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Rate Constants and Mechanism for Reactions of Ketenes with OH Radicals in Air at 299 ± 2K

Shiro HATAKEYAMA,* Shigeo HONDA,† Nobuaki WASHIDA, and Hajime AKIMOTO
Division of Atmospheric Environment, The National Institute for Environmental Studies, P.O. Tsukuba-gakuen, Ibaraki 305
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Rate constants for reactions of OH radicals with four kinds of simple ketenes (ketene, methylketene: MK, ethylketene: EK, and dimethylketene: DMK) were measured in 1 atm of air at 299±2 K by use of a competitive reaction method. The photolysis of CH_3ONO in air was used to generate OH radicals. The rate constants for OH reactions obtained are $(1.8\pm0.2)\times10^{-11}$, $(7.6\pm1.4)\times10^{-11}$, $(11\pm3)\times10^{-11}$ and $(10\pm3)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for ketene, MK, EK, and DMK, respectively. The major product was a carbonyl compound; HCHO from ketene, CH_3CHO from MK, and CH_3COCH_3 from DMK; the yield was ≈80%, 72±17%, and 70±3%, respectively. It is proposed that the reaction proceeded mainly *via* an OH addition to the olefinic carbons of ketenes and the adduct decomposes to give a carbonyl compound and CO as final products in air.

Ketenes are known to be products of ozone–alkene reactions[1] and $O(^3P)$–alkene or alkyne reactions.[2] They are also produced during the combustion of alkynes and alkenes.[3,4] Therefore, a knowledge of oxidation rates of ketenes is significant for modeling the atmospheric life cycle and the combustion of hydrocarbons. However, there have been few reports concerning an experimental investigation of the oxidation of ketenes. Recently, we reported on the reactions of ketenes with $O(^3P)$.[5]

Although the OH radical reaction plays an important role in the atmospheric oxidation and combustion processes of ketenes, little has been reported regarding the rate constants of these reactions. Faubel *et al.*[6] reported that the lower limit of the rate constant for ketene+OH is $\approx1.7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. In computer-modeling studies regarding the combustion of ethylene[3] and acetylene,[4] rate constants of 1.7×10^{-11} [3] and 4.7×10^{-11} cm^3 $molecule^{-1}$ s^{-1},[4] respectively, were adopted without any experimental basis. Rate constants for other substituted ketenes have never appeared in the literature. No experimental study on the mechanism of an OH reaction with ketenes has been reported.

In the work reported here we measured the rate constants for the reactions of OH radicals with four kinds of simple ketenes (ketene, methylketene: MK, ethylketene: EK, dimethylketene: DMK) by use of CH_3ONO photolysis in air as a source of OH radicals. A competitive reaction method was employed. The mechanism for reactions of OH with the ketenes are also discussed in terms of both the linear dependence of the logarithms of the rate constants on the ionization potential and the results of product analyses.

Experimental

Ketene, MK, EK, and DMK were prepared by the pyrolysis of their corresponding dimers at 550 °C,[7] purified by repeated trap-to-trap distillation, and stored at liquid-nitrogen temperature. Dimers of ketene and DMK are commercially available (Tokyo Kasei). Those of MK and EK were prepared by the dehydrochlorination of propionyl chloride and butyryl chloride, respectively, with triethylamine.[8] UV-visible spectra were recorded using a Hitachi 220A spectrometer for given pressures of the ketenes (measured with an MKS Baratron capacitance manometer).

Kinetic measurements were performed in an 11 L cylindrical quartz vessel (120 mm i.d., 1000 mm long), and the changes in the concentration of reactants and products were monitored by means of long-path Fourier-transform infrared spectroscopy (LP-FTIR). The path length was 40 m, and 32 scans at a 1 cm^{-1} resolution were accumulated (≈1 min). The absorptivities (base 10, $Torr^{-1}$ m^{-1} at 30 °C) used were as follows: CH_2CO, 2.11 (2164 cm^{-1}); MK, 2.02 (2140 cm^{-1}); EK, 2.63 (2134 cm^{-1}); DMK, 2.60 (2134 cm^{-1}); HCHO, 0.25 (2780 cm^{-1}, peak to valley); CH_3CHO, 4.05×10^{-2} (2706 cm^{-1}); CH_3COCH_3, 0.173 (1218 cm^{-1}); cyclohexane, 3.31 (2934 cm^{-1}); propylene, 0.384 (912 cm^{-1}). The concentrations of CO and CO_2 were determined by use of calibration curves which were previously reported from this laboratory.[9]

The light source for photolysis was four 20-W black-light lamps (Toshiba FL 20S. BLB, $300<\lambda<400$ nm, $\lambda_{max}=360$ nm) which surrounded the reactor coaxially. The light intensity (measured by the NO_2 photodissociation rate, k_1) was 0.191 min^{-1}. To check for the existence of reactive intermediates such as an OH radical (which can consume ketenes during photolysis) photolyses of ketenes in the presence of 2-methylpropene were also carried out.

OH radicals were generated by the photolysis of methyl nitrite in air, as depicted by following equations.

$$CH_3ONO + h\nu \longrightarrow CH_3O + NO \quad (1)$$

$$CH_3O + O_2 \longrightarrow HO_2 + HCHO \quad (2)$$

$$HO_2 + NO \longrightarrow OH + NO_2 \quad (3)$$

CD_3ONO (in place of CH_3ONO) was also employed for ketene in order to distinguish the product formaldehyde from that produced in reaction 2.

The rate constants were measured on the basis of a competitive reaction method in the presence of cyclohexane or propylene as a reference compound. Typically, CH_3ONO (≈20 mTorr) (1 Torr=133.322 Pa)–ketenes (2—7 mTorr)–reference compound (R.C. 2—7 mTorr) in 1 atm of purified

†On study leave from the University of Tsukuba, Sakura, Ibaraki 305.

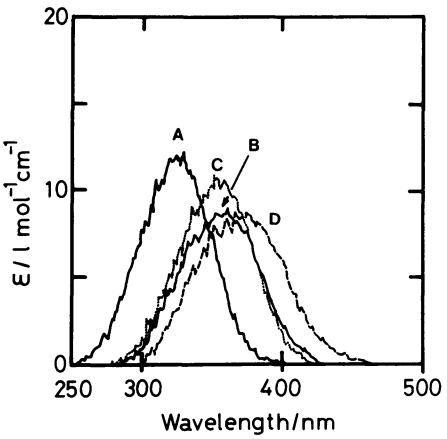

Fig. 1. UV-visible spectra of four kinds of ketenes. A: Ketene, B: methylketene, C: ethylketene, D: dimethylketene.

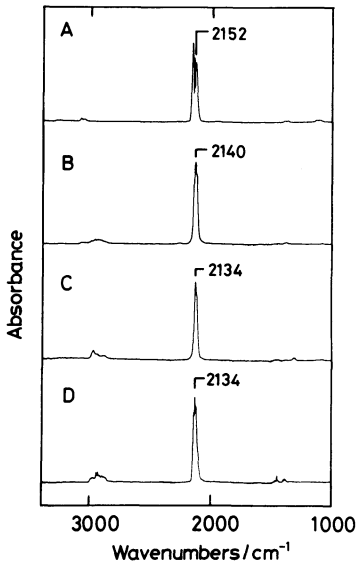

Fig. 2. IR spectra of four kinds of ketenes. A: Ketene, B: methylketene, C: ethylketene, D: dimethylketene.

air was irradiated for 10 min. IR spectra were taken at a constant interval. The reaction temperature was 299±2 K.

Results and Discussion

I. Rate Constants for OH+Ketenes. Figure 1 shows the UV-visible spectra of four kinds of ketenes. The λ_{max} and ε_{max} for ketene, MK, and DMK are in good agreement with those reported earlier.[10-12] That of EK (in a gas phase) has not been measured so far. All of the spectra show diffuse structures. Such structures have been reported for ketene.[13,14] Figure 2 shows the IR spectra of ketenes; the peaks at $\approx$2150 cm^{-1} correspond to the antisymmetric C=C=O stretching bands and were used for the concentration measurements.

An irradiation of the ketenes in 1 atm of air produced a first-order decay of each ketene. In order to check for the possibility that some reactive species, such as an OH radical which consumes ketenes, is produced in the course of photolysis, photolyses in the presence of 2-methylpropene (the rate constant for OH reaction is 5.07×10^{-11} cm^3 $molecule^{-1}$ s^{-1} [15]) were performed. No change in the concentration of 2-methylpropene was observed during 20 min of photoirradiation. Thus, it can be concluded that the decay of each ketene is solely due to photolysis. From the slope of the first-order decay of the ketenes, the photolysis rate constants in this system were calculated to be 9.5×10^{-3}, 3.5×10^{-3}, 3.0×10^{-3}, and 3.1×10^{-3} min^{-1} for ketene, MK, EK, and DMK, respectively.

The rate constants for reactions of the OH radical with ketenes were measured by use of CH_3ONO as a source of OH radicals. Thus, an irradiation of the ketenes–CH_3ONO–R.C. was carried out. The reactions which took place in the system were as follows.

$$\text{OH} + \text{ketenes} \longrightarrow \text{products} \quad (4)$$

$$\text{OH} + \text{R.C.} \longrightarrow \text{products} \quad (5)$$

$$\text{ketenes} + h\nu \longrightarrow \text{products} \quad (6)$$

The decay rate of the ketenes and R.C. are described according to the next equations.

$$-\,\mathrm{d[ketenes]}/\mathrm{d}t = k_4[\mathrm{OH}][\mathrm{ketenes}] + k_6[\mathrm{ketenes}] \quad (7)$$

$$-\,\mathrm{d[R.C.]}/\mathrm{d}t = k_5[\mathrm{OH}][\mathrm{R.C.}] \quad (8)$$

Thus,

$$\ln([\mathrm{ketenes}]_{t_0}/[\mathrm{ketenes}]_t) = k_4\int_{t_0}^{t}[\mathrm{OH}]\mathrm{d}t + k_6(t-t_0) \quad (9)$$

$$\ln([\mathrm{R.C.}]_{t_0}/[\mathrm{R.C.}]_t) = k_5\int_{t_0}^{t}[\mathrm{OH}]\mathrm{d}t \quad (10)$$

From Eqs. 9 and 10 the following equation can be derived.

$$\ln([\mathrm{ketenes}]_{t_0}/[\mathrm{ketenes}]_t) - k_6(t-t_0) = (k_4/k_5)\ln([\mathrm{R.C.}]_{t_0}/[\mathrm{R.C.}]_t) \quad (11)$$

Figure 3 shows a plot of Eq. 11 for four different ketenes. The data, which were obtained during several runs, are almost on the same straight line for each ketene. In this plot, the above photolysis rate constants were used as k_6. From the slopes of those plots and k_5 (cyclohexane: 7.85×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, propylene: 2.51×10^{-11} cm^3 $molecule^{-1}$ s^{-1})[15] k_4 can be calculated. Results are listed in Table 1. The rate constant for MK was measured by use of not only cyclohexane but also propylene as a R.C. The rate constants obtained for the two R.C. agreed well (within experimental error). However, since a large difference in the rate constants between cyclohexane and MK against OH may introduce a systematic error, the rate constant obtained by use of propylene as a R.C. should be more reliable.

In the case of EK and DMK, propylene, the same compound used as the R.C., may be formed during the isomerization of the carbenes produced in the

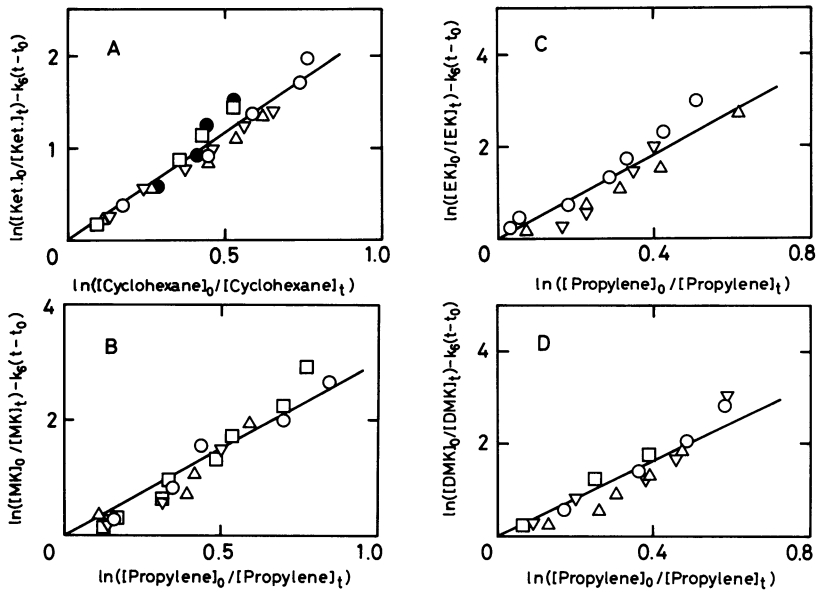

Fig. 3. Plot of Eq. 11 for four kinds of ketenes. Different symbols correspond to different runs. A: Ketene ($CH_3ONO \approx 22$ mTorr-Ketene ≈ 2 mTorr-$C_6H_{10} \approx 2$ mTorr), B: MK ($CH_3ONO \approx 22$ mTorr-MK ≈ 7 mTorr-$C_3H_6 \approx 7$ mTorr), C: EK ($CH_3ONO \approx 23$ mTorr-EK $\approx$ 6.5 mTorr-$C_3H_6 \approx 7.5$ mTorr), D: DMK ($CH_3ONO \approx 23$ mTorr-DMK ≈ 6.5 mTorr-$C_3H_6 \approx 7.5$ mTorr).

Table 1. Rate constants for the reaction of ketenes with OH radicals

Ketene	Reference Compound	k_4/k_5	$k_4/1\times10^{-11}$ cm^3 molecule^{-1} s^{-1}
Ketene	Cyclohexane[a)]	2.3±0.3	1.8±0.2
MK	Cyclohexane	8.0±1.7	6.4±1.4
MK	Propylene[b)]	3.0±0.5	7.6±1.4
EK	Propylene	4.5±1.1	11±3
DMK	Propylene	4.1±1.1	10±3

a) $k_5=7.95\times10^{-12}$ cm^3 molecule^{-1} s^{-1}.[15] b) $k_5=2.51\times10^{-11}$ cm^3 molecule^{-1} s^{-1}.[15] Estimated errors are 95% confidence limits.

photolysis. However, propylene was not detected during the 20-min photolysis of EK and DMK. This is, perhaps, due to the scavenging of the carbenes by O_2. Thus, the production of propylene can be neglected in our reaction system.

Only one study has previously been reported regarding the rate constants for the reaction of OH with ketene. Faubel *et al.*[6] estimated the lower limit of the rate constant for the OH+ketene reaction to be 1.7×10^{-12} cm^3 molecule^{-1} s^{-1} by means of a discharge flow-MS method in the course of their study on the C_3O_2+OH reaction. OH reactions with other ketenes have never been studied before. Our value for ketene, 1.8×10^{-11} cm^3 molecule^{-1} s^{-1}, is consistent with the lower limit given by Faubel *et al.*,[6] and is in good agreement with the value used in the numerical model study reported by Levy[3] ($\approx1.7\times10^{-11}$ cm^3 molecule^{-1} s^{-1}, no temperature dependence was assumed).

II. Reaction Mechanism of OH+Ketenes. No information is available concerning the mechanism of the reaction of ketenes with OH. In the field of combustion chemistry, the reaction of OH with ketene has been thought to proceed *via* the following reaction[3,4] without any experimental evidence.

$$CH_2CO + OH \longrightarrow HCHO + HCO \qquad (12)$$

In order to get an insight into the mechanism of the reaction, logarithms of the rate constants for OH+alkenes[15] and OH+ketenes were plotted against the ionization potential of alkenes and ketenes[16-18] (Fig. 4), as proposed by Bayes and co-workers.[19] The points for ketenes seem to fall on a straight line (the lower solid line), similar to the points for olefins (the upper solid line). This indicates that the reaction of OH with ketenes proceeds *via* a path similar to that for OH+alkenes (a reaction path on which the charge-transfer surface has an important contribution and the transition state is somewhat polarized). Thus, the reaction of OH with ketenes should proceed *via* addition.

In the reaction of OH with ketene, MK, and DMK, HCHO, CH_3CHO, and CH_3COCH_3 were detected, respectively. Figures 5 and 6 show the amount of acetaldehyde and acetone plotted against the amount of the corresponding ketenes consumed during several runs. The apparently straight lines were obtained in both systems. From the slopes of the lines shown in Figs. 5 and 6 the average ratios of the carbonyl-compounds-formed to ketenes-consumed were calculated to be 0.72±0.17 and 0.70±0.03 for acetaldehyde from MK and acetone from DMK, respectively. Since, in

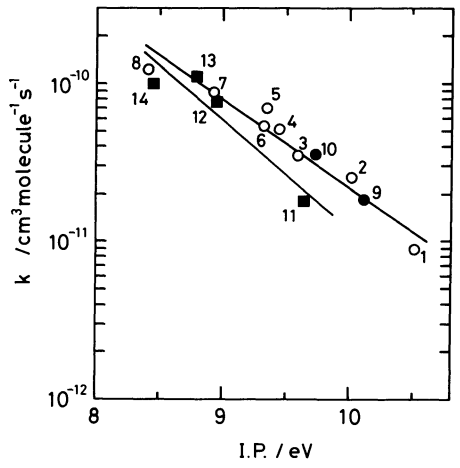

Fig. 4. Log(rate constant) *vs.* ionization potential for alkenes and ketenes. 1: Ethylene, 2: propylene, 3: 1-butene, 4: 2-methylpropene, 5: *trans*-2-butene, 6: *cis*-2-butene, 7: 2-methyl-2-butene, 8: 2,3-dimethyl-2-butene, 9: acrylaldehyde, 10: crotonaldehyde, 11: ketene, 12: methylketene, 13: ethylketene, 14: dimethylketene. Upper solid line was obtained by the least square calculation for compounds 1—10. Lower solid line was obtained by the least square calculation for ketenes.

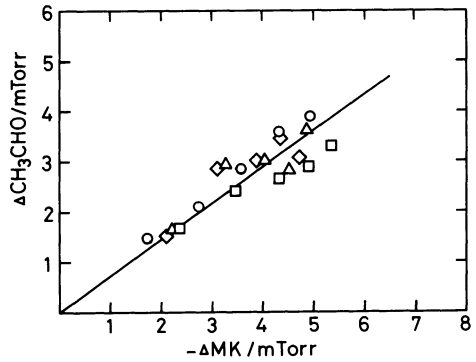

Fig. 5. Concentration of produced acetaldehyde plotted against decreased amount of methylketene. Different symbols correspond to different runs. $[MK]_0$=5.0—6.1 mTorr, $[CH_3ONO]_0$=≈22 mTorr.

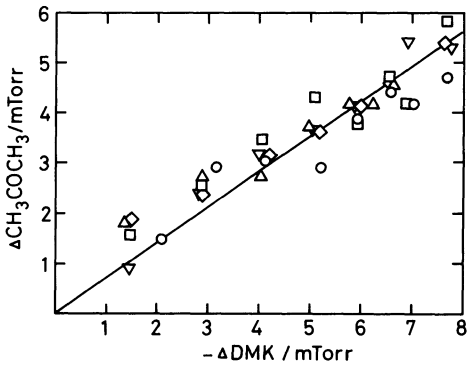

Fig. 6. Concentration of produced acetone plotted against decreased amount of dimethylketene. Different symbols correspond to different runs. $[DMK]_0$= 6.6—7.7 mTorr, $[CH_3ONO]_0$=≈23 mTorr.

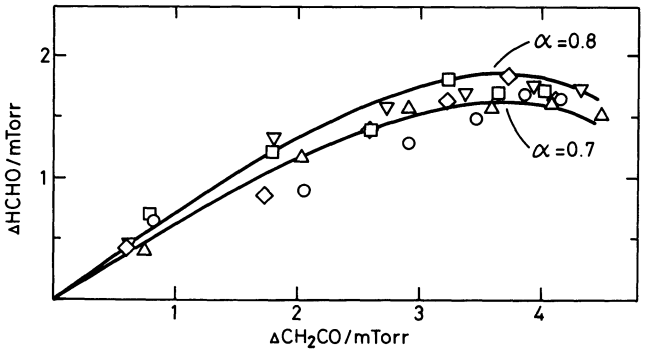

Fig. 7. Concentration of produced formaldehyde plotted against decreased amount of ketene. Different symbols correspond to different runs. $[Ketene]_0$= 4.7—5.4 mTorr, $[CD_3ONO]_0$=≈25 mTorr. Solid lines are the plot of the amount of formaldehyde formed against the amount of consumed ketene calculated by Eqs. 15 and 16 with α=0.8 and α=0.7.

each case, the photolysis of the product carbonyl compounds and the secondary OH reactions of products tend to decrease their yields, the yields estimated above should be taken as lower limits.

For ketene, the plot shows no lineality, and the final yield of formaldehyde is indicated to be much lower (Fig. 7). It is because the OH+HCHO reaction has a rate constant (1.01×10^{-11} cm³ molecule^{-1} s^{-1})[20] comparable to that for OH+ketene; the secondary reaction of OH with formaldehyde (as well as its photolysis) significantly lowers the apparent yield of formaldehyde.

In order to simulate the concentration change of ketene and formaldehyde, the following reaction scheme was used.

$$\text{ketene} + \text{OH} \xrightarrow{k_4} \alpha\text{HCHO} + \text{other products} \quad (4')$$

$$\text{ketene} + h\nu \xrightarrow{k_6} \text{products} \quad (6)$$

$$\text{HCHO} + \text{OH} \xrightarrow{k_{13}} \text{products} \quad (13)$$

$$\text{HCHO} + h\nu \xrightarrow{k_{14}} \text{products} \quad (14)$$

Here α ($\leq$1) is the yield of formaldehyde. Thus, next equations were obtained using a constant OH (OD) radical concentration (≈2×10^8 molecule cm^{-3}), which was measured[21] for about 10 min of irradiations in 5 runs.

$$[\text{ketene}] = [\text{ketene}]_0 \exp\{-(k_4[\text{OH}]+k_6)t\} \quad (15)$$

$$[\text{HCHO}] = \frac{\alpha k_4[\text{OH}][\text{ketene}]_0}{k_{13}[\text{OH}]+k_{14}-k_4[\text{OH}]-k_6} \times [\exp\{-(k_4[\text{OH}]+k_6)t\} - \exp\{-(k_{13}[\text{OH}]+k_{14})t\}] \quad (16)$$

Here $[ketene]_0$ is the initial ketene concentration. The solid lines in Fig. 7 are plots of the amounts of formaldehyde formed against the amounts of consumed ketene as calculated by Eqs. 15 and 16 with α=0.7 and α=0.8 by the use of $k_{13}=1.0\times10^{-11}$ cm³ molecule^{-1} s^{-1} and $k_{14}=2.6\times10^{-5}$ s^{-1}.[22] Most of the experimental points fall between the two lines; thus, we can assume

that the inital yield of formaldehyde in the reaction of OH (OD) with ketene was 70—80%. Therefore, it can be concluded that the reaction of OH with various ketenes at room temperature gives corresponding carbonyl compounds as the main products.

By an *a priori* consideration, the site attacked by an OH can be regarded to be the olefinic carbon of the ketenes, where the electron density is the greatest.[23] The formation of carbonyl compounds from the adduct can be explained in two ways. One is,

$$RR'C{=}C{=}O + OH \longrightarrow \left[\begin{array}{l} RR'C\text{-}C{=}O \\ \quad\;\; | \\ \quad\;\; OH \end{array}\right]^{\ddagger} \longrightarrow$$

A

$$RR'COH + CO \qquad (17)$$

$$\Delta H = -35.1 \text{ kcal mol}^{-1} \text{ for R,R}' = H^{24)}$$

Since it is known[26-28] that the RR'COH radical yields RR'CO in the presence of O_2, the formation of formaldehyde, acetaldehyde, and acetone in the reaction of ketene, MK, and DMK, respectively, can be regarded as the products of the reaction of RR'COH radicals with O_2.

The other is the hypothesized route used in the modeling studies[3,4] mentioned above

$$RR'C{=}C{=}O + OH \longrightarrow \mathbf{A} \longrightarrow RR'CO + HCO \qquad (18)$$

$$\Delta H = -31.9 \text{ kcal mol}^{-1} \text{ for R,R}' = H.^{24)}$$

HCO reacts with O_2 to give $CO+HO_2$, almost exclusively.[25] Thus, the total reaction in air is the same for both cases, as described by the following equation.

$$RR'C{=}C{=}O + OH + O_2 \longrightarrow RR'CO + CO + HO_2 \qquad (19)$$

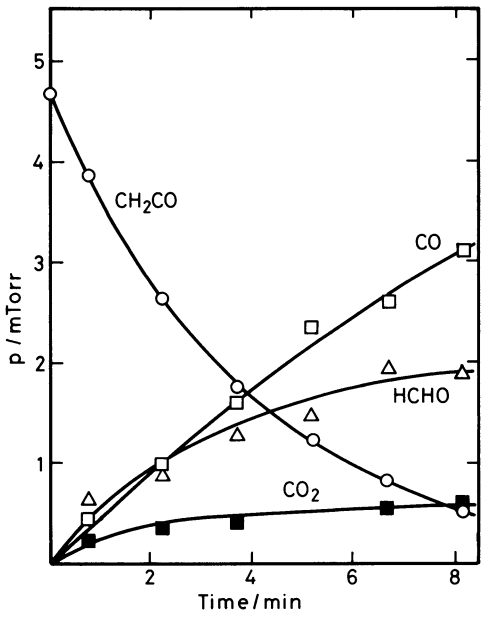

Fig. 8. Typical time profile of the concentration of the reactant and the products in CD_3ONO (22.5 mTorr)-CH_2CO (4.7 mTorr)-air-irradiation system.

The reaction paths in 17 and 18 could not be distinguished in the kinetic experiments and the product analyses performed in this study.

Since **A** is an OH-substituted acetyl radical, the formation of a PAN-type compound ($RR'C(OH)C(O)OONO_2$) can be expected if the radical is stabilized under atmospheric conditions. In the present study, however, no IR band corresponding to PAN-type compounds was detected. Thus, we can assume that the lifetime of **A** is much shorter than the collision interval, even under atmospheric conditions.

Figure 8 shows a typical time profile for the concentration of a reactant and its products in a CD_3ONO-ketene-air-irradiation system. As can be seen in this figure, the CO yield is much higher than CO_2.[29] This strongly supports the above mechanism as being the major pathway. However, the small amount of CO_2 produced may correspond to the pathway of the OH-attack on the carbonyl carbon of the ketenes.

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22) The photolysis rate constant in the reaction system employed in this study was calculated by the summation of $\sum_{\lambda} J_{\lambda}\sigma_{\lambda}\phi_{\lambda}$, where J, σ, and ϕ are effective light intensity, absorption cross section, and quantum yield, respectively, by use of the absorption cross section and quantum yield given by Ref. 20.

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29) Since CO and CO_2 can be produced by the photochemical reaction of RONO and photodesorption from the cell wall, the contribution of those by-products is corrected in the data shown in Fig. 8 in the following manner. Production rate of CO and CO_2 was estimated as a function of the consumption of nitrite as an average of several runs of photolysis of CH_3ONO or CD_3ONO in air. The yield of CO and CO_2 was estimated by the subtraction of the yield calculated with these functions from the apparent yield.