γ-Radiolysis of Gaseous Carbon Dioxide at High Densities

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Summary G(CO) from γ-irradiated gaseous carbon dioxide at 50 ± 1 °C showed a marked increase with density increase above 0·2 g/ml, owing to the increased probability of geminate recombination of ion pairs at high densities.

THE effect of density in gas-phase radiolysis has been the subject of several studies. In a few cases a sharp decrease in decomposition was observed at higher densities, which was attributed to ion-cluster formation[1] or collisional deactivation of excited ions,[2] *etc.* We have observed an abrupt increase of G(CO) at $d >$ *ca.* 0·2 g/ml in the γ-radiolysis of gaseous CO_2 at 50 ± 1 °C (Figure), which we interpret as the result of geminate recombination of ion pairs. The yield of CO was determined by gas chromatography using Molecular Sieve 5A with He carrier gas. The G value was calculated from the dose rate, determined by a Fricke dosimeter after correction for the electron density,† *i.e.*, $1{\cdot}00 \times 10^{18}$ eV/g h in CO_2. Total doses were in the range 10^{19}—10^{20} eV/g; most of the samples in the higher density region received *ca.* 5×10^{19} eV/g. G.l.c. analysis of CO_2 processed in the same manner as the irradiated samples showed no detectable organic impurity.‡

Gaseous carbon dioxide is noted for its stability to low LET radiation except at very high dose rate,[3,4] though it readily decomposes in the condensed phase.[5] This high stability is due to reverse reactions which maintain the yield of CO at a steady state value which is proportional to the dose rate.[6] In the present study the yield was found to be linear with dose even at low densities [*e.g.* at $d = 0{\cdot}33 \pm 0{\cdot}04$ g/ml, $G(\text{CO}) = 0{\cdot}37 \pm 0{\cdot}04$], and also a fivefold increase in the dose rate did not affect the yield. Therefore our lower G-values are not due to the steady state attainment. The species principally responsible for the re-oxidation of CO was found to be ionic and in the formation of this species oxygen was involved.[5,7] The higher yield in the condensed phase is attributed to the

† It was previously shown that such extrapolation was justified in the density range of this work.[1a]

‡ The yield of oxygen was not measured for all the samples, since a small amount of air leaked in during analysis (for the analytical procedure, see M. Nishikawa and N. Shinohara, *Radiation Res.*, 1968, **33**, 194). A correction for the presence of this air gave variable oxygen yields. Addition of small amount of hydrocarbons sharply increased the yield of CO, which was not depressed by the addition of SF_6. Therefore this scatter cannot be due to the presence of organic impurities.

rapid geminate recombination of ion pairs which inhibits the formation of the oxidizing species.[5] The larger G-values found at higher densities in the present study are consistent with the above interpretation, since geminate charge neutralization is facilitated by higher density.[8]

Addition of a small amount of SF_6 reduced $G(CO)$ drastically throughout the density range studied. SF_6 is known to scavenge low-energy electrons efficiently and not to react with oxygen atoms.[9] It is generally accepted that neutralization of positive ions by SF_6^- does not result in dissociation. Thus in this density region CO is produced principally by reaction (1). The finding is not necessarily contradictory to that of Anderson and Best[10] who found

$$CO_2^+ + e^- \rightarrow CO_2^* \rightarrow CO + O \qquad (1)$$

that SF_6 enhances $G(CO)$ in the radiolysis of CO_2 at *ca.* 300 mmHg. Since there is no geminate neutralization at this low pressure,[11] the reverse reaction by an ionic mechanism predominates. SF_6, however, interferes with the formation of the negatively charged oxidizing species. In fact, SF_6 was found to reduce $G(CO)$ at a similar pressure but at a much higher dose rate where neutralization is expected to be more important.

According to the argument advanced by Baulch *et al.*,[5] reaction (1) must involve geminate pairs since a very small amount of oxygen was shown to suffice for scavenging electrons and/or CO_2^+.[12] The fact that the concentration of SF_6 required to decrease the CO yield at $d = ca.\ 0{\cdot}5$ g/ml is much higher (*ca.* 1·5 mole %) than is usual in gas-phase radiolysis at atmospheric pressures also suggests the geminate character of the neutralization.

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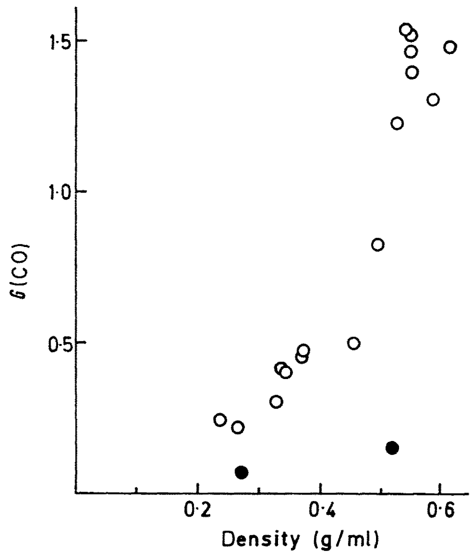

FIGURE. *Dependence of* CO *yield* (molecules/100 eV) *on density in the irradiation of gaseous* CO_2 *by* ^{60}Co-γ *rays at* 50 ± 1 °C; ○ *no additives*; ● SF_6 (> *ca.* 1·5 *mol* %) *added.*

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