil, Michael, and Yeh, Ref. 14. b) Hg, mercury photosensitization; PA, pulse radiolysis; PH, photolysis; PRA, product analysis; RA, resonance absorption. c) The value in parentheses is less reliable.

ecule^{-1} s^{-1},[12)] $k_c=6.0\times10^{-11}$ cm^3 molecule^{-1} s^{-1},[13)] and $[\text{H}]_0=6.0\times10^{12}$ molecule cm^{-3}. The result is shown in Fig. 7.

In the present experiment, $[\text{olefin}]_0/[\text{H}]_0>10^2$ and k_a/k_c is of the order of 10^{-2}. Therefore, the value of γ must be lower than 1.1. This means that no correction is needed for the present measurement of k_a.

Comparison with Other Measurements. Table 1 compares some of the measurements made for obtaining the absolute rate constants of reaction of hydrogen atoms with simple olefins.

As Mihelcic and coworkers summarized, numerous measurements have been reported for the reaction with ethylene.[2)] The rate constants reported range from 0.15 to 1.5×10^{-12} cm^3 molecule^{-1} s^{-1}. The value obtained by Hikida *et al.* is $0.91\pm0.09\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. The present result lies between the values obtained by two measurements in which the pulse radiolysis technique was used.

On the other hand, Table 2 compares our result with the relative rate constants obtained by Cvetanović and coworkers[3—5)] and Cowfer *et al.*[14)] Except for the values obtained with 2-methyl-1-propene and 2-methyl-2-butene, the present result is in good agreement with those reported by Cvetanović.

References

1) T. Hikida, J. A. Eyre, and L. M. Dorfman, *J. Chem. Phys.*, **54**, 3422 (1971).

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

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

4) R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, **50**, 4705 (1969).

5) G. R. Woolley and R. J. Cvetanović, *J. Chem. Phys.*, **50**, 4697 (1969).

6) C. Willis, O. A. Miller, A. E. Rothwell, and A. W. Boyd, *Adv. Chem. Ser.*, **81**, 539 (1968).

7) T. Terao and R. A. Back, *J. Phys. Chem.*, **73**, 3884 (1969).

8) K. Okazaki and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 3523 (1975).

9) J. V. Michael and R. E. Weston, Jr., *J. Chem. Phys.*, **45**, 3632 (1966).

10) J. M. Warman and M. C. Sauer, Jr., *J. Chem. Phys.*, **62**, 1971 (1975).

11) S. Sato, K. Okazaki, M. Yamabe, H. Umemoto, S. Tsunashima, T. Ueno, A. Yokoyama, and Y. Hatano, *Chem. Lett.*, **1976**, 385.

12) J. A. Kerr and A. F. P. Dickenson, *Prog. React. Kinet.*, **1**, 105 (1961).

13) M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, **53**, 2776 (1970).

14) J. A. Cowfer, D. G. Keil, J. V. Michael, and C. Yeh, *J. Phys. Chem.*, **75**, 1584 (1971).

15) A. F. Dodonov, G. K. Lavrovskaya, and V. L. Tal'roze, *Kinet. Katal.*, **10**, 22 (1969).

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

17) E. E. Daby, H. Niki, and B. Weinstock, *J. Phys. Chem.*, **75**, 1601 (1971).

18) W. Braun and M. Lenzi, *Discuss. Faraday Soc.*, **44**, 252 (1967).

19) M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, **54**, 4662 (1971).