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Absolute Rate Constants for the Reactions of $O(^3P)$ with Several Molecules

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Absolute rate constants were measured for several reactions of ground-state oxygen atoms at 296±2 K. The pulse-radiolysis of O_2, CO, or CO_2 in the He diluent was used to produce oxygen atoms, and the atomic concentration was monitored by the resonance absorption. The measurements were made in the pressure range from 50 to 950 Torr (1 Torr $\simeq$133.3 Pa). The rate constants thus obtained were $(2.5\pm0.3)\times10^{-34}$ for $O+O_2+He$ and $(1.0\pm0.2)\times10^{-35}$ for O+CO+He in units of cm^6 $molecule^{-2}$ s^{-1} (1 cm^6 $molecule^{-2}$ $s^{-1}\simeq3.626\times10^{35}$ m^6 mol^{-2} s^{-1}). For simple olefins, the following bimolecular rate constants ($k/10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) were obtained: Ethylene (1.0±0.2), propene (4.7±0.3), 1-butene (4.7±0.5), *trans*-2-butene (23±3), *cis*-2-butene (20±3), 2-methylpropene (17±2), 2-methyl-2-butene (55±5), 1,3-butadiene (20±2), (1 cm^3 $molecule^{-1}$ $s^{-1}\simeq6.022\times10^{17}$ m^3 mol^{-1} s^{-1}). These rate constants were in fair agreement with the literature values.

The reactions of oxygen atoms with unsaturated hydrocarbons have been investigated by a variety of techniques. Cvetanović used a system of product analysis for the determination of the relative rate constants in his early studies.[1] For the production of oxygen atoms, the mercury-photosensitized decomposition of dinitrogen oxide and the photolysis of nitrogen dioxide were employed. The absolute rate constants were measured in discharge-flow systems combined with a mass spectrometer[2-5] or ESR.[6,7] This technique can, however, be used in only a limited low-pressure range, and it often needs stoichiometry corrections, because of the small difference in concentration between atoms and reactants in the reaction system.

Instead of the discharge-flow method, two other techniques have been employed so as to investigate the reactions under relatively high pressures, at which the concentration of the oxygen atoms is generally much lower than that of the reactants, and where no stoichiometry corrections are necessary. One is the flash-photolysis technique, which is often employed together with the method of resonance fluorescence[4,8-12] or the chemiluminescence of NO_2^*[13-15] for the time-resolved measurement of the oxygen-atom concentration. The other is the modulation-phase shift technique, in which oxygen atoms are produced by the modulated mercury-photosensitization of dinitrogen oxide, and the rate constants are obtained as the phase shift between the incident radiation and the NO_2^* chemiluminescence.[16-21]

Although a number of rate constants for the reactions of oxygen atoms with unsaturated hydrocarbons have been obtained by using these methods, there remain large discrepancies between the determined values. For example, the rate constant for the reaction of oxygen atoms with ethylene, which is one of the most investigated hydrocarbons, ranges from 5.0×10^{-13} to 1.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Therefore, it is of interest to measure the rate constant using other techniques.

Recently we reported the absolute rate constants at room temperature for the reactions of H and D atoms with seven olefins, using a pulse radiolysis-resonance absorption technique.[22,23] The H and D atoms were generated in hydrogen and deuterium of some hundreds of Torr by the irradiation of an electron pulse, and were monitored by means of the light absorption at the Lyman-α line. This technique was initiated by Bishop and Dorfman[24] and developed by Mihelcic *et al.*[25] The results showed good agreement with those of previous works, and confirmed the validity of our apparatus and technique. This technique was extended to the rate constant measurements on the reactions of nitrogen atoms in the ground state with nitrogen monoxide, seven olefins, acetylene, and 1,3-butadiene.[26] The quenching rate coefficients of $N(^2D)$ and $N(^2P)$ by N_2 were also obtained.[27]

In the present work, this technique is extended to the measurement of the absolute rate constants for the reactions of oxygen atoms.

Experimental

The details of the apparatus and technique were given in the previous paper;[22] hence, only additional improvements and the major features will be described here.

Figure 1 shows the apparatus schematically. As the source of oxygen atoms, O_2(1.2—6.0 Torr), CO($\approx$11 Torr), or CO_2 ($\approx$2.6 Torr) diluted with He (50—950 Torr) was used, and the gas mixture was irradiated with an electron pulse (pulse width, 3 ns; upper-limit energy, 600 keV) generated by Febetron 706 (Hewlett Packard Co.). The energy absorbed by 900 Torr He was estimated to be 4×10^{16} eV per pulse at a 25 kV DC charging voltage of

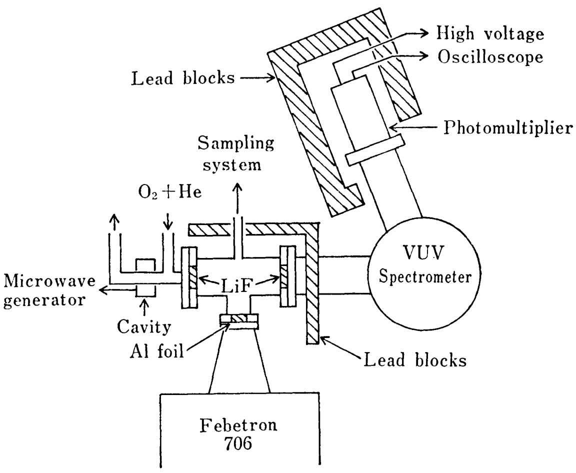

Fig. 1. Schematic diagram of the apparatus.

Febetron 706, on the basis of the measurement of the yields of nitrogen and oxygen in the pulse-irradiated dinitrogen oxide at 900 Torr. The values of 12.4 and 2.1 were taken as the *G*-values of nitrogen and oxygen,[28] and the energy absorption was assumed to be proportional to the electron density.

The concentration of oxygen atoms was followed by observing the light absorption of the resonance triplet lines of oxygen atoms around 130 nm. The resonance lamp used previously was a water-cooled capillary discharge lamp powered by a DC-current regulator. Since the output of the lamp fluctuated in the time range of μs ($S/N=5$ in the worst case), it was replaced by an electrodeless discharge lamp made of a Pyrex glass tube, 8 mm in inside diameter. A 2450 MHz microwave generator (Ito Chotanpa Co.) was operated at 70 W. A mixture of O_2 (10%) and He was made to flow at the total pressure of 5 Torr. Under these conditions, the highest intensity was obtained at the resonance line of the oxygen atoms. The resonance triplet lines ($^3S_1 \rightarrow {}^3P_{2,1,0}$: 130.217, 130.487, and 130.604 nm) emitted from the lamp passed through the reaction cell, on both sides of which LiF windows (Harshow Chem. Co.) were mounted, and were isolated with a vacuum ultraviolet spectrometer (Shimadzu, Model SGV-50). Since the slit width was open wide (1 mm), the triplet was not resolved. Consequently, the rate constants obtained in the present work are those of the overall reactions of oxygen atoms in the $^3P_2$, $^3P_1$, and $^3P_0$ states. The vacuum ultraviolet light was directly detected with a head-on-type photomultiplier (Hamamatsu TV Co., R976) amplified and monitored with an oscilloscope (Tektronix 465). Lead blocks were placed as is shown in Fig. 1 in order to protect the photomultiplier from the X-rays generated by the electron pulse.

The high-purity, dried He (Nihon Helium Co.) was passed through a trap filled with molecular sieve 4A at 77 K before use. The O_2 (Nihon Sanso Co.) and CO (Takachiho shoji Co.) were used without further purification. Research-grade olefins and CO_2 (Takachiho Shoji Co.) were used after thorough degassing.

Results

For the time-resolved measurements of the concentration of oxygen atoms, we used the resonance absorption method based on Lambert-Beer's law:

$$I_{tr} = I_0 \exp(-D), \qquad \text{(I)}$$

$$D = \varepsilon[\mathrm{O}]l. \qquad \text{(II)}$$

The relative intensities of the incident and transmitted light, I_0 and I_{tr}, were evaluated from photographs such as Fig. 3a, and the optical density, D, was calculated by means of Eq. I. Since the molar absorption coefficient, ε, and the light-pass length, l, are constant, the oxygen-atom concentration, [O], should be proportional to D. However, Beer's law (II) does not always hold, because the line shape of the emission from a lamp is generally broader than that of the absorption in the reaction cell. Figure 2 shows the initial optical density as a function of the He pressure in the range from 50 to 950 Torr. The oxygen pressure was fixed at 3.0 Torr. In the present experiment, the absorption of energy by the gas mixture occurs through He, since O_2 is a minor component, and oxygen atoms are generated in proportion to the He pressure. Consequently, the plots shown in Fig. 2 correspond to the relationship between [O] and D. Evidently a linearity holds below the unity of D. In only this range of D, the photographs obtained were analyzed. As will be described below, the unity of D corresponds to the oxygen-atom concentration of 3×10^{13} cm^{-3}.

The System of O_2 in He. Figure 3a exhibits the transmittance, I_{tr}/I_0, as a function of the time obtained with the O_2 system in He. With this system, all the decay curves obtained fit a first-order decay plot, such as Fig. 3b. The slope of this linear rela-

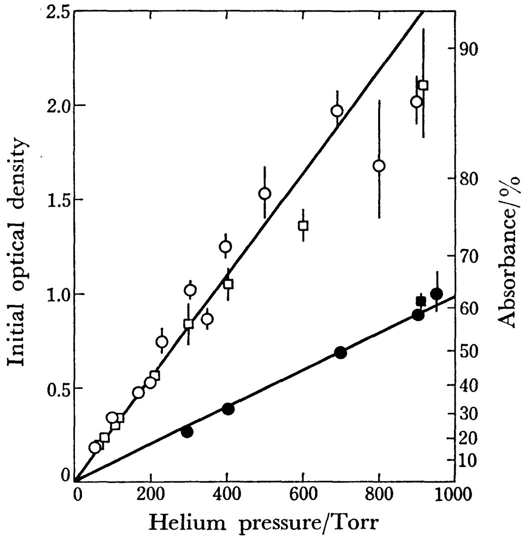

Fig. 2. Initial optical density and absorbance as a function of He pressure.
Charging voltage of Febetron is set at 25 kV (●, ■) and 28 kV (○, □). Circles were obtained with the mixture of 3 Torr oxygen and He. Squares were obtained with the same mixtures in the presence of 0.05 Torr ethylene.

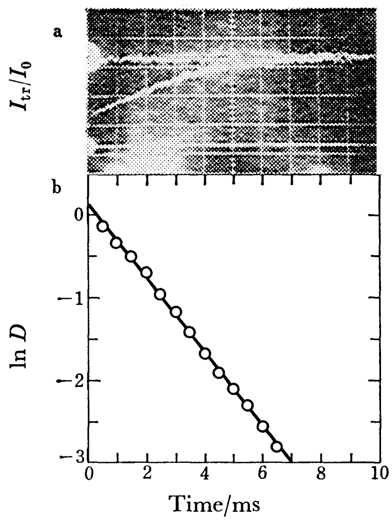

Fig. 3. Time dependence of the transmitted light at 130 nm (a) and the logarithm of the optical density (b).
This photograph was obtained within 10 ms with the mixture of 3.06 Torr oxygen and 604 Torr helium. Charging voltage of Febetron was 27 kV.

tionship gives the decay rate of the oxygen atoms. The reactions occuring in this system may be described by the next two termolecular reactions:

$$O + O_2 + He \longrightarrow O_3 + He, \qquad (1)$$

$$O + O_2 + O_2 \longrightarrow O_3 + O_2. \qquad (2)$$

The decay rate, k_{dr}, should, then, be given by this equation:

$$k_{dr} = k_1[O_2][He] + k_2[O_2]^2. \qquad (III)$$

Here, k_1 and k_2 are the rate constants of Reactions 1 and 2 respectively. The He pressure dependence of the decay rate is shown in Fig. 4, where the oxygen pressures are fixed at 1.2 and 3.0 Torr. The slope and intercept of this linear relationship should correspond to $k_1[O_2]$ and $k_2[O_2]^2$ respectively. Figure 5 shows the O_2 pressure dependence of the decay rate, where the $k_{dr}[O_2]^{-2}$'s are plotted as a function of $[O_2]^{-1}$, with two fixed pressures of He. The slope and intercept should correspond to $k_1[He]$ and k_2 respectively. From these figures, k_1 and k_2 were obtained to be $(2.5\pm0.3)\times10^{-34}$, and $(1\pm3)\times10^{-33}$ cm^6 molecule^{-2} s^{-1} respectively. Since the pressure range of oxygen could not be changed widely, the error limit for k_2 was very large.

The System of CO in He. Figure 6a was obtained by the pulse radiolysis of the mixture of 10.5 Torr of CO and 905 Torr of He at 294 K. The first-order decay plot, Fig. 6b, exhibits that the decay of oxygen atoms seems to occur in two stages. In order to explain this decay curve, we considered the participation of carbon atoms in this reaction system:

$$C + CO + M \longrightarrow C_2O + M \ (M{=}He,\ CO) \qquad (3)$$

$$O + CO + He \longrightarrow CO_2 + He \qquad (4)$$

$$O + CO + CO \longrightarrow CO_2 + CO \qquad (5)$$

$$O + C_2O \longrightarrow 2CO. \qquad (6)$$

The decay rate of the concentration of oxygen atoms is, then, given by this equation:

$$k_{dr} = k_4[CO][He] + k_5[CO]^2 + k_6[C_2O]. \qquad (IV)$$

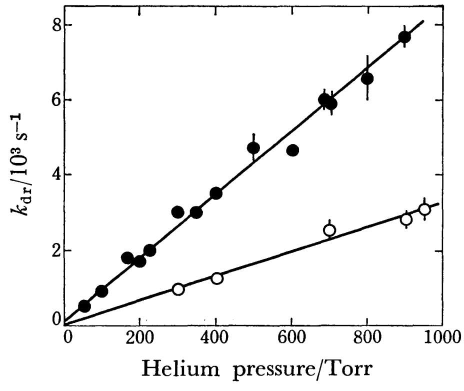

Fig. 4. Decay rate, k_{dr}, as a function of helium pressure.
The oxygen pressure is fixed at 1.2 Torr (○) and 3.0 Torr (●).

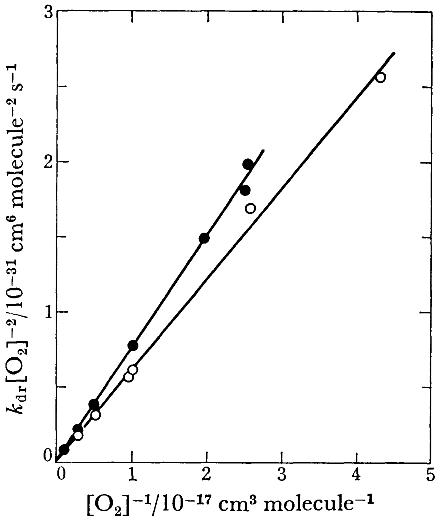

Fig. 5. $k_{dr}[O_2]^{-2}$'s as a function of $[O_2]^{-1}$.
The helium pressure is 700 Torr (○) and 900 Torr (●).

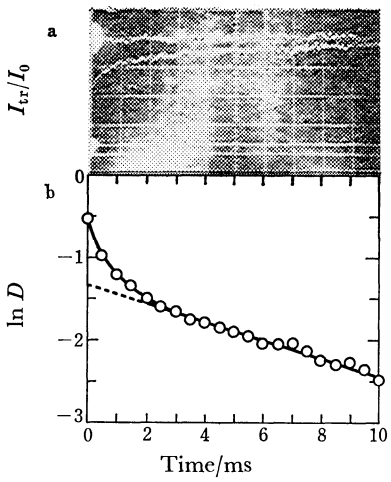

Fig. 6. Time dependence of the transmitted light at 130 nm (a) and the logarithm of the optical density (b).
Carbon monoxide pressure is 10.5 Torr and helium pressure 905 Torr.

TABLE 1. ABSOLUTE RATE CONSTANTS FOR THE $O+O_2+He \rightarrow O_3+He$ REACTION AT ROOM TEMPERATURE

Author[a]	KK	S	MW	DHK	This work
Method[b]	DF/CL	PR/AO$_3$	P, DF/CL	FP/RA	PR/RA
Pressure/Torr	0—5	(2.0—5.7)×10^4	1—8	150—543	50—950
$k/10^{-34}$ cm^6 molecule^{-2} s^{-1}	4	1.9±0.3	6.3±0.3	4.6±2.6	2.5±0.3

a) KK: Kaufman and Kelso, Ref. 34; S: Sauer, Ref. 35; MW: Mulcahy and Williams, Ref. 36; DHK: Donovan, Husain, and Kirsch, Ref. 37. b) DF: Discharge flow; CL: chemiluminescence; PR: pulse radiolysis; AO$_3$: absorption of ozone; P: pyrolysis; FP: flash photolysis; RA: resonance absorption.

The initial fast decay of oxygen atoms shown in Fig. 6b may be due to the last term of Eq. IV.

Using the rate constant of Reaction 3 (6.3×10^{-32} cm^6 molecule^{-2} s^{-1})[29] and the concentration of oxygen atoms, as will be stated below, we could estimate the rate constant of Reaction 6 to be larger than 5×10^{-11} cm^3 molecule^{-1} s^{-1}.

If this reaction mechanism is correct, the rate constants of Reactions 4 and 5 can be estimated from the slow first-order decay shown in Fig. 6b, as has been done in the case of the O_2 in the He system. Figures 7 and 8 show the pressure dependence of k_{dr} on CO and He respectively. From these figures, the rate constants of Reactions 4 and 5 can be estimated as follows: $k_4=(1.0\pm0.2)\times10^{-35}$ and $k_5=(3\pm2)\times10^{-35}$ in units of cm^6 molecule^{-2} s^{-1}.

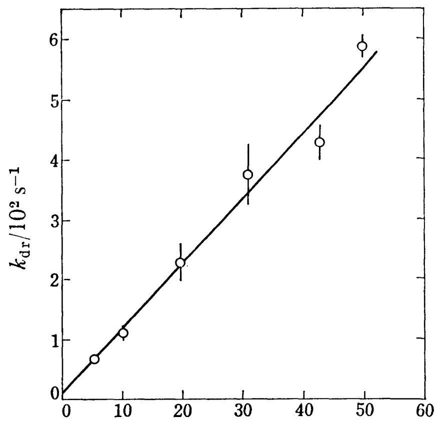

Fig. 7. The decay rate, k_{dr}, of oxygen atoms in the reaction O+CO+He as a function of carbon monoxide pressure. Helium pressure is 900 Torr.

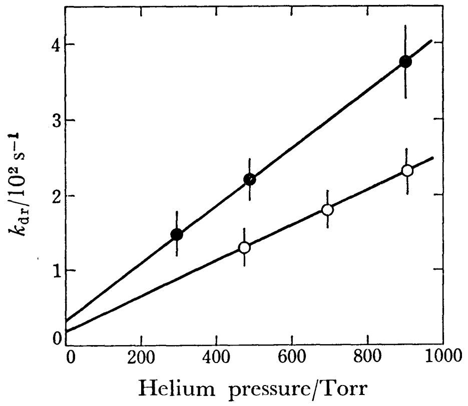

Fig. 8. The decay rate, k_{dr}, of oxygen atoms in the reaction O+CO+He as functions of helium pressure. The carbon monoxide pressures are fixed at 20 (○) and 30 (●) Torr.

The System of CO_2 in He. Similar measurements of the decay rate of oxygen atoms produced in the mixture of 2.6 Torr of carbon dioxide and He, the pressure ranging from 50 to 900 Torr, were carried out. Very slow first-order decays were found. If the oxygen atoms in this system react as follows:

$$O + CO_2 + He \longrightarrow CO_3 + He, \qquad (7)$$

then the upper limit of the rate constant of this reaction is estimated to be $(4\pm2)\times10^{-36}$ cm^6 molecule^{-2} s^{-1}.

The Reactions with Olefins. When a small amount of an olefin is present in any of the three systems of O_2 in He, CO in He, and CO_2 in He, a fast decay of the oxygen atoms can be observed. Figures 9a and b show the decay curves obtained in the absence and presence of propene respectively, with the same sweep time of 0.2 ms per division. Figure 9c represents the first-order decay plots.

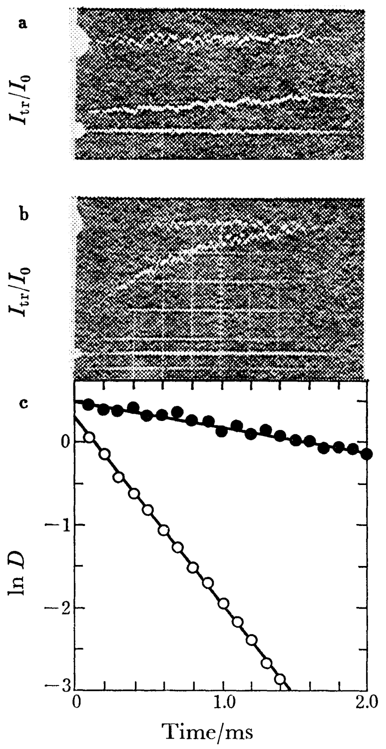

Fig. 9. Time dependence of the transmitted light at 130 nm. (a) was obtained with the mixture of 1.97 Torr O_2 and 904 Torr He, and (b) with the mixture of 0.010 Torr C_3H_6, 3.04 Torr O_2, and 903 Torr He. (c) is the first order plots of the decay curves of (a) (●) and (b) (○).

TABLE 2. ABSOLUTE RATE CONSTANTS FOR THE $O+CO+He\rightarrow CO_2+He$ REACTION AT ROOM TEMPERATURE

Author[a]	DHK	SB	SN	This work
Method[b]	FP/RA	FP/RF	FP/CL	PR/RA
Pressure/Torr		30—200	20—450	300—950
$k/10^{-35}$ cm^6 molecule^{-2} s^{-1}	<4.8	0.6 ± 0.15	0.17 ± 0.05	1.0 ± 0.2

a) DHK: Donovan, Husain, and Kirsch, Ref. 37; SB: Slanger and Black, Ref. 38; SN: Stuhl and Niki, Ref. 39. b) FP: flash photolysis; RA: resonance absorption; RF: resonance fluorescence; CL: chemiluminescence; PR: pulse radiolysis.

Figure 10 shows the decay rates of the oxygen atoms obtained by using four different sources of oxygen atoms as a function of the ethylene pressure. The slopes of these linear relationships correspond to the rate constant of the reaction of oxygen atoms with ethylene, and the intercepts, to the decay rates of oxygen atoms in each source of oxygen atoms in the absence of ethylene, *i.e.*, O_2 (3 and 6 Torr), CO (11 Torr), and CO_2 (2.6 Torr) in He (900 Torr). Evidently, the same rate constant for the reaction of the oxygen atoms with ethylene was obtained irrespective of the source of the oxygen atoms. Figure 11 shows that the rate constant is also independent of the helium pressure in the range from 50 to 1000 Torr. From these data, the rate constant of the addition reaction of the oxygen atoms to ethylene was estimated to be $(1.0\pm0.2)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. Table 3 compares previous studies of this reaction.

When the ratio of $[C_2H_4]/[He]$ was smaller than 10^{-4}, the apparent rate constant of the reaction of

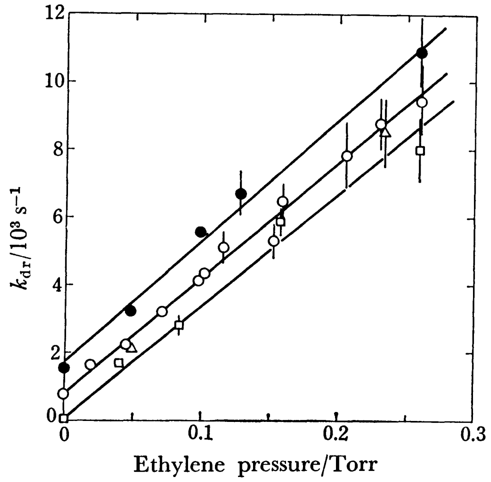

Fig. 10. The decay rates, k_{dr}, of oxygen atoms as a function of ethylene pressure.
The oxygen atom sources are 3.0 Torr O_2 (○), 6 Torr O_2 (●), 11 Torr CO (△), and 2.6 Torr CO_2 (□). Helium pressure is fixed at 900 Torr.

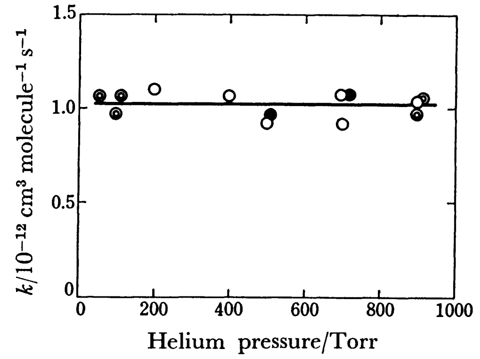

Fig. 11. The rate constant, k, for the reaction of $O+C_2H_4$ as a function of helium pressure.
The ethylene pressures are 0.20 (○), 0.10 (●) and 0.05 (◎) Torr.

TABLE 3. RATE CONSTANT FOR THE REACTION OF OXYGEN ATOMS WITH ETHYLENE AT ROOM TEMPERATURE

Author$^{a)}$	Method$^{b)}$	Pressure/Torr	$[C_2H_4]/[O]_0$	$k/10^{-13}$ cm^3 molecule^{-1} s^{-1}
ES	DF/CL	0.25—7.5	0.30—2.3	$12\pm4^{c)}$
E	DF/MS	1.4—2.4	0.38—1.6	9.5
BT	DF/ESR	1.4—2.8		5.3 ± 0.7
NDW	DF/MS	1.0—2.3	0.010—0.047	5.2 ± 0.4
WD	DF/ESR	0.90—1.33		7.5 ± 0.5
DHHKB	DF/MS	1.30—2.27	0.33—0.54	$8.67^{d)}$
SPG	DF/MS	0.78—2.14	0.010—0.018	7.7
SN	FP/CL	≈10	$>10^3$	$6.3^{+0.3}_{-0.9}$
DHHKB	FP/RF	5—240	100—1500	$8.36^{d)}$
DHHKB	FP/RA	≈50	>80	$8.80^{d)}$
SN	FP/CL	5—20	$40—1.6\times10^5$	6.25 ± 0.63
KH	FP/RF		$>1.8\times10^4$	7.96 ± 0.80
AP	FP/CL	≈26	500—2000	7.61 ± 0.76
AC	HgS/PS	23—107		5.0 ± 0.4
AP	HgS/PS	57—116		6.64 ± 0.66
FACC	HgS/PS	30—50		7.18 ± 0.75
SC	HgS/PS	30—90		6.67 ± 0.85
This work	PR/RA	50—950	100—600	10 ± 2

a) ES: Elias and Schiff, Ref. 40; E: Elias, Ref. 2; BT: Brown and Thrush, Ref. 6; NDW: Niki, Daby, and Weinstock, Ref. 3; WD: Westenberg and de Haas, Ref. 7; DHHKB: Davis, Huie, Herron, Kurylo, and Braun, Ref. 4; SPG: Slagle, Pruss, and Gutman, Ref. 5; SN: Stuhl and Niki, Refs. 13 and 14; KH: Kurylo and Huie, Ref. 8; AP: Atkinson and Pitts, Refs. 15, 20, and 21; AC: Atkinson and Cvetanović, Refs. 16 and 17; FACC: Furuyama, Atkinson, Colussi, and Cvetanović, Ref. 18; SC: Singleton and Cvetanović, Ref. 19. b) DF: discharge flow; FP: flash photolysis; HgS: Hg-photosensitization; CL: chemiluminescence; MS: mass spectrometry; ESR: electron-spin resonance; RF: resonace fluorescence; RA: resonance absorption; PS: phase shift. c) Calculated from the Arrhenius expression. d) Means of the data in the tables of Ref. 4.

the oxygen atoms was found to be a little larger than that obtained above. This is probably due to the fact that, since the amount of ethylene is small, the radicals produced in the reaction of the oxygen atoms with ethylene can compete with ethylene for the oxygen atoms. Therefore, we took the value obtained with the ratio, $[C_2H_4]/[He]$, larger than 10^{-4}. Such an anomaly could not be observed with any olefins other than ethylene.

Figure 12 summarizes the decay rates of oxygen atoms obtained with all olefins examined, as functions of olefin pressure. The rate constants thus obtained are summarized in Tables 4 and 5 together with those previously reported.

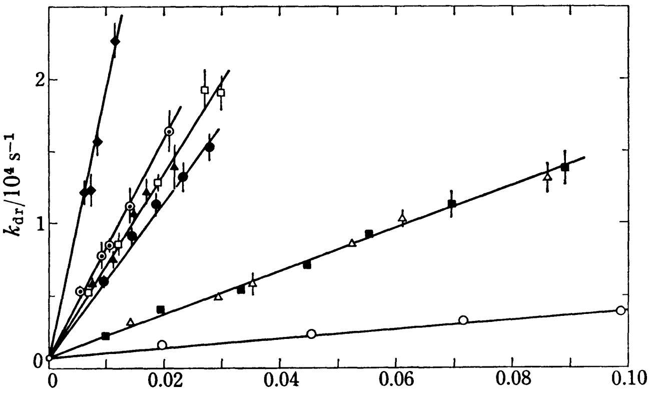

Fig. 12. The decay rates, k_{dr}, of oxygen atoms in the reactions of oxygen atoms with olefins.
Oxygen pressure is 3.0 Torr and helium pressure 900 Torr. ○: ethylene, ■: propene, △: 1-butene, ⊙: *trans*-2-butene, ▲: *cis*-2-butene, ●: 2-methylpropene, ◆: 2-methyl-2-butene, □: 1,3-butadiene.

Discussion

Initial Concentration of Oxygen Atoms. When helium containing a small amount of oxygen is irradiated with high-energy electrons, the ionization and excitation of helium occurs first, and then, the oxygen atoms in the ground (^3P) and metastable (^1D and ^1S) states are generated by the decomposition of oxygen through energy transfer from excited helium or through charge transfer from ionized helium, followed by neutralization with electrons.

Boyd *et al.* measured the *G*-value of ozone from a mixture of oxygen and helium, using Febetron 705 as the source of high-energy electrons; they found that $G(O_3)=16$ at total pressures higher than 300 Torr and with oxygen mole fractions ranging from 0.1 to 0.3.[30] In the present experiment, the mole fraction of oxygen is less than 0.06, so that the *G*-value of ozone may be smaller than 16.

In order to estimate the initial concentration of the oxygen atoms produced in a mixture of 3 Torr oxygen and 900 Torr helium, we used the following values: $G(O)=12.8$,[31] 4×10^{16} eV per pulse for absorbed dose, and 150 cm^3 for the effective volume of the reaction cell. The initial concentration of the oxygen atoms thus calculated was 3×10^{13} cm^{-3}, a value which corresponds to the unity of *D* in Fig. 2.

Influence of Other Active Species. When pulse radiolysis is used for the production of atoms, many different active species are generated together with the atoms required. As was discussed in a previous paper,[22] the participation of ionic species is completed within 10 μs after pulse irradiation; therefore, the only active species we have to consider here are two metastable oxygen atoms, ^1D and ^1S.

Resently Schofield summarized the rate constants

Table 4. Rate constants for the reactions of oxygen atoms with simple olefins at room temperature

Author[a]	Method[b]	Pressure /Torr	$k/10^{-12}$ cm^3 molecule^{-1} s^{-1}						
			Propene	1-Butene	*trans*-2-Butene	*cis*-2-Butene	2-Methyl-propene	2-Methyl-2-butene	1,3-Butadiene
E	DF/MS	0.75—3.0		5.2		21	16.5		
CS	FP/ACS	≈100		3.2±0.5			13±2		
AC	HgS/PS	23—107	1.96±0.10	2.57±0.20			10.3±2.5		
SN	FP/CL	≈10	$3.6\ ^{+0.2}_{-0.4}$						
K	FP/RF	25—258	3.69±0.21[c]						
FACC	HgS/PS	30—50	3.36±0.29	3.99±0.54		15.0±3.0	16.4±2.3	51.7±5.0	
AP	HgS/PS	57—116	3.34±0.37						
HHD	FP/RF	10—200		4.01±0.40[c]					
DHH	FP/RF	20—40				16.7±1.7[c]			
SC	HgS/PS	30—90	3.69±0.20	3.90±0.26		17.5±0.7	17.3±1.2		
ML	DF/RF	0.78—2.5	3.95±0.41						
AP	FP/CL	≈26	4.47±0.45	4.54±0.46	23.5±2.4	18.1±1.8	15.3±1.5		19.4±1.9
This work	PR/RA	200—1000	4.7±0.3	4.7±0.5	23±3	20±3	17±2	55±5	20±2

a) CS: Callear and Smith, Ref. 41; K: Kurylo, Ref. 11; ML: Michael and Lee, Ref. 42; HHD: Huie, Herron, and Davis, Refs, 9 and 10; DHH: Davis, Huie, and Herron, Ref. 12; for other abbreviations, see Table 3. b) ACS: absorption of CS radicals; for other abbreviations, see Table 3. c) Calculated from the Arrhenius expression.

TABLE 5. RELATIVE RATE CONSTANTS FOR THE REACTIONS OF OXYGEN ATOMS WITH SIMPLE OLEFINS AT ROOM TEMPERATURE

Author[a)] Method[b)]	C HgS/PA	E DF/MS	CS FP/ACS	AC HgS/PS	DHHKB HHD DHH FP/RF	FACC HgS/PS	SC HgS/PS	AP FP/CL	This work PR/RA
Ethylene	0.17	0.18		0.19	0.21	0.17	0.17	0.17	0.21
Propene	1.0			0.76		0.84	0.95	0.98	1.0
1-Butene	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
trans-2-Butene	4.9							5.2	4.9
cis-2-Butene	3.9	4.0			4.2	3.8	4.5	4.0	4.3
2-Methylpropene	4.3	3.2	4.0	4.0		4.1	4.4	3.4	3.6
2-Methyl-2-butene	14					13			12
1,3-Butadiene	4.2							4.3	4.3

a) C: Cvetanović, Ref. 1; for other abbreviations, see Tables 3 and 4. b) PA: product analysis; for other abbreviations, see Tables 3 and 4.

for the reactions of metastable oxygen atoms, ^1D and ^1S, with a number of molecules including oxygen, carbon monoxide, carbon dioxide, and olefins.[32)] All rate constants reported are much larger than those obtained with the ground-state ^3P oxygen atoms. Simple calculations using these data can show that the reactions of the ^1D and ^1S oxygen atoms, even if they are produced in the present experimental systems, are all completed before the measurement of the decay of the ^3P oxygen atoms. For example, the $O(^1D)$ atoms are quenched to $O(^3P)$ atoms within 0.3 μs in the system containing 3 Torr of oxygen. Similarly, $O(^1S)$ atoms, if produced in the system containing 0.1 Torr ethylene, are removed within one μs.

Influence of Secondary Reactions. Ozone, which is a product of the reaction of $O+O_2+M$, cannot affect the decay of oxygen atoms in the system of O_2 in helium, because the concentration of ozone produced is small ($<10^{13}$ cm^{-3}) and the rate constant for the reaction of $O+O_3$ is known to be not very large ($(2.5\pm0.5)\times 10^{-14}$ cm^3 molecule^{-1} s^{-1}).[33)]

As has been stated in the Results section, when carbon monoxide was used as the source of oxygen atoms, the decay curve for the oxygen atoms was not a simple first-order one. We tentatively explained this as the result of the participation of C_2O in the reaction. This is obviously a subject for further investigation. This complication however, can be ignored in the measurement of the rate constants of the reactions of O+olefins, since the amount of olefins used was much larger than that of the C_2O produced and since the reactions of O+olefins are fast.

In the study of the reaction of oxygen atoms with ethylene, we found the anomaly presented in the Results section. Consequently, we made extensive measurements of this reaction. Some of the results are shown in Fig. 13, where it can be seen that the apparent rate constant for the reaction of oxygen atoms with ethylene increased with the decrease in the ratio of $[C_2H_4]/[O]_0$ below 100. Here, $[O]_0$ stands for the initial concentration of the oxygen atoms.

It is well known that the reaction of $O+C_2H_4$ does not give a stable addition product, but such radicals as CH_3 and CHO, even at atmospheric pressure, while olefins larger than ethylene produce the corresponding addition products.[1)] Consequently, the participation of radicals cannot be ignored in the case of ethylene. Let us consider the following simplified reaction mechanism:

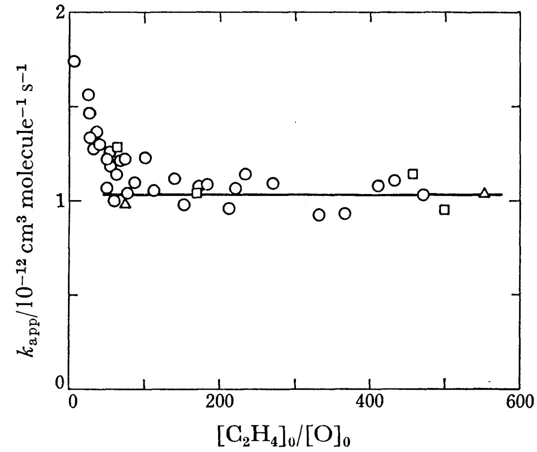

Fig. 13. The apparent rate constant, k_{app}, for the reaction of $O+C_2H_4$ as a function of the ratio, $[C_2H_4]/[O]_0$.
The O_2 (○), CO (△), and CO_2 (□) are used as the source of oxygen atoms.

$$O + C_2H_4 \longrightarrow R + \text{residue} \qquad k$$
$$R + O_2 + M \longrightarrow RO_2 + M$$
$$O + R \longrightarrow \text{products} \qquad k_R$$
$$O + RO_2 \longrightarrow \text{products} \qquad k_{RO_2}$$

Here, R stands for a radical, and k, k_R, and k_{RO_2}, for the rate constants for each reaction. The amounts of radicals are, of course, time-dependent, but they may be regarded as being in proportion to the initial concentration of the oxygen atoms. Then, the apparent decay rate, k_{app}, of the oxygen atoms may be written by the following equation:

$$k_{app} = k + k_R\frac{[R]}{[C_2H_4]} + k_{RO_2}\frac{[RO_2]}{[C_2H_4]}$$
$$\simeq k\left(1+\alpha(t)\frac{[O]_0}{[C_2H_4]}\right)$$

Therefore, we concluded that the k_{app} value obtained at higher ratios of $[C_2H_4]/[O]_0$ corresponds to the rate constant we are concerned with.

Comparison with Literature Values for the Reactions with Olefins. The rate constants previously obtained for the reaction of $O+C_2H_4$ are summarized in Table 3. They are classified by the method of measurement. The present result is slightly larger than those obtained by the flash-photolysis and modulation-phase-shift techniques, but within the limits of experimental error. Table 4 lists the rate constants for other olefins. The present results agree well with those obtained by Atkinson and Pitts.15) In addition, the relative rate constants are tabulated in Table 5. All the data are in good agreement with each other, irrespective of the method of measurement.

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