The Rate Constants for H and D-Atom Additions to O_2, NO, Acetylene, and 1,3-Butadiene

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Pulse radiolysis has been combined with Lyman-α absorption spectroscopy for the measurement of absolute rate constants for the addition reactions of H and D-atoms to oxygen, nitrogen monoxide, acetylene-d_0 and -d_2, and 1,3-butadiene at room temperature. The rate constants obtained with O_2 and NO were in good agreement with the results previously reported and no H/D isotope effect was found. With acetylenes and 1,3-butadiene, the following rate constants were obtained (units of cm^3 $molecule^{-1}$ s^{-1}): $(3.8\pm0.4)\times10^{-13}$ for $H+C_2H_2$; $(2.6\pm0.2)\times10^{-13}$ for $D+C_2H_2$; $(3.8\pm0.2)\times10^{-13}$ for $H+C_2D_2$; $(2.5\pm0.2)\times10^{-13}$ for $D+C_2D_2$; $(8.5\pm1.5)\times10^{-12}$ for $H+1,3\text{-}C_4H_6$; $(7.5\pm0.6)\times10^{-12}$ for $D+1,3\text{-}C_4H_6$. These results are compared to previous studies, and the H/D isotope effect discussed.

In previous papers the absolute rate constants for the addition reactions of H and D-atoms to seven mono-olefins were reported.[1,2] The technique used for the measurement can readily be extended to the reactions with other reactants. This paper describes the results obtained with oxygen, nitrogen monoxide, acetylene-d_0 and -d_2, and 1,3-butadiene.

Experimental

The apparatus and procedures used in this study are the same as those previously described for the reactions of hydrogen and deuterium atoms with olefins.[1,2]

Research grade oxygen, nitrogen monoxide, acetylene-d_0, and 1,3-butadiene (Takachiho Shoji Co.) were used without further purification. Acetylene-d_2 was synthesized by the reaction of D_2O (99.99% up; Merck Co.) with CaC_2 (Tokyo Kasei Co.), which was heated at approximately 500 °C for 70 h in vacuum prior to use. The acetylene-d_2 thus obtained was introduced into a flask containing sulfuric acid and shaken for 1 h to remove hydrogen sulfide, ammonia, and phosphine. The mass and infrared spectra showed that the purity of acetylene-d_2 was better than 99%.

Results and Discussion

Reaction with Oxygen. Figure 1 shows the oscillogram for the time dependence of the concentration of H-atoms obtained with 747 Torr (1 Torr ≃133.322 Pa) hydrogen containing 0.93 Torr oxygen, and the first order decay rates thus obtained are plotted as functions of the initial pressures of hydrogen and oxygen in Figs. 2 and 3, respectively. The linear relationships obtained are consistent with the widely accepted reaction mechanism, *i.e.*, a third order combination reaction of hydrogen atoms with oxygen:

$$H + O_2 + H_2 \longrightarrow HO_2 + H_2$$

The rate constant was calculated to be $(3.0\pm0.6)\times10^{-32}$ cm^6 $molecule^{-2}$ s^{-1}, a value somewhat smaller than that reported by Hikida *et al.*, $(4.7\pm1.1)\times10^{-32}$ cm^6 $molecule^{-2}$ s^{-1}.[3]

A similar experiment employing deuterium in place of hydrogen gave a rate constant for the reaction,

$$D + O_2 + D_2 \longrightarrow DO_2 + D_2$$

as $(2.9\pm1.3)\times10^{-32}$ cm^6 $molecule^{-2}$ s^{-1}. No H/D isotope effect was found.

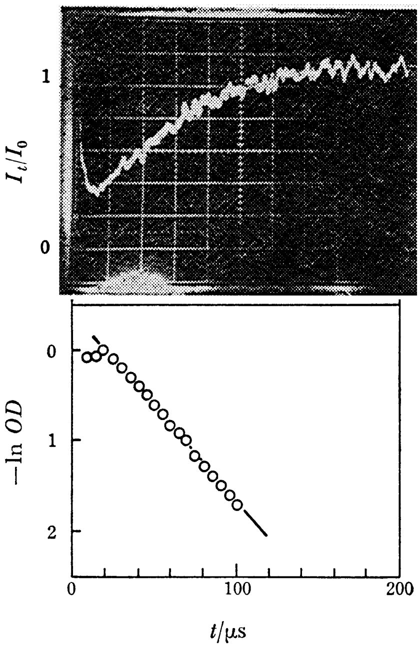

Fig. 1. The decay curve of hydrogen atoms due to the reaction of $H+O_2+H_2 \rightarrow HO_2+H_2$, and the first order plot of this decay curve. Temperature is 298 K. The pressure of hydrogen is 747 Torr; pressure of oxygen 0.93 Torr.

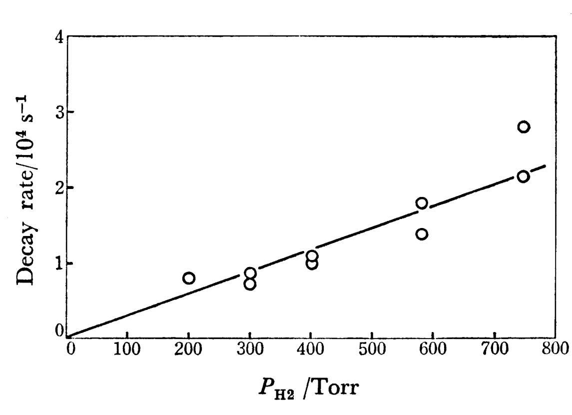

Fig. 2. The decay rate as a function of the pressure of hydrogen. The pressure of oxygen is 0.95 ± 0.02 Torr.

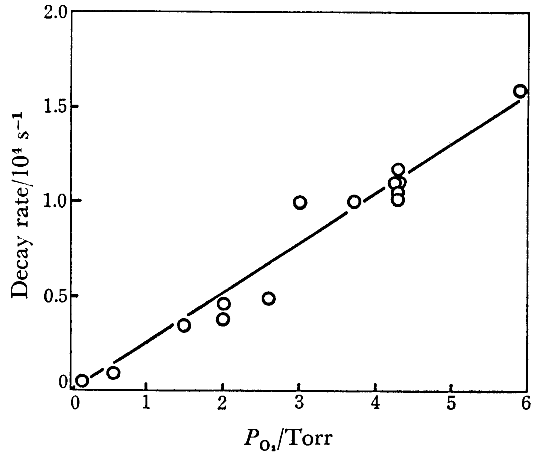

Fig. 3. The decay rate as a function of the pressure of oxygen. The pressure of hydrogen is 750±4 Torr.

Reaction with Nitrogen Monoxide. This is a well documented third order reaction. Thirty measurements, in which the hydrogen and deuterium pressures were changed from 100 to 900 Torr and the nitrogen monoxide pressure from 0.05 to 0.85 Torr, gave the following rate constant: $(4.6\pm0.6)\times10^{-32}$ cm^6 molecule^{-2} s^{-1} for the reaction:

$$H + NO + H_2 \longrightarrow HNO + H_2$$

and $(4.4\pm1.0)\times10^{-32}$ cm^6 molecule^{-2} s^{-1} for the reaction:

$$D + NO + D_2 \longrightarrow DNO + D_2.$$

Again no isotope effect could be observed. Table 1 compares previous studies for this reaction where it can be seen that agreement is within experimental error.

TABLE 1. THE RATE CONSTANT OF REACTION FOR $H+NO+H_2 \rightarrow HNO+H_2$ AT ROOM TEMPERATURE

Author[a]	P_{total}/Torr	Technique[b]	$k/10^{-32}$ cm^6 molecule^{-2} s^{-1}	Ref.
CT	0.7—3	DF-CL	4.1±0.4	6, 7)
HT	0.4—3	DF-CL	5.7±0.5	8)
HED	100—1500	PR-RA	3.9±0.6	3)
Present	100—900	PR-RA	4.6±0.6	

a) CT: Clyne and Thrush; HT: Hartley and Thrush; HED: Hikida, Eyre, and Dorfman. b) DF: Discharge flow; PR: pulse radiolysis; CL: chemiluminescence of HNO*; RA: resonance absorption.

Reaction with Acetylene. Figure 4 shows the oscillogram for the time-dependence of hydrogen atom concentration obtained with 752 Torr hydrogen containing 47 mTorr acetylene after irradiation of pulsed electrons, and the first order plot for the optical density, from which the decay rate of hydrogen atoms was estimated. The decay rates thus obtained with various pressures of hydrogen, from 300 to 1200 Torr, and with a constant pressure, 73 mTorr, of acetylene are plotted in Fig. 5. The decay rate appears to be independent of hydrogen pressure in the range studied.

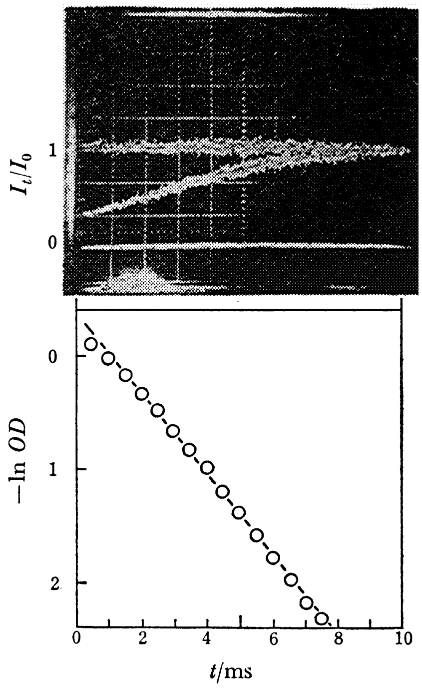

Fig. 4. The decay curve of hydrogen atoms due to the reaction of $H+C_2H_2 \rightarrow C_2H_3$, and the first order plot of this decay curve. Temperature is 298 K. The pressure of hydrogen is 752 Torr; pressure of acetylene 47 mTorr.

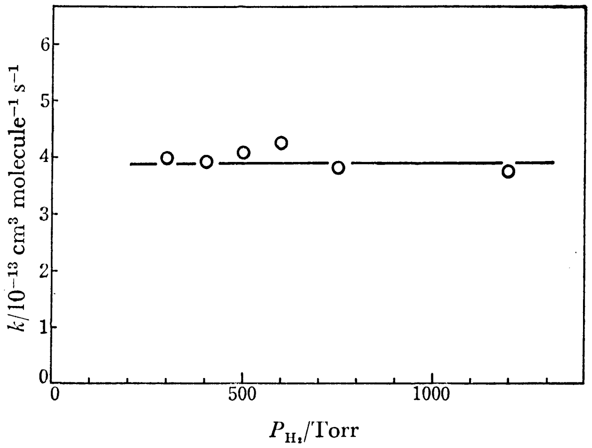

Fig. 5. The rate constant of reaction of hydrogen atoms with acetylene as a function of the pressure of hydrogen. The pressure of acetylene is 73 mTorr.

It is known that the apparent decay rate of hydrogen atoms in the reaction with acetylene is pressure dependent at low total pressure, because the reverse reaction: $C_2H_3^* \rightarrow H+C_2H_2$ cannot be ignored.[4] The present result suggests that such a reverse reaction becomes important only below 300 Torr in hydrogen. Unfortunately, the present method cannot be applied to low pressures, since the amount of hydrogen atoms produced by pulse irradiation is proportional to the total pressure and the concentration obtained below 300 Torr is too small for decay measurement.

Figures 6 and 7 show the decay rates of H and D-atoms as functions of the pressure of acetylene-d_0 and

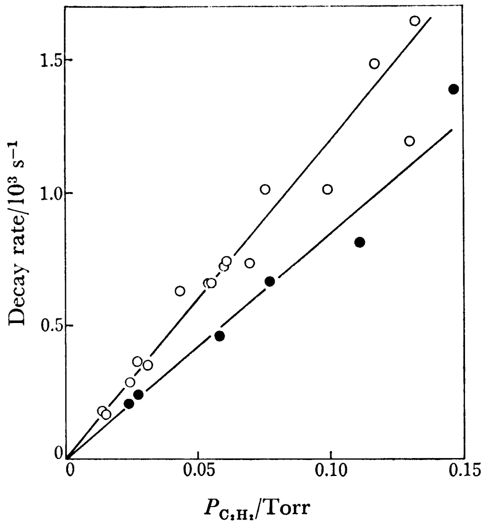

Fig. 6. The decay rates of hydrogen (○) and deuterium (●) atoms as a function of the pressure of acetylene-d_0.

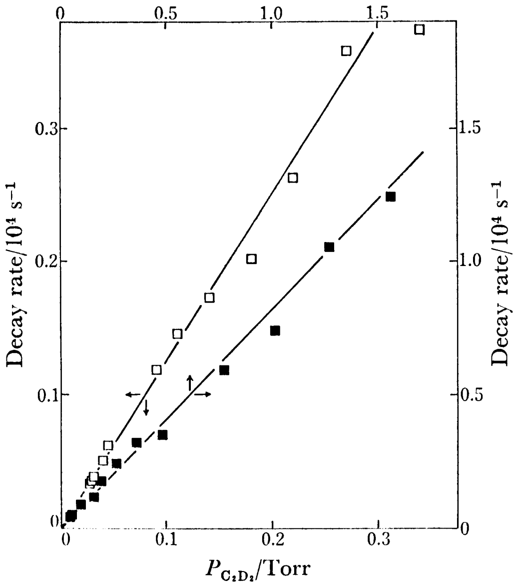

Fig. 7. The decay rates of hydrogen (□) and deuterium (■) atoms as a function of the pressure of acetylene-d_2.

Table 2. The rate constants of the reactions of hydrogen or deuterium atoms with acetylene-d_0 or -d_2 at room temperature

Reactant	$10^{13} k_H$ / cm³ molecule⁻¹ s⁻¹	$10^{13} k_D$ / cm³ molecule⁻¹ s⁻¹
C_2H_2	3.8±0.4	2.6±0.2
C_2D_2	3.8±0.2	2.5±0.2

Table 3. The rate constant of reaction for $H+C_2H_2$ at room temperature

Author[a)]	P_{total}/Torr	Technique[b)]	$k/10^{-13}$ cm³ molecule⁻¹ s⁻¹	Ref.
TL	1.0—15 (H_2)	DF-CP	0.86	9)
DL	3.5 (H_2)	DF-CP	0.134	10)
GGM	3.0 (H_2)	DF-WG	2.66	11)
MW	0.7—17.3 (He)	DF-RA	5.98(∞)[c)]	12)
MN	1.67 (He)	DF-MS	0.37	4)
HWW	0.5—30 (He)	DF-ESR	0.57(∞)	13)
IT	650 (H_2)	Hg-PA	0.91	14)
PS	10—700 (He)	FP-RF	1.56(∞)	15)
Present	200—1100 (H_2)	PR-RA	3.8	

a) TL: Tollefson and LeRoy; DL: Dingle and LeRoy; GGM: Girouard, Graber, and Myers; MW: Michael and Weston; MN: Michael and Niki; HWW: Hoyermann, Wagner, and Wolfrum; IT: Ibuki and Takezaki; PS: Payne and Stief. b) DF: Discharge flow; Hg: mercury photosensitization; FP: flash photolysis; PR: pulse radiolysis; CP: catalytic probe; WG: Wrede gauge; RA: resonance absorption; MS: mass spectrometer; ESR: electron spin resonance; PA: product analysis; RF: resonance fluorescence. c) Obtained by extrapolating to infinite pressure.

-d_2, where the pressure of hydrogen and deuterium is approximately 750 and 600 Torr respectively. It should be noted here that in the reaction of $D+C_2D_2$, the acetylene-d_2 pressure could be raised to 1.56 Torr, which is approximately 10 times that used in the other three reactions. The absorption coefficient of acetylene-d_2 appears to be very small at the resonance line of D-atoms.

The rate constant for the reaction of hydrogen atoms with acetylene is one order of magnitude smaller than those obtained with olefins. Consequently it was presumed that the vinyl radicals produced in the reaction of hydrogen atoms with acetylene participate in the decay of hydrogen atoms.[1)] However, the fact that a linear relationship between the decay rate of D-atoms and the C_2D_2 pressure exists up to 1.56 Torr of acetylene-d_2, suggests that the decay rates observed in the present experiments do correspond to the reactions of H or D-atoms with acetylene-d_0 or -d_2.

Table 2 summarizes the rate constants obtained in the present experiments, and Table 3 compares some previous studies in the reaction of $H+C_2H_2$. Most previous measurements were conducted using the discharge flow system under low pressures, where the reverse reaction, *i.e.*, the decomposition of excited vinyl radicals reproducing hydrogen atoms, may be important. Therefore, the value obtained here must be compared with those obtained by extrapolation to infinite pressure.

In a previous paper,[1)] the rate constant in the reaction of $H+C_2H_4$ was reported and compared with previous studies. The value reported by Payne and Stief was in very good agreement with that of the present authors. The value for $H+C_2H_2$ obtained by Payne and Stief however, was less than a half. No proper interpretation for this discrepancy has been found.

Reaction with 1,3-Butadiene. The rate constants of hydrogen and deuterium atoms with 1,3-butadiene at room temperature were measured by an analogous method. The hydrogen pressure was 500 to 600 Torr and the 1,3-butadiene pressure from 0.02 to 0.09 Torr. The decay rates of hydrogen and deuterium atoms were found to be linearly proportional to the pressure of 1,3-butadiene. The rate constants obtained were as follows (units of cm³ molecule⁻¹ s⁻¹):

$$k(\mathrm{H}+1{,}3\text{-butadiene}) = (8.5\pm1.5)\times10^{-12}$$

$$k(\mathrm{D}+1\text{-}3\text{-butadiene}) = (7.5\pm0.6)\times10^{-12}$$

These results are in fair agreement with those reported by Daby *et al.*, $(8.3\pm1.1)\times10^{-12}$ for the reaction of H +1,3-butadiene and $(5.3\pm1.1)\times10^{-12}$ for D+1,3-butadiene.[5] Daby *et al.* used a discharge flow system combined with a mass spectrometer. This agreement suggests that vibrationally excited radicals formed by the addition reaction do not release a hydrogen atom under low total pressure.

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