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Radiation Chemical Reactions in Carbon Dioxide–Propane System. II. Reoxidation of Carbon Monoxide at Low Propane Concentration

Yasumasa Ikezoe and Shoichi Sato
Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-11

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In the γ-radiolysis of carbon dioxide, the back reaction or reoxidation of carbon monoxide, proceeds at a moderate rate with propane concentration less than 0.5%, reducing the apparent G(CO) value. Concerning the total pressure and dose rate dependence of the G(CO) value with such small propane addition, it was found that the back reaction was accelerated by raising the total pressure and by lowering the dose rate. The following reactions of clustered negative ions are considered to explain the pressure and dose rate effects:

$$X^- + CO \rightarrow CO_2 + Y^- + Z_1,$$
$$X^- + C_3H_8 \rightarrow Y^- + Z_2,$$
$$X^- + X^+ \rightarrow mCO_2 + Z_3,$$

where X^- stands for a clustered negative ion.

Radiolysis of carbon dioxide has been studied extensively,[1–3] since Harteck and Dondes[4] irradiated the gas with radon α-rays and reactor radiations in 1955 and 1957. Apparent stability towards ionizing radiation at moderate dose rates ($\approx 10^{16}$ eV/g s) was attributed to a rapid reoxidation reaction, by which carbon monoxide formed is reoxidized to carbon dioxide. However, the detailed mechanism of the reoxidation, or back reaction still remains unclarified. The oxidizing species has not yet been identified, in spite of many species, such as O, O_3, O^+, O_2^+, O^-, O_2^-, CO_3^-, and CO_4^- being proposed. Recently, Parkes[5] suggested that highly clustered ions might be involved in the back reaction.

In this study, we attempted to clarifiy the nature of the back reaction when a small amount of propane is added to carbon dioxide. A controlled amount of propane was added to make the back reaction proceed at a moderate rate, under such conditions, the relation between the apparent G(CO) value and the rate of the back reaction being expected to be connected.

Experimental

Carbon dioxide (Takachiho Chemical, pure gas, stated 99.99% up) and propane (Takachiho Chemical, research grade, stated 99.7% up) were used after removing uncondensable gas with a liquid nitrogen trap. Pyrex glass ampoules (64 ml and 160 ml) were thoroughly washed with distilled water and evacuated to a vacuum of 1×10^{-4} Torr while being heated with a gas burner. The reactant gases were then, introduced into the ampoules, their pressures being measured by a stainless steel Bourdon gage. The total pressure was in the range 0.5—3.2 atm.

The ampoules were irradiated by ^{60}Co γ-rays at exposure rates in the range 0.32—4.2 MR/h. The absorbed dose was determined by the decomposition of ethylene ($G(H_2) \equiv 1.3$) in the same ampoules as those used for sample irradiation, with a correction for the stopping power ratios of the gases to the secondary electrons.

The uncondensable products (CO, H_2, CH_4) were measured volumetrically by using a Toepler pump. The composition of the products was determined by mass spectrometry and confirmed by gas chromatography. Details were the same as described previously.[3]

Results

Propane Addition and the Back Reaction. In the preceding paper,[3] 1% propane was found sufficient to suppress the back reaction. In this study the propane concentration at which maximum G(CO) value could be obtained was first surveyed. Reactions were carried out at slightly smaller propane concentration, when the back reaction might be expected to proceed at a moderate rate.

The G(CO) value is shown in Fig. 1 as a function of the initial propane concentration. G(CO) values were determined at a constant dose (6.7 Mrad). After irradiation the propane added was consumed to some extent, *e.g.*, 0.55 to 0.39% and 0.27 to 0.18%. The maximum 4.5 was obtained at 0.55% propane concentration. This maximum is greater than the one previously obtained (3.6) by γ and $(n+\gamma)$ rays, but smaller than the one (6.7) by fission fragments.[3]

The gradual decrease in G(CO) with propane concentration higher than 0.55% is the same as our previous results.[3] The effect could be related to the suppression of the formation of carbon monoxide from cationic species by propane.

The gradual decrease in G(CO) with the less than 0.55% decrease in propane concentration is attributable

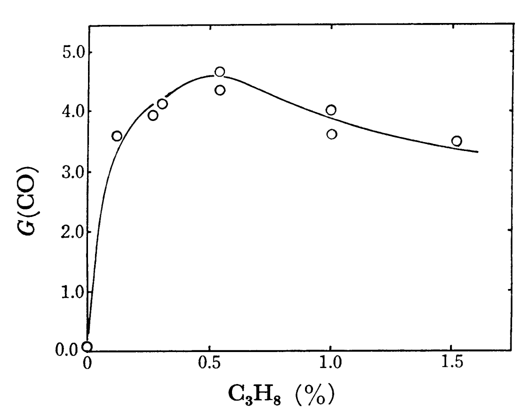

Fig. 1. Effect of propane addition on G(CO). 160-ml glass ampoule, CO_2; 1 atm, γ-rays; 0.95 MR/h, absorbed dose; 6.7 Mrad.

to the back reaction. The lower the concentration of propane, the more pronounced will be the effect of the back reaction. However, when the initial concentration of propane is extremely low (less than 0.1%), the total amount of reaction products, mainly, butane, isobutane, ethane, 2-propanol, and acetone, becomes greater than that of propane at a very small dose.

The radiolysis was carried out mainly at a propane concentration of 0.27%, the middle point between 0.55 % (at which the back reaction became apparent) and 0% (at which the complete back reaction took place). At this propane concentration, dynamic balance was expected between the back reaction and its suppression, no significant interference from the reaction products taking place with the reaction course at the absorbed dose employed. Under these conditions, the quantity of carbon monoxide formed was found to be the same order of magnitude as that of propane present in the reaction system during most of the radiolysis.

Pressure Effect. The pressure dependence of G(CO) at propane concentration less than 0.5% is of special interest, since it may be related to the mechanism of the back reaction.

The pressure dependence of *G*(CO) at propane concentrations of 0.27, 1.1, and 1.6% is shown in Fig. 2. The pressure dependence of *G*(CO) at 0.27% clearly differs from that at 1.1 and at 1.6%. The *G*(CO) value at 0.27% propane decreases from 4.1 to 3.6 with a total pressure rise from 0.4 to 3.2 atm, while the other *G*(CO) values remain constant (4.0 and 3.6).

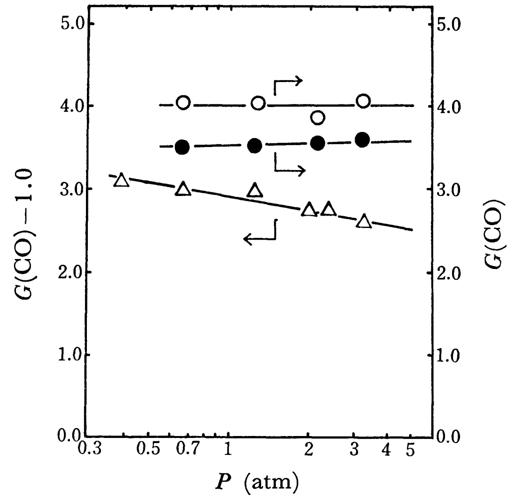

Fig. 2. Pressure dependence of *G*(CO). 64- and 160-ml glass ampoule, γ-rays; 0.95 MR/h, 6.7 Mrad. ●; C_3H_8 1.6%, ○; C_3H_8 1.1%, △; C_3H_8 0.27%.

This result indicates that higher pressure is favorable for the back reaction. This pressure dependence of the back reaction does not necessarily contradict the result by Yoshimura *et al.*[2] who found that the back reaction is suppressed at much higher density (0.5 g/ml), since there is a large difference between our density of the reaction system (1.8×10^{-3} g/ml) and theirs and a quite different mechanism can be considered as regards the back reaction.

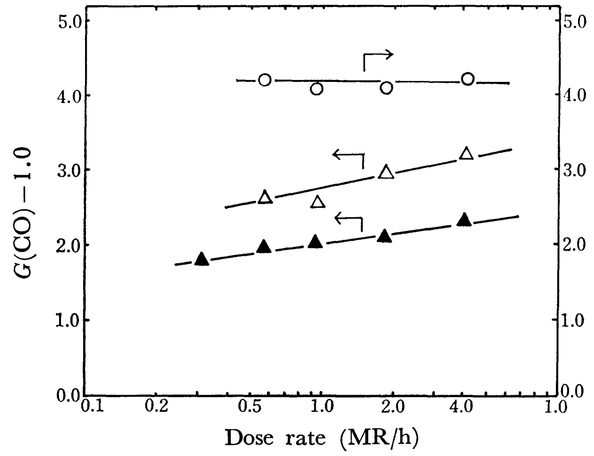

Fig. 3. Dose rate dependence of *G*(CO). 64-ml glass ampoule, 3.2 atm, 6.7 Mrad. ○; C_3H_8 0.82%, △; C_3H_8 0.27%, ▲; C_3H_8 0.06%.

Dose Rate Effect. The dose rate dependence of *G*(CO) is shown in Fig. 3 at the low propane concentration. At 0.82% propane, where the back reaction can be assumed to be quenched, the *G*(CO) value is independent of the dose rate. On the other hand, the *G*(CO) value at 0.27% propane increases from 3.6 to 4.2 with the dose rate increase from 0.57 to 4.2×10^6 R/h. The *G*(CO) at 0.06% propane shows a similar dependence on the dose rate. The dose rate dependence of *G*(CO) obtained here is in agreement with that by Anderson and Best.[7] They found that the *G*(CO) value increased with the dose rate when 0.05% SF_6 was added to carbon dioxide, but remained constant when 1% SF_6 was added.

With respect to the dose rate dependence of the radiolysis of carbon dioxide, it was further found that the steady state concentration of carbon monoxide is proportional to the square root of the dose rate,[8] and that at extremely high dose rate (2×10^{27} eV/g s) carbon dioxide is decomposed with a high *G*(CO) value (7.8).[9]

All these effects of dose rate indicate that the back reaction becomes less effective at high dose rate.

Discussion

Oxidizing Species. Three kinds of active species, *i.e.*, neutral atomic oxygen, positive and negative ions containing an oxygen atom or molecule,[5] are conceivable as the oxidizing species responsible for the back reaction in the radiolysis of carbon dioxide. Since propane added can scavenge all of them,[2,10] the fact that the back reaction is suppressed by propane affords no information on the nature of the oxidizing species. However, the finding that the back reaction and its suppression is balanced even at 0.27% propane (Fig. 1) indicates that the oxidizing species responsible should have a reactivity of the same order of magnitude for reactions with propane and with carbon monoxide as well.

Of the three kinds of oxidizing species, atomic oxygen is much more reactive with propane than with carbon monoxide.[1] Positive ions containing an oxygen atom or molecule are also more reactive with propane than with carbon monoxide, because the ionization potential of an oxygen atom (13.6 eV) or of oxygen (12.1 eV) is higher than that of propane (11.1 eV) and lower than that of carbon monoxide (14.0 eV). If two species were the oxidizing species, the balancing between the back reaction and its suppression should have taken place at much lower propane concentration.

On the other hand, negative ions seem to have a similar reactivity both with propane and with carbon monoxide.[11] Negative ions are known to be clustered in carbon dioxide at atmospheric pressure and ambient temperature.[12] Thus, the clustered negative ion containing an oxygen atom or molecule is presumed to be the most probable species responsible for the reoxidation of carbon monoxide in this system.

Parkes[5] has suggested that the following reactions of clustered ions may be responsible for the reoxidation of carbon monoxide.

$$O_2^{\pm}(CO_2)_n + CO \rightarrow O^{\pm}(CO_2)_n + CO_2, \qquad (1)$$

$$O^{\pm}(CO_2)_n + CO \rightarrow (CO_2)_n^{\pm} + CO_2. \qquad (2)$$

Simple negative ions,[7,8] such as O^-, O_2^-, CO_3^-, and CO_4^-, were found not to be responsible for the rapid back reaction.

Mechanism of the Back Reaction. From the results (Figs. 2 and 3), it is obvious that the back reaction is accelerated by raising the pressure and by lowering the dose rate. The following reactions seem plausible to account for the experimental results:

$$X^- + CO \xrightarrow{k_3} CO_2 + Y^- + Z_1, \qquad (3)$$

$$X^- + C_3H_8 \xrightarrow{k_4} Y^- + Z_2, \qquad (4)$$

$$X^- + X^+ \xrightarrow{k_5} mCO_2 + Z_3, \qquad (5)$$

$$Y^- + X^+ \xrightarrow{k_5} nCO_2 + Z_4. \qquad (5')$$

In these reactions, X^- denotes a clustered negative ion containing an oxygen atom or molecule, Y^- an electron or a negative ion other than X^-, X^+ any possible positive ion, and Z neutral reaction products. Reaction 3 is the back reaction, Reaction 4 the scavenging of X^- by propane, and Reaction 5 and 5′ the neutralization of ionic species.

The ratio, R, of the rate of Reaction 3 to that of all reactions of X^-, becomes

$$R = \frac{k_3[CO]}{k_3[CO]+k_4[C_3H_8]+k_5[X^+]} = \frac{1}{1+K_1[C_3H_8]/[CO]+K_2[X^+]/[CO]}, \qquad (6)$$

where $K_1=k_4/k_3$ and $K_2=k_5/k_3$.

The concentrations of propane and carbon monoxide are proportional to the total pressure at a constant dose. The concentration of X^+ is proportional to the square root of pressure and dose rate, since it is determined by the balance between the ionization of carbon dioxide by radiations and the neutralization of ionic species.[13] Accordingly, the dependence of R on dose rate and pressure is

$$R = \frac{1}{A+B\cdot I^{1/2}\cdot P^{-1/2}}, \qquad (7)$$

where I is the dose rate, P the total pressure, and A and B are constants. R increases with the rise of pressure and with the lowering of dose rate, in qualitative agreement with the dependence of the back reaction on dose rate and pressure.

Pressure and Dose Rate. R can be approximated by the ratio between the reduction in G(CO) due to the back reaction and the ideal G(CO) value, G_0, which would be obtained when no back reaction occurred.

$$R = \frac{G_0-G(CO)}{G_0}. \qquad (8)$$

From Eqs. 7 and 8, we have

$$\frac{G_0}{G_0-G(CO)} = A + B\cdot I^{1/2}\cdot P^{-1/2}. \qquad (9)$$

The ratio, $G_0/(G_0-G(CO))$, should be linearly dependent on $(I^{1/2}P^{-1/2})$, from the mechanism of the back reaction proposed.

The values of $G_0/(G_0-G(CO))$ are plotted as a function of $(I^{1/2}P^{-1/2})$ in Fig. 4, where G(CO) is taken from the experimental values at 0.27% propane addition (Figs. 2 and 3), and G_0 is estimated to be 5.6 from the primary yields of carbon monoxide obtained by Willis and Boyd.[15,16] It seems possible to draw a straight line in Fig. 4, despite a little scatter at low pressure and high dose rate.

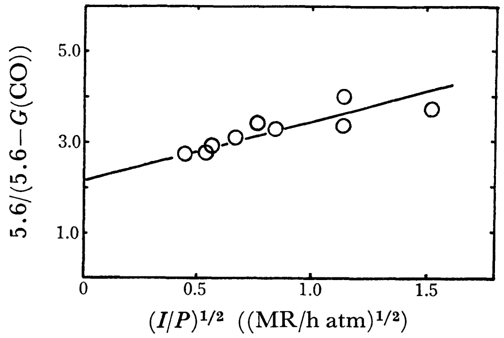

Fig. 4. $G_0/(G_0-G(CO))$ *vs.* $(I/P)^{1/2}$.

From the intercept and the slope of the straight line in Fig. 4, the ratios of the rate constants can be estimated to be $k_4/k_3=1/3$, $k_5/k_3=6.2\times10^7$, using the experimentally determined concentrations of carbon monoxide and propane. k_3 and k_4 become 1.6×10^{-13} and 0.5×10^{-13} $cm^3\ molecule^{-1}\ s^{-1}$, respectively, if we adopt 10×10^{-6} $cm^3\ molecule^{-1}\ s^{-1}$ for the value of k_5.[15] Because of the scatter in Fig. 4 and the approximation included in the above discussion, no accuracy is claimed in these values, though their orders of magnitude seem reasonable when we compare them with those of analogous reactions of a simple negative ion.[17] Clustered ions will have somewhat lower reactivity to the same reactant than ions not clustered.

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11) For example, O^- ion reacts with ethylene ($k=6\times10^{-10}$ cm^3 molecule^{-1} s^{-1})$^{10)}$ and with carbon monoxide ($k=7\times10^{-10}$ cm^3 molecule^{-1} s^{-1})$^{6)}$ with the rate constants of the same order of magnitude.

12) H. W. Ellis, R. Y. Pai, I. R. Gatland, and E. W. McDaniel, *J. Chem. Phys.*, **64**, 3935 (1976).

13) The concentration of X^+ can be estimated as follows. When the exposure rate is $I\times10^6$ R/h, the pressure of carbon dioxide P atm, and the G value of ionization 3, the rate of ion formation per unit volume, F is

$$F=(I\times10^6\ \mathrm{R/h})\ (2.41\times10^{15}\ \mathrm{eV/R\ mol\ CO_2})\ (3\ \mathrm{molecule}/100\ \mathrm{eV})\times(P\ \mathrm{atm})/(3600\ \mathrm{s/h})/(2.45\times10^4\ \mathrm{atm\ cm^3/mol\text{-}CO_2})=0.82\times10^{12}PI(\mathrm{molecule/cm^3\ s}).$$

The rate of disappearance of the ions, D is

$$D=k_5[X^+][X^-+Y^-]=k_5[X^+]^2(\mathrm{molecule/cm^3\ s}).$$

The equilibrium concentration of X^+ is obtained by putting $D=F$. If we use 10×10^{-6} cm^3 molecule^{-1} s^{-1} for the value of k_5, the concentration of X^+, $[X^+]$ is

$$[X^+]=2.8\times10^8P^{1/2}I^{1/2}(\mathrm{molecule/cm^3}).$$

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16) G_0 is determined from the equation

$$G_0=g(CO)+g(CO^+)+2g(C^+)+g(O^+)$$
$$=4.72+0.51+0.14+0.21=5.6$$

17) $O^-+CO\rightarrow CO_2+e^-$ ($k=6\times10^{-10}$ cm^3 molecule^{-1} s^{-1})$^{6)}$

$O^-+C_2H_6\rightarrow C_2H_6O+e^-$ ($k=0.2\times10^{-10}$ cm^3 molecule^{-1} s^{-1}).$^{18)}$

18) T. O. Tiernan, "Interaction between Ions and Molecules," ed by P. Ausloos, Plenum Press, New York (1974), p. 382.