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Mechanism of Chlorine Catalytic Oxidation of CO in the Gas Phase

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The mechanism of the title reaction is determined under steady state conditions by the irradiation of the mixtures of Cl_2, CO, O_2, and N_2 at 300 K with black blue fluorescence lamps using infrared spectroscopy. The pressure dependence of the ratio of the formation rate of carbon dioxide to that of phosgene($COCl_2$) and the other results indicated that the oxidation of CO proceeded *via* intermediates ClCO and $ClC(O)O_2$ as the termolecular process rather than the bimolecular oxidation by ClOO and/or ClO. The ratio of the competitive reactions of chloroformyl radicals, k_8/k_{9a}, was found to be $(6.5\pm0.4)\times10^{-2}$ in the total pressure range from 30 to 755 Torr (1 Torr = 133 Pa); $ClCO+Cl_2\rightarrow COCl_2+Cl$ (8), $ClCO+O_2\rightarrow ClC(O)O_2{}^*$ (9a). And also, the ratio of the competitive reactions of the vibrationally excited intermediates, k_{9b}/k_{9c}, was $(3.4\pm0.3)\times10^{18}$ molecule/cm^3; $ClC(O)O_2{}^*\rightarrow ClCO+O_2$ (9b), $ClC(O)O_2{}^*+M\rightarrow ClC(O)O_2+M$ (9c). The role of this reaction in the stratosphere is discussed and estimated to be unimportant.

Accumulation of CO_2 in the atmosphere has been discussed to affect the temperature of the erath in future.[1] In addition to the direct emission of CO_2 by combustion, breathing, and respiration, the chemical oxidation of CO is believed to occur in the atmosphere. The major pathway is the oxidation by OH radicals.[2] Catalytic oxidation cycle of Cl atoms, which are formed from the ultraviolet photolysis of chlorofluorocarbons in the stratosphere, may contribute to the conversion as another possible path. And any reaction involving Cl atoms is essential to understand chlorine reaction in the atmosphere.

The oxidation of CO by Cl atoms in the presence of O_2 was found as early as 1930's.[3,4] Brenschede,[5] in illuminating mixtures of CO, O_2, and Cl_2, found the ratio of formed CO_2 to formed $COCl_2$ to be given by Eq. 1,

$$\frac{[CO_2]}{[COCl_2]}=A\frac{[O_2]_0}{[Cl_2]_0}, \tag{1}$$

where A increases with total pressure at first rapidly and then slowly. But his interpretation on mechanism involved uncertainty, because he did not analyze the pressure dependence behavior and the value of the proportionality constant in terms of kinetics. A probable mechanism for chlorine catalytic oxidation of CO is Reaction 2 and/or 3 as proposed by Prinn,[6] but very little information is available on the rate constant involving ClO_x. The other is Reaction 4 proposed by Spence *et al.*[7] by observing $ClC(O)OONO_2$ as an oxidation product of the ultraviolet irradiation of Cl_2, NO_2, and CO mixtures in air, though the possibility of Reaction 2 and/or 3 is not excluded from their experiments.

$$ClOO+CO\longrightarrow ClO+CO_2 \tag{2}$$

$$ClO+CO\longrightarrow Cl+CO_2 \tag{3}$$

$$Cl+CO\longrightarrow ClCO\xrightarrow[O_2]{}ClC(O)O_2\longrightarrow ClCO_2\longrightarrow Cl+CO_2 \tag{4}$$

In this paper, we try to analyze the relation (1) to get more information on the mechanism of the reaction system by irradiating the mixture of Cl_2, CO, O_2, and N_2 with varying the initial conditions and add some facts that supports the mechanism involving ClCO and $ClC(O)O_2$. And also the role of the reaction in the atmosphere is discussed.

Experimental

Chlorine from a cylider (Fujimoto Sanso) was pumped through a trap immersed in isopentane-liquid nitrogen bath (160 °C). The condensed fraction was used for the experiments. CO, O_2, and N_2 form research grade steel cylinders were used without further purification. Experimental apparatus was described previously.[8] In brief, reactant gases Cl_2, CO, and O_2 and inert gas N_2 were mixed in a 10 cm Pyrex-body infrared absorption cell of 4 cm diameter (window was NaCl). The cell was mounted in the sample beam of the infrared spectrometer. Two 20-W black blue light lamps irradiated into the cell from 7 cm above at 27±1 °C. Concentration-time profile of the products, CO_2 and $COCl_2$, increased lineary within the irradiation time of 50 s. Thus, measurement of the initial rates was made after light exposure of less than 30 s duration. The concentration was determined by measuring the peak intensity. The peak and absorption coefficients used were the same as those in the previous publication except $COCl_2$. $COCl_2$ was measured by the more sensitive absorption at 852 cm^{-1} in this work.

Results and Discussion

It is well confirmed by early works[9] that when mixtures of CO, Cl_2, and O_2 are illuminated with light which is absorbed by Cl_2, part of CO is changed to $COCl_2$ and part to CO_2, and that, at relatively high pressures of O_2, CO_2 formation occurs almost exclusively, whereas at low O_2 pressures $COCl_2$ formation is predominant.

The mechanism of the formation of $COCl_2$ is well established by Burns and Dainton[10] to be the reactions (5) to (8) in this system. In the later work by Jacox and Milligan,[11] the formation of chloroformyl radical, ClCO, from the reaction of Cl with CO was confirmed using an argon matrix by infrared spectroscopy.

$$Cl_2+h\nu\longrightarrow 2Cl \tag{5}$$

$$Cl+CO+M\rightleftharpoons ClCO+M \tag{6,$-$6}$$

$$ClCO+Cl\longrightarrow Cl_2+CO \tag{7}$$

$$ClCO+Cl_2\longrightarrow COCl_2+Cl \tag{8}$$

As a first series of experiment, each initial pressure of Cl_2 and O_2 was held constant at 10 Torr (1 Torr = 133 Pa) and CO pressure was varied while keeping

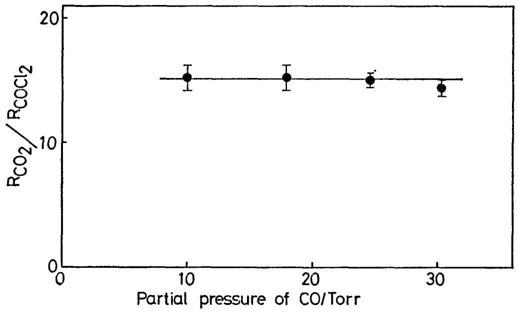

Fig. 1. The function, R_{CO_2}/R_{COCl_2}, *vs.* partial pressure of CO in the photolysis of $Cl_2/CO/O_2/N_2$; $[Cl_2]_0 = [O_2]_0 = 10$ and $[\text{total pressure}]_0 = 755$ Torr.

the total pressure at 755 Torr. The value R_{CO_2}/R_{COCl_2} was plotted against the partial pressure of CO (Fig. 1). The value was independent on the partial pressure of CO as found in the previous work.[5] If the reaction intermediates ClOO and/or ClO were important for the CO oxidation, Cl would have two competitive paths: one is the association with O_2 to form CO_2 *via* Reactions 2 and/or 3 and the other is association with CO to form $COCl_2$ *via* Reactions 6 and 8, R_{CO_2}/R_{COCl_2} would decrease as the initial pressure of CO increases. Thus, the oxidation of CO seems to occur *via* the intermediate ClCO, not *via* ClOO or ClO.

Then, the effect of the total pressure on the ratio of the initial formation rates, R_{CO_2}/R_{COCl_2}, was examined at total pressure ranging from 30 to 755 Torr by changing the amount of added N_2 to a mixture of 10 Torr of Cl_2, 10 Torr of CO, and 10 Torr of O_2. The infrared spectra were taken after filling N_2 up to 755 Torr following the photolysis, since IR intensities of CO and CO_2 depend on the total pressure. The logarithm of R_{CO_2}/R_{COCl_2} is plotted against that of the total pressure (Fig. 2). Typical fall-off behavior is appeared in the figure. Since stripping reaction such as Reaction 8 is not usally pressure dependent, the observed pressure effect is due to the pressure dependence in the CO_2 formation process, and this reaction seems to proceed *via* a stabilized adduct $(ClC(O)O_2)$ from a vibrationally excited intermediate $(ClC(O)O_2{}^*)$. High pressure limit appears a little above the highest pressure used in our experiment, and it is higher than the limit observed for $C_2H_5 + O_2$ by Plumb and Ryan[11] as expected from the consideration of the number of degrees of freedom.

Consequently, let us assume the following reaction mechanism involving ClCO and $ClC(O)O_2$.

$$ClCO + O_2 + M \longrightarrow ClC(O)O_2 + M \tag{9}$$

$$ClC(O)O_2 + ClC(O)O_2 \longrightarrow 2ClCO_2 + O_2 \tag{10}$$

$$ClCO_2 \longrightarrow Cl + CO_2 \tag{11}$$

In order to make some estimation for the fall-off region, the combination reaction 9 is decomposed into the steps 9a to 9c.

$$ClCO + O_2 \longrightarrow ClC(O)O_2{}^* \tag{9a}$$

$$ClC(O)O_2{}^* \longrightarrow ClCO + O_2 \tag{9b}$$

$$ClC(O)O_2{}^* + M \longrightarrow ClC(O)O_2 + M \tag{9c}$$

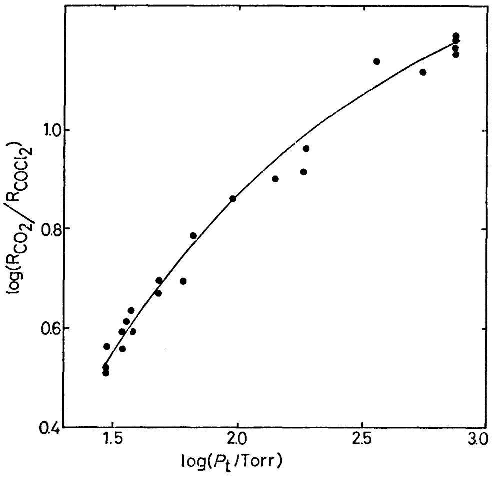

Fig. 2. Total pressure (P_t) dependence of the function, R_{CO_2}/R_{COCl_2} in the photolysis of $Cl_2/CO/O_2/N_2$; $[Cl_2]_0 = [O_2]_0 = [CO]_0 = 10$ Torr.

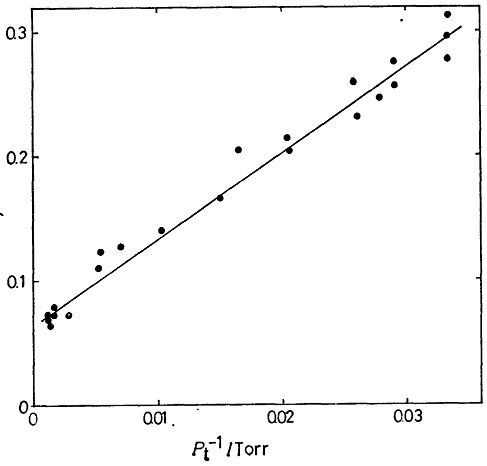

Fig. 3. The function, R_{COCl_2}/R_{CO_2} *vs.* inverse of total pressure (P_t) in the photolysis of $Cl_2/CO/O_2/N_2$; $[Cl_2]_0 = [CO]_0 = [O_2]_0 = 10$ Torr.

The steady state treatment with respect to $ClC(O)O_2{}^*$ gives,

$$[ClC(O)O_2{}^*] = \frac{k_{9a}[ClCO][O_2]}{k_{9b} + k_{9c}[M]}. \tag{12}$$

The formation rate of CO_2 is expressed by Eq. 13, if we apply the steady state treatment also to $ClC(O)O_2$ and $ClCO_2$.

$$R_{CO_2} = k_{9c}[ClC(O)O_2{}^*][M] = \frac{k_{9a}k_{9c}[ClCO][O_2][M]}{k_{9b} + k_{9c}[M]} \tag{13}$$

And,

$$R_{COCl_2} = k_8[ClCO][Cl_2]. \tag{14}$$

Then,

$$\frac{R_{COCl_2}}{R_{CO_2}} = \frac{[Cl_2]}{[O_2]}\left(\frac{k_8}{k_{9a}} + \frac{k_8 k_{9b}}{k_{9a}k_{9c}[M]}\right). \tag{15}$$

To correlate Eq. 15 with the pressure dependence, the value, R_{COCl_2}/R_{CO_2}, from the same data used in Fig. 2 is replotted *vs.* inverse of total pressure (Fig. 3). The plots gave a straight line which is fit by

Eq. 15 under our experimental conditions. Assume $[Cl_2]/[O_2]$ is 1 during the course of the irradiation in the experiment of total pressure variation, since the initial concentration of Cl_2 and O_2 were 10 Torr and the photolysis did not exceed 10% of the reactants. We obtained the values of k_8/k_{9a} and $k_8k_{9b}/k_{9a}k_{9c}$ from the intercept and the slope in Fig. 3, respectively.

$$k_8/k_{9a} = (6.45\pm0.41)\times10^{-2}\ \text{Torr} \qquad (16)$$

$$k_8k_{9b}/k_{9a}k_{9c} = (6.89\pm0.21)\ \text{Torr}, \qquad (17)$$

where error is a standard deviation of the least-squares analysis.

Then,

$$\begin{aligned} k_{9b}/k_{9c} &= (108\pm8)\ \text{Torr} \\ &= (3.4\pm0.3)\times10^{18}\ \text{molecule/cm}^3 \end{aligned} \qquad (18)$$

Eq. 16 and the literature value,10) $k_8=2.91\times10^{-14}$ cm^3 molecule^{-1} s^{-1} at 300 K, gives $k_{9c}=4.51\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. The k_{9a} value is ten times smaller than the rate constant for a similar recombination $C_2H_5+O_2\rightarrow C_2H_5O_2^*$ reported by Plumb and Ryan.12) It is also important to note that $ClCO+O_2$ addition (9a) is faster than the competing reaction of Cl abstraction by ClCO from Cl_2 (8).

To evaluate the obtained value of Eq. 18, 3.4×10^{18} molecule/cm^3, k_{9b} and k_{9c} may be estimated from a quantum RRK theory for unimolecular decomposition of energized molecule. Necessary parameters are assumed as: the proportionality constant is to be 10^{14} s^{-1} from the Arrhenius A factor for the unimolecular decomposition of alkyl-$O_2$13): the bond strength of ClC(O)–O_2 is 28 kcal/mol from that of alkyl-$O_2$13): the geometrical mean frequency is guessed at 640 cm^{-1} by assigning 600 Cl–C st. from $ClC(O)CH_3$ in Ref. 14, 1800 for C=O st. from $ClC(O)OONO_2$ in Ref. 7, 1200 for C–O st. in Ref. 15, 880 for O–O st. from HO_2NO_2 in Ref. 16, 400 for O–O–C bend,15) 420 for O=C–O,15) 360 for O=C–Cl,15) and 400 for O–C–Cl,15) all in units of cm^{-1}. If we choose 9 as the number of effective oscillators, k_{9b} is about 10^8 s^{-1}. By substituting k_{9b} in Eq. 18, k_{9c} becomes 3×10^{-11} cm^{3}molecule^{-1} s^{-1}. Although we do not have enough knowledge what value less than 9 is proper for the number of effective oscillations, the k_{9c} derived from crude calculation is near collision frequency under our experimental conditions. Hence, the value (18) obtained here appears reasonable.

Next, we find k_8/k_9 at 755 Torr from the equations obtained. From Reaction 9,

$$R_{ClC(O)O_2} = k_9[ClCO][O_2][M] = R_{CO_2}. \qquad (19)$$

From the comparison of Eq. 19 with 13,

$$k_{9a} = \frac{k_{9a}\,k_{9c}}{k_{9b}+k_{9c}[M]}. \qquad (20)$$

From this,

$$\frac{k_8}{k_9} = \frac{k_8}{k_{9a}}\left(\frac{k_{9b}}{k_{9c}}+[M]\right). \qquad (21)$$

By substituting the values of $k_8/k_{9a}=6.45\times10^{-2}$ and $k_{9b}/k_{9c}=107$ Torr found before,

$$\frac{k_8}{k_9} = 0.0645(107+[M]). \qquad (22)$$

When $[M]=755$ Torr, k_8/k_9 is calculated to be 55.6 Torr.

Rollefson, in the previous work,17) assumed Reaction 23 in place of the set of the Reactions 9, 10, and 11. He disregarded the pressure effect on the products distribution and obtained the value 0.2 for k_8/k_{23} by finding that the number of moles of Cl_2 and O_2 reacting to be equal when the Cl_2 pressure was five times that of oxygen.

$$ClCO + O_2 \longrightarrow CO_2 + ClO. \qquad (23)$$

The ratio k_8/k_{23} by Rollefson corresponds to $k_8/(k_9[M])$ in our mechanism. Since he did not show the total pressure of each run, we guess mean value for the total pressure [M] as 50 Torr from the list of the partial pressure of three reactants. Then, $k_8/(k_9[M])$ becomes 0.2 that agrees very well with the results shown by Rollefson.

In order to compare the derived value of k_8/k_9 with the value obtained experimentally at constant total pressure, we determined A in Eq. 1 in different initial conditions. First, by keeping the constant total pressure of 755 Torr and the initial concentration of Cl_2 and CO at 10 Torr, the pressure of O_2 was varied. Plot of the values of R_{CO_2}/R_{COCl_2} against the initial pressure of O_2 gave a straight line (Fig. 4). From the relations (14) and (19),

$$\frac{R_{CO_2}}{R_{COCl_2}} = \frac{k_9[M]}{k_8[Cl_2]}[O_2]. \qquad (24)$$

The relation (24) fits to the line. The slope is 1.48, which corresponded to $k_9[M]/(k_8[Cl_2])$. Thus,

$$k_8/k_9 = 51.0\ \text{Torr}. \qquad (25)$$

Secondly, by keeping the total pressure, initial pressure of CO and O_2 constant, 755, 10, and 10 Torr, respectively, the partial pressure of Cl_2 was varied. The plot of the value of R_{COCl_2}/R_{CO_2} against the partial pressure of Cl_2 gave also a straight line with a slope of 0.00645 (Fig. 5). The slope must be equal to $k_8/(k_9[M][O_2])$. Then,

$$k_8/k_9 = 48.7\ \text{Torr}. \qquad (26)$$

In view of the consumption of O_2 and Cl_2 during the irradiation that will cause error, the value 55.6 Torr

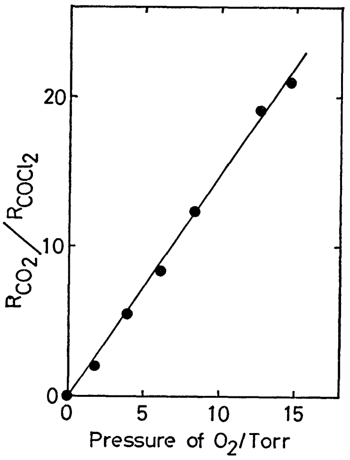

Fig. 4. The function, R_{CO_2}/R_{COCl_2} *vs.* partial pressure of O_2 in the photolysis of $Cl_2/CO/O_2/N_2$; $[Cl_2]_0=[CO]_0=10$ and $[\text{total pressure}]_0=755$ Torr.

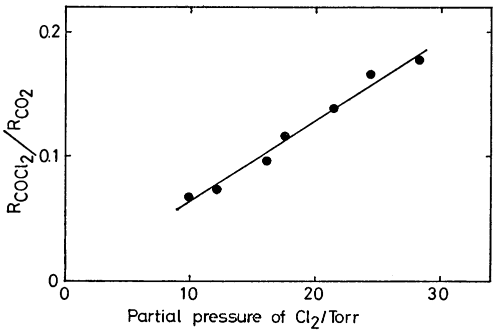

Fig. 5. The function, R_{COCl_2}/R_{CO_2} *vs.* partial pressure of Cl_2 in the photolysis of $Cl_2/CO/O_2/N_2$; $[CO]_0=[O_2]_0=10$ and $[\text{total pressure}]_0=755$ Torr.

for k_8/k_9 determined from the assumption of termolecular process agrees with the results (25) and (26) obtained from the different experiments.

In consideration of all the points discussed above, the termolecular process via ClCO and $ClC(O)O_2$ is confirmed to be the major pathway for the oxidation of CO by Cl atoms at the pressure range of 30 to 755 Torr.

It is of interset to discuss the role of this termolecular reaction in the atmosphere. The most important reaction of Cl in the stratosphere is beleived to be Reaction 27, whose rate constant is $2.7\times10^{-11}\exp(-257/RT)$ cm^3 $molecule^{-1}$ s^{-1}.[18)]

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (27)$$

k_6 was determined to be $10^{14.5}$ cm^6 $molecule^{-2}$ s^{-1} or 8.73×10^{-34} cm^6 $molecule^{-2}$ s^{-1} at 300 K by Clark *et al.*[19)] Since the Arrhenius parameters for the rate constant was not given, let us compare k_{27} with $k_6[M]$ at 300 K and 1 atmospheric pressure to get a rough idea on the role of ClCO mechanism in the stratosphere: k_{27} is 10000 times larger than $k_6[M]$. In the upper atmosphere at low pressure, $k_6[M]$ becomes smaller, and moreover, the concentration of ozone is higher than that of CO in the region.[20,21)] Thus, Reaction 27 is predominant over Reaction 6. Even when ClCO is formed and becomes adduct, $ClC(O)O_2^*$, it dissociates very easily, since the atmospheric density is too low to make three-body reaction effective. Therefore, the oxidation of CO by Cl catalytic cycle is not important in the atmosphere.

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