Reactions of Ketene, Methylketene, Ethylketene, and Dimethylketene with Ozone in Air

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Synopsis. Rate constants for reactions with ozone were measured for four kinds of simple ketenes (ketene, methylketene, ethylketene and dimethylketene) in 1 atm of air. The rate constants were obtained as upper limits; $<1\times10^{-21}$, 7×10^{-19}, 1×10^{-18}, and 4×10^{-17} cm^3 molecule^{-1} s^{-1}, respectively. The mechanism of the reactions was proposed to be similar to that for the liquid-phase reaction.

Formation and loss process of oxygen-containing secondary pollutants in the atmosphere is of great interest in the area of atmospheric chemistry. In addition to the well-known oxygen-containing secondary pollutants such as aldehydes, ketones, and carboxylic acids, α-dicarbonyl compounds, ketenes, and peroxides are also observed in the atmosphere. Among these compounds ketenes are known as products of ozone–alkene reactions.[1)]

As to the homogeneous loss processes of ketenes in the atmosphere, photolysis and reactions with OH, ozone, and O(^{3}P) should be important. Recently, we reported the reaction of ketenes with O(^{3}P),[2)] and with OH.[3)] However, little is known about the kinetics of the reactions of ketenes with ozone. To our knowledge, mechanisms of the ozone reactions of ketenes in the gas phase have not been studied so far. For the liquid phase several investigations[4—7)] were reported.

In this paper we report the measurement of rate constants for the reactions of ketenes with ozone. The reaction mechanism is also discussed.

Experimental

Ketene, methylketene (MK), ethylketene (EK), and dimethylketene (DMK) were prepared in the same manner as reported before.[2)] $^{18}O_2$ (99%) was obtained from Nippon Sanso.

Kinetic measurements were performed both in an 11 L cylindrical quartz vessel (120 mm i.d., 1000 mm long), and in a large volume (6 m^3) smog chamber,[8)] whose inner surface is coated with Teflon. The change in the concentration of reactants and products was monitored by means of long-path Fourier transform infrared spectroscopy (LP-FTIR). Path length is 40 m and 221.5 m for the quartz cell and the smog chamber, respectively. Absorptivities used are reported in the previous paper.[3)] All the IR spectra were taken at 1 cm^{-1} of resolution. Scans accumulated were 32 times (≈1 min) and 128 times (≈4 min) in the quartz cell runs and in the smog chamber runs, respectively.

Measurements of the rate constant for the reaction of ketene with ozone were performed in the 11 L quartz cell with 2.8 mTorr (1 Torr=133.322 Pa) of ketene and 24—100 mTorr of ozone or with 5.8 mTorr of ozone and 58 mTorr of ketene at room temperature. Those for other ketenes were performed in the smog chamber with ≈0.2 mTorr of ketenes and 1—6 mTorr of ozone at 30±1 °C in the presence of ≈15 mTorr of CH_3CHO as a scavenger of free radicals.

Results and Discussion

Even in the presence of a large excess of ketene (58 mTorr), the decay of ozone (5.8 mTorr) was under detection limit. In the presence of a large excess of ozone (24—100 mTorr), the decay rate of ketene (initial concentration 2.8 mTorr) did not show any dependence on the concentration of ozone as shown in Fig. 1. Thus, the reaction of unsubstituted ketene with ozone is concluded to be very slow. Ketene decay observed in Fig. 1 should be attributed to wall decay of ketene. Decay rate shown in Fig. 1 is three to four times as high as that in the absence of ozone, so it seems that excess ozone enhances the wall decay of ketene. From the results obtained above the upper limit of the rate constant was estimated to be $<1\times10^{-21}$ cm^3 molecule^{-1} s^{-1}. The other ketenes were found to react with ozone more than 100 times faster than ketene. Therefore, the 6 m^3 smog chamber was used as the reactor in order to use much lower concentration of ketenes. Decay of ketenes (initial concentration is about 0.2 mTorr) in the presence of excess ozone (1—6 mTorr) and CH_3CHO (≈15 mTorr) as a scavenger of free radicals was first order. From the dependence of the decay rates on the initial concentrations of ozone as shown in Fig. 2, second order rate constants were calculated to be $(6.7\pm1.9)\times10^{-19}$, $(9.8\pm3.4)\times10^{-19}$, and $(3.7\pm0.5)\times10^{-17}$ cm^3 molecule^{-1} s^{-1} for MK, EK, and DMK respectively. In these plots the intercepts are in good agreement with the wall decay rates of ketenes (filled circles in Fig. 2).

However, stoichiometry of the reaction for three kinds of ketenes are not unity: consumption of ozone is always smaller than that of ketenes in a factor of about 0.7 under the conditions employed for the smog chamber runs and the discrepancy of stoichiometry

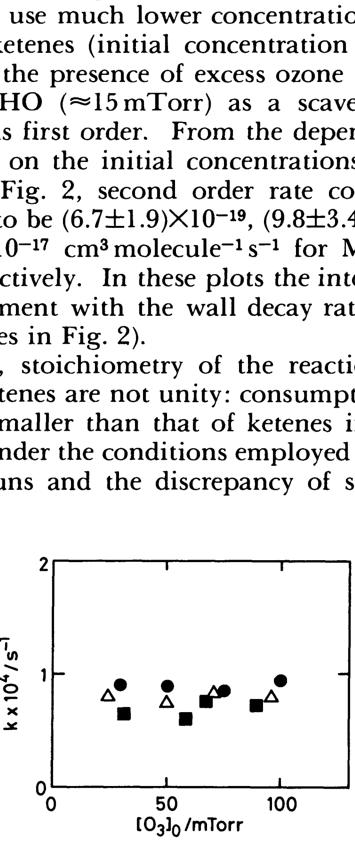

Fig. 1. Dependence of decay rate of ketene on the concentration of ozone. $[Ketene]_0\cong2.8$ mTorr.

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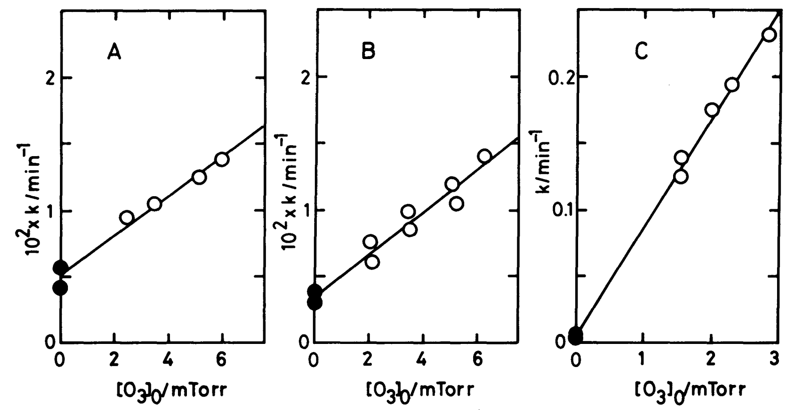
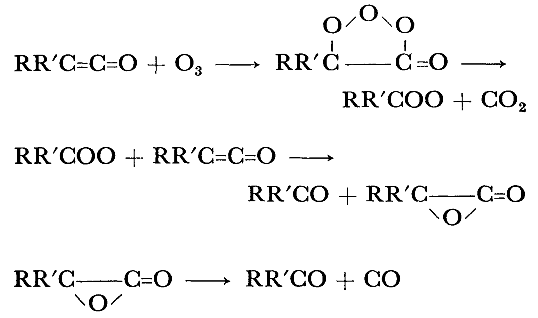


Fig. 2. Dependence of decay rates of MK, EK, and DMK on the concentration of ozone. Solid circles indicate the wall decay. $[\mathrm{Ketene}]_0 \cong 0.2$ mTorr.

becomes larger when the concentration of reactants is higher. In the runs with low concentration of ozone and excess ketenes first order decay of ozone was not observed. These facts indicate the contribution of secondary reactions which cannot be prohibited even in the presence of excess CH_3CHO. Thus, the rate constants obtained here may be also regarded as upper limits.

To our knowledge, the gas phase reaction of ozone with ketenes has never been investigated. As for the liquid phase reaction of ozone with ketenes, several reports have been presented.[4,7] In these papers the reaction mechanism is described as follows:



$$RR'C{=}C{=}O + O_3 \longrightarrow RR'\overset{O\diagup^{O}\diagdown O}{C\text{——}C}{=}O \longrightarrow RR'COO + CO_2 \qquad (1)$$

$$RR'COO + RR'C{=}C{=}O \longrightarrow RR'CO + RR'\underset{\diagdown O \diagup}{C\text{——}C}{=}O \qquad (2)$$

$$RR'\underset{\diagdown O \diagup}{C\text{——}C}{=}O \longrightarrow RR'CO + CO \qquad (3)$$

In the present study formation of CO, CO_2, and RR′CO (CH_3CHO, C_2H_5CHO, and CH_3COCH_3 from MK, EK and DMK, respectively) was observed, but the stoichiometry of the reaction is not so good enough to discuss the product yields quantitatively. However, the formation of methane, formaldehyde and a small amount of ketene in MK ozone reactions strongly indicates the existence of CH_3CHOO biradical when the mechanism of the decomposition of this biradical,[9] as depicted by following equations, is taken into account.

$$CH_3CHOO \longrightarrow CH_3 + H + CO_2 \qquad (4)$$

$$\longrightarrow CH_4 + CO_2 \qquad (5)$$

$$\longrightarrow CH_3 + CO + OH \qquad (6)$$

$$\longrightarrow CH_2C{=}O + H_2O \qquad (7)$$

Radical species formed by the reactions 4 and 6 can consume ketenes, which results in the poor stoichiometry.

An interesting result was obtained in the experiments using $^{18}O_3$ as a reactant. Produced CO_2 mainly consists of $C^{16}O^{18}O$, which supports the occurrence of reaction 1. However, since even a large excess of acetaldehyde cannot trap the biradical (ozonides were not detected), the biradical seems to decompose very quickly and the reaction 2 does not take place in the gas phase.

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