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Radiation Chemical Reactions in Carbon Dioxide–Propane System. III. Formation of Oxygen Containing Products

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The *G* value of water and 2-propanol as well as that of carbon monoxide decreased with decrease in propane concentration below 0.5%, the value of acetone remaining constant. Considering the effects of dose rate and irradiation temperature on the product yields, the results indicate that the formation of water and 2-propanol competes with the back reaction, or the reoxidation of carbon monoxide. A clustered negative ion, $O^-(CO_2)_n$ seems to be the oxidizing species responsible both for the back reaction and the formation of water and 2-propanol. The *G* value of $O^-(CO_2)_n$ was estimated to be 1.3. The formation of acetone is independent of the back reaction.

In the radiolysis of carbon dioxide, reoxidation of carbon monoxide, or the back reaction, is of great interest.[1] The back reaction in the carbon dioxide-propane system was studied at a low propane concentration,[2] and found to be accelerated by raising the total pressure or lowering the dose rate.

In order to clarify the relation between the two reactions and the properties of the oxidizing species present in the reaction system, we have examined the formation of oxygen containing products at the low propane concentration, where the back reaction competes with the formation of oxygen containing products.

Experimental

Carbon dioxide (Takachiho Chemical, pure gas, stated 99.99% up) and propane (Takachiho Chemical, research grade, stated 99.7% up) were used after uncondensable gas had been removed with a liquid nitrogen trap. Pyrex ampoules (160 and 64 ml) were washed with distilled water thoroughly. The reactant gas was introduced into the ampoules connected to a vacuum line, their pressure being measured with a stainless steel Bourdon gauge. Irradiation of the ampoules by ^{60}Co γ-rays and the dosimetry were carried out as described previously.[2] High temperature irradiation was carried out in an electric furnace, in which the temperature was controlled to an accuracy of ± 2 °C.

The irradiated gas was analyzed by means of mass spectrometry and gas chromatography. Three columns were used to separate eleven products; column I (molecular sieve 5A, 70 cm, 30 °C) was used to analyze carbon monoxide and methane, column II (Porapak R, 1.5 m, 120 °C) 2-propanol and hexanes,[3] column III (Porapak T; 2 m+Porapak T coated with 0.5% polyethylene glycol; 5 cm, 120 °C) water, acetone, propylene oxide, isobutane, butane, isopentane and pentane. The analysis of a small amount of water ($\approx 10^{-7}$ mol) required particular attention because of its adsorption on the wall surface of the analytical vacuum line. The effect of adsorption was minimized by conditioning the wall surface with the irradiated gas before its introduction. Details were described elsewhere.[4]

Results

Effect of Propane Concentration. The effects of propane concentration below 1.1% on the *G* values of various products are shown in Figs. 1 and 2. The *G* values were obtained at a constant dose 6.7 Mrad, total pressure 1.88×10^5 Pa, temperature 308 K and exposure rate 0.95 MR/h. The maximum *G*(CO) value 4.3 ± 0.1 and the concentration of propane 0.5% at which the maximum *G*(CO) value was obtained agree with our previous results within experimental error.[2] The decrease in *G*(CO) value with the reduction of propane concentration less than 0.5% is attributed to the back reaction.

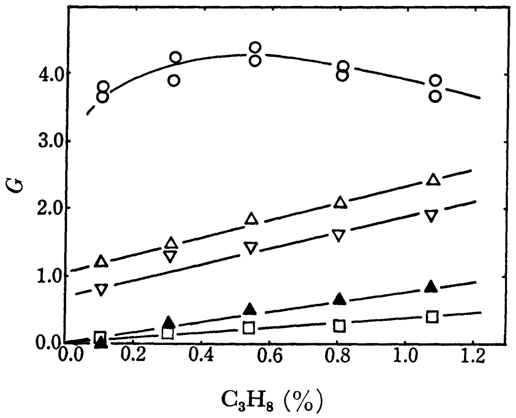

Fig. 1. Effect of propane concentration, I. 160 ml glass ampoule, $CO_2+C_3H_8$; 1.88×10^5 Pa, γ exposure rate; 0.95 MR/h, absorbed dose; 6.7 Mrad. ○; CO, △; $H_2\times 3$, △; $CH_4\times 3$, ▲; (hexanes)$\times 5$, □; (isopentane) $\times 5$.

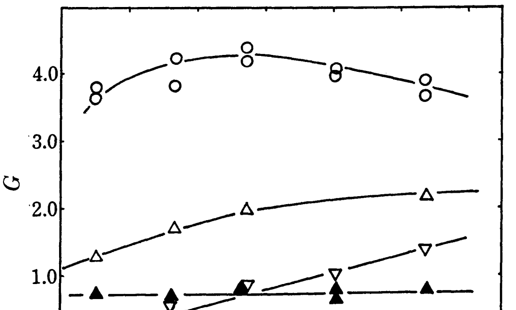

Fig. 2. Effect of propane concentration, II. ○; CO, △; H_2O, ▽; *i*-PrOH$\times 10$, ▲; (acetone)$\times 10$.

The occurrence of the back reaction should necessarily lead to a variation in the *G* values of the products in this reaction system. The *G* values of hydrogen and methane (Fig. 1) decreased linearly with the reduction in propane concentration, but their extrapolated values at the propane concentration of zero per cent did not reach zero. The values of isopentane and hexanes were small (<0.2), apparently converging to zero.

The effect of propane concentration on the formation of oxygen containing products is directly related to the reaction of the oxidizing species responsible for the back reaction. In the range of propane concentration investigated, formation of oxygen containing products competes with the back reaction.

Three oxygen containing products, water, 2-propanol and acetone, besides carbon monoxide were identified and measured. The G value of water (1—3) was the largest of the three. The G values of 2-propanol and acetone were of the same order of magnitude (0.1—0.2), those of other oxygen containing products, such as methanol, ethanol and propylene oxide, being smaller than 0.03. Neither propanal nor 1-propanol was detected. From the material balance of oxygen, it is obvious that unidentified oxygen containing products, not detected by the analytical procedures employed, still remain.

The G value of acetone did not decrease with decrease in propane concentration, remaining constant (0.08 ± 0.01) in the whole range of propane concentration investigated (Fig. 2). This indicates that acetone is formed by the reaction of an oxidizing species not responsible for the back reaction.

The G values of water and 2-propanol decreased with decrease in propane concentration. The G value of 2-propanol decreased linearly and converged to zero at zero per cent propane, while the G value of water did not converge to zero. This suggests that both water and 2-propanol are formed by the reaction of the oxidizing species responsible for the back reaction, but the mechanisms of their formations differ.

Effects of Dose Rate and Temperature. For the propane concentration 0.27%, the back reaction and its suppression are dynamically balanced. The back reaction has been found to be retarded by raising the dose rate, resulting in an apparent increase in G(CO) value.[2] The formation of the oxygen containing products seems to depend on the dose rate.

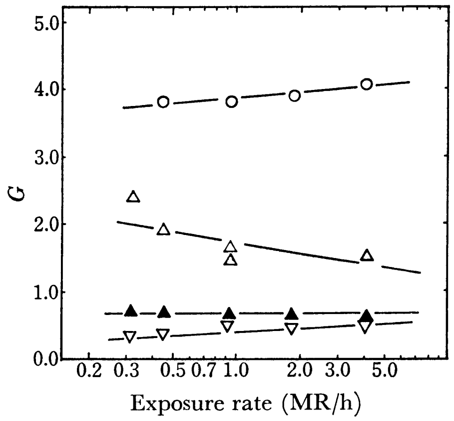

Fig. 3. Effect of dose rate. 160 ml glass ampoule, $CO_2 + C_3H_8$; 1.12×10^5 Pa, C_3H_8; 0.27%, absorbed dose; 6.7 Mrad. ○; CO, △; H_2O, ▽; *i*-PrOH × 10, ▲; (acetone) × 10.

The effect of dose rate at 0.27% propane on the G value of carbon monoxide, water, 2-propanol, and acetone is shown in Fig. 3. The G values of other products such as hydrogen, methane, isopentane, and hexanes were also examined. They remained constant in the whole range of dose rate investigated.

The G(CO) value increased with the dose rate in agreement with the previous result.[2] The G value of water decreases with the rate, that of acetone remaining constant (0.07 ± 0.01). The G value of 2-propanol at 0.27% propane was very small (<0.05), increasing slightly with dose rate. The retardation of the back reaction by the rise in dose rate is accompanied by a decrease in the formation of water and a slight increase in the formation of 2-propanol.

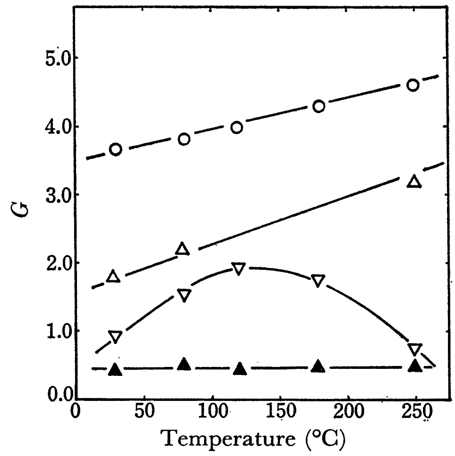

Fig. 4. Effect of irradiation temperature. 64 ml glass ampoule, $CO_2 + C_3H_8$; 4.58 mg/ml, C_3H_8; 1.1%, γ exposure rate; 0.45 MR/h, absorbed dose; 6.7 Mrad. ○; CO, △; H_2O, ▽; *i*-PrOH × 5, ▲; (acetone) × 5.

The effect of irradiation temperature on the G values of carbon monoxide, water, 2-propanol and acetone is shown in Fig. 4. Conditions were as follows: irradiation temperature 30—250 °C, with the other conditions constant; gas density 4.58 mg/ml, propane concentration 1.1%, exposure rate 0.45 MR/h, and absorbed dose 6.7 Mrad. We see from Figs. 1 and 2 that at 1.1% propane the formation of oxygen containing products predominates over the back reaction. The mechanism of their formation seems to be the same as that at 0.27% propane.

The G value of 2-propanol shows an interesting behavior. At first, it increased from 0.2 to 0.4 with the rise in temperature from 30 to 120 °C, decreasing to 0.15 at 250 °C. That of acetone remained constant (0.1 ± 0.01).

The G values of carbon monoxide and water increased steadily with the irradiation temperature. This is in constrast to the effect of the dose rate on the G values (Fig. 3).

Discussion

Oxygen Containing Products and the Back Reaction. The formation of oxygen containing products results from the reactions of the same oxidizing species responsible for the back reaction. The following reactions were proposed for the mechanism of such reactions.[2)]

$$X^- + CO \longrightarrow CO_2 + Y^- + Z_1 \qquad (1)$$

$$X^- + C_3H_8 \longrightarrow Y^- + Z_2 \qquad (2)$$

$$X^- + R^+ \longrightarrow mCO_2 + Z_3 \qquad (3)$$

$$Y^- + R^+ \longrightarrow nCO_2 + Z_4 \qquad (4)$$

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^-, R^+ any possible positive ion, and Z a neutral product.

Reactions 2 and 3 contribute to the formation of oxygen containing products. Reaction 3 contributes not only to the formation of oxygen containing products but also to the back reaction, depending on the identity of R^+.[5)] Reaction 2, the scavenging of X^- by propane, leads to the formation of oxygen containing products other than carbon monoxide, competing with Reactions 1 and 3. The yield of the product in Reaction 2 becomes low with decrease in propane concentration.

Oxygen containing products are formed by reactions of the oxidizing species other than X^-. An oxygen atom (ground and excited) and the positive ion containing an oxygen atom or molecule[7)] are conceivable. They are expected to react preferentially with propane even at the reduced concentration of propane, because of their high reactivity with propane. In this case propane concentration has little effect on the yield of the oxygen containing products.

Water and 2-Propanol. The results show that the G values of water and 2-propanol, as well as of carbon monoxide depend in a complicated way on propane concentration, dose rate, and irradiation temperature, indicating that there is a certain relation between the back reaction and the formation of water and 2-propanol.

It is impossible to determine the exact mechanism of the formation of water and 2-propanol which explains all the experimental results. However, the following reactions seem plausible for qualitative explanation.

ionic mechanism of water formation

$$O^-(CO_2)_n + C_3H_8 \longrightarrow (OH)^-(CO_2)_n + C_3H_7 \qquad (2')$$

$$(OH)^-(CO_2)_n + C_3H_8 \longrightarrow H_2O + nCO_2 + C_3H_7 + e^- \qquad (5)$$

radical mechanism of water formation

$$O + C_3H_8 \longrightarrow OH + C_3H_7 \qquad (6)$$

$$OH + C_3H_8 \longrightarrow H_2O + C_3H_7 \qquad (7)$$

mechanism of 2-propanol formation

$$(OH)^-(CO_2)_n + C_3H_7 \longrightarrow i\text{-PrOH} + nCO_2 + e^- \qquad (8)$$

Water should be formed by at least two processes, ionic and radical. In the former, other ionic species such as $O_2^-(CO_2)_n$, $O^+(CO_2)_n$ and $O_2^+(CO_2)_n$, have been considered, in addition to $O^-(CO_2)_n$, to be the probable oxidizing species in pure carbon dioxide.[8)] However, in the present reaction system, $O_2^-(CO_2)_n$ seems to be negligible since the formation of oxygen is inhibited by propane. The contribution of $O^+(CO_2)_n$ and $O_2^+(CO_2)_n$ was neglected because of their low yields.[5,7)] On the other hand, O^- (and $O^-(CO_2)_n$) can be formed by the dissociative attachment of an electron to carbon dioxide.[9)]

By the above mechanism, the yield of water by the ionic process will depend on the concentration of propane because of the competing back reaction 1. On the other hand, the yield by the radical process will not depend on it, since O atom preferentially reacts with propane. The G value of water which is due to the radical process, $G(H_2O)_r$, can be approximated by the extrapolated G value 1.1 of water to zero per cent propane (Fig. 1). The G value of water due to the ionic process, $G(H_2O)_i$, could be estimated by subtracting $G(H_2O)_r$ from the experimental G value of water. The maximum $G(H_2O)_i$ thus obtained is 1.1.

Formation of 2-propanol seems to be due to the ionic process (Reactions 2′ and 8). The rate of Reaction 8 should depend on the dose rate more strongly than that of Reaction 5, since the concentration of C_3H_7 is a function of dose rate, but not that of propane. Thus, the above mechanism satisfies qualitatively the experimental effect of dose rate on the formation of water and 2-propanol (Fig. 3). Reaction 8 is expected to depend on the irradiation temperature.[10)]

If the above mechanism holds for the formation of water and 2-propanol, the G value of $O^-(CO_2)_n$ can be estimated by

$$G(O^-(CO_2)_n) \approx G(H_2O)_i + G(i\text{-PrOH}) = 1.3. \qquad (9)$$

Acetone. The G value of acetone is costant irrespective of the reduction in propane concentration (Fig. 2). Consequently, the oxidizing species, $O^-(CO_2)_n$, responsible for the back reaction in the present reaction system, is excluded from the precursor of acetone. Moreover it kept a constant value irrespective of the variation in dose rate and irradiation temperature (Figs. 3 and 4). The results suggest that acetone is a product of a reaction of highly excited species formed by the direct action of the ionizing radiations on carbon dioxide, having a high reactivity with propane.

Excited oxygen atoms and atom ions are known to be formed in quantity in the primary process in the radiolysis of carbon dioxide.[12)] Among them, $O(^1D)$ reacts with paraffins to form ketone.[13,14)]

$$O(^1D) + RH \longrightarrow H_2 + \text{ketone} \qquad (10)$$

The formation of acetone could be explained by an analogous reaction of $O(^1D)$ with propane, if Reaction 10′ were independent of the propane concentration and irradiation temperature.

$$O(^1D) + C_3H_8 \longrightarrow CH_3COCH_3 + H_2 \qquad (10')$$

However, in the reaction system investigated, $O(^1D)$ would preferentially react with carbon dioxide and be deactivated to the ground state, $O(^3P)$.[15)] The rate of Reaction 10′ should depend on the concentration of propane. Reaction 10′ for the formation of acetone is thus not compatible with the experimental result (Fig. 2). This is confirmed by the lack of 1-propanol formation, since 1-propanol is formed in a greater amount than 2-propanol[16)] and probably acetone,[14)] when $O(^1D)$ reacts with propane. The formation of acetone should be ascribed to the excited species other than $O(^1D)$. So far the precursor of acetone can not be identified further.

The precursor of acetone differs from the oxidizing species which is responsible for the back reaction in the present reaction system. However, the possibility that the highly excited species responsible for the formation of acetone plays a role in the back reaction in pure carbon dioxide cannot be excluded. The back reaction in pure carbon dioxide is probably not identical to that in the carbon dioxide–propane system even at very low propane concentration.

References

1) A. R. Anderson and D. A. Dominey, *Radiat. Res. Rev.*, **1**, 269 (1968).

2) Y. Ikezoe and S. Sato, *Bull. Chem. Soc. Jpn.*, **51**, 33 (1978).

3) A mixture of 2-methylpentane and 2,3-dimethylbutane.

4) S. Sato, Y. Ikezoe, S. Shimizu, H. Nakajima, and T. Kobayashi, JAERI-M 7316 (1977).

5) The most abundant positive ions in the reaction system seem to be $(C_3H_8)^+(CO_2)_n$ and $(C_3H_7)^+(CO_2)_n$, the reaction of which with X^- probably contributes to the formation of oxygen containing products. $(CO_2)^+(CO)(CO_2)_n$ and $(CO_2)^+(CO_2)_n$ are also conceivable positive ions. The reaction of $(CO_2)^+(CO)(CO_2)_n$ with X^- contributes to the back reaction, and that of $(CO_2)^+(CO_2)_n$ with X^- only to neutralization.

6) Y. Ikezoe and S. Sato, *J. Nucl. Sci. Technol.*, **13**, 503 (1976).

7) In pure carbon dioxide, $(CO_2)^+(CO_2)_n$, $O^+(CO_2)_n$, and $O_2^+(CO_2)_n$ are major positive ions.[8] But in the present reaction system, the positive charge is expected to be concentrated on propane and its fragments, because of the low ionization potential of propane (11.1 eV) as compared with those of carbon dioxide (13.9 eV), an oxygen atom (13.6 eV), and oxygen (12.1 eV).

8) D. A. Parkes, *J. Chem. Soc., Faraday Trans. 1*, **69**, 198 (1973).

9) D. A. Parkes, *J. Chem. Soc., Faraday Trans. 1*, **68**, 627 (1972).

10) When the temperature is raised, clustered ions become less clustered.[11] Under such conditions, 2-propanol, even if formed by Reaction 8, would at once be decomposed by the excess heat of reaction.

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

12) C. Willis and A. W. Boyd, *Int. J. Radiat. Phys. Chem.*, **8**, 71 (1976).

13) R. K. M. Jayantry, R. Simonaitis, and J. Heicklen, *Int. J. Chem. Kinet.*, **8**, 107 (1976).

14) A. J. Colussi and R. J. Cvetanovic, *J. Phys. Chem.*, **79**, 1891 (1975).

15) G. Paraskevopoulos and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **91**, 7572 (1969).

16) H. Yamazaki and R. J. Cvetanovic, *J. Chem. Phys.*, **41**, 3703 (1964).