# *The Radiation-Induced Exchange Reaction of Oxygen Atoms in Carbon Dioxide*

By Kozo HIROTA, Hideo TERASAKI and Motoyoshi HATADA

(Received July 12, 1962)

There have been several reports on the radiation-induced reactions of carbon dioxide since the classical paper of Lind[1]. Recently Harteck and Dondes[2] obtained a small $G$ value on the decomposition of carbon dioxide in relation to the study on the production of carbon suboxide and its polymers. However, they concluded[3] that this is due to the presence of the backward reaction, because the $G$-value became higher by the inhibition of the backward reaction with nitrogen dioxide. In relation to the above conclusion on the decomposition of carbon dioxide by Harteck

1) S. C. Lind and D. C. Barwell, *J. Am. Chem. Soc.*, **47**, 2675 (1925).

2) P. Harteck and S. Dondes, *J. Chem. Phys.*, **23**, 902 (1955); **26**, 1727 (1957).

3) P. Harteck and S. Dondes, *Z. Elektrochem.*, **64**, 983 (1960).

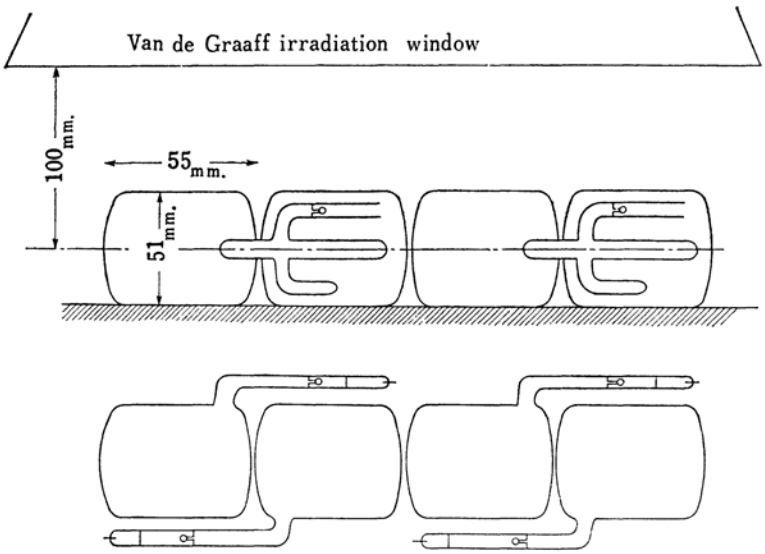


Fig. 1. Arrangement of the irradiation ampoules.

et al., it will be interesting to study the radiation-induced oxygen exchange between normal and labeled carbon dioxide: $C^{18}O_2 + C^{16}O_2 \rightarrow 2C^{16}O^{18}O$. Our purpose in the present paper is to report the investigation actually carried out on this line.

## Experimental

**Labeled Carbon Dioxide $C^{18}O_2$.** — The enriched carbon dioxide $C^{18}O_2$ used in this experiment was prepared by the thermal diffusion method at the Faculty of Science, Osaka University[4]. The $^{18}O$ content was ca. 29 atom % and the ratio $C^{16}O_2$ : $C^{16}O^{18}O$ : $C^{18}O_2$ was 51.1 : 39.9 : 8.5*.

**Normal Carbon Dioxide.** — Commercial carbon dioxide was used after vacuum distillation.

**Irradiation.** — Definite amounts of the normal and the labeled carbon dioxide were taken and introduced into a cylindrical glass ampoule (80 cc.) with a break-off-tip by using liquid nitrogen cold trap. A set of such ampoules were arranged as shown in Fig. 1 and was irradiated simultaneously with 1.5 MeV. electron beam from the Van de Graaff accelerator (High Voltage Eng. Co., Model AKS).

**Analysis.** — After the irradiation, the samples were taken out from the ampoules and were analyzed by use of a mass-spectrometer (Hitachi, RMU-5 type).

## Results and Discussion

The results in addition to the conditions of the irradiation are described in Table I. In the case of No. 4, glass wool was inserted into the ampoule.

**Effect of the Irradiation Time.** — The logarithm of the excess amount of heavy carbon dioxide in mole from the equilibrium value is plotted against the irradiation time $t$. The rate constant $k$ was estimated to be $1.5_2\ hr^{-1}$, assuming that this exchange reaction proceeds according to 1st order, i. e.,

$$\ln\frac{[CO_2^*] - [CO_2^*]_\infty}{[CO_2^*]_0 - [CO_2^*]_\infty} = -kt$$

and reaches the equilibrium, the thermal equilibrium constant of which is as follows.

$$[COO^*]^2/[CO_2^*]\,[CO_2] = 4.0$$

where $[COO^*]$, $[CO_2^*]$ and $[CO_2]$ are the amounts of $COO^*$, $CO_2^*$ and $CO_2$ in mol./unit volume, respectively.

**Determination of the Apparent $G$ Value.** — The $G^{exc}$-value of the exchange reaction is given by the decrease of $CO_2^*$ as follows:

$$G(-CO_2^*) = \frac{\text{Number of the } CO_2^* \text{ exchanged} \times 100}{\text{Energy absorbed in eV.}} \quad (1)$$

This value will be called an apparent one of $G^{exc}$, because only the value of the labeled $CO_2$ is determined.

In order to evaluate the energy absorbed by carbon dioxide in Eq. 1, effective thickness of the ampoules was calculated to be 2.1 mm. in No. 1—3, while it was estimated to be 2.2 mm. in No. 4 by considering the thickness corresponding to a half amount of the glass wool besides. The dose rate $I$ thus calculated in

4) K. Hirota, Y. Kobayashi, M. Takahashi and Y. Yoshikawa, *Isotopes and Radiation (Tokyo)*, **2**, 235 (1959).

* Hereafter $O^{18}$ will be denoted by O* while $^{16}O$ by O.

* In the equation $N_A$ is the Avogadro number.

Table I. Experimental results

| | | Blank | No. 1 | No. 2 | No. 3 | No. 4 |
|---|---|---|---|---|---|---|
| Dose rate $\times 10^5$ rad/sec. | | 0 | 0.88 | 0.88 | 0.88 | 0.55[b] |
| Irradiation time, min. | | 0 | 60 | 120 | 180 | 180 |
| Before the irradiation | Labeled carbon[a] dioxide, $\times 10^{-5}$ mol. | 5.23 | 5.41 | 5.50 | 5.48 | 4.02 |
| | Normal carbon dioxide, $\times 10^{-5}$ mol. | 16.24 | 16.11 | 16.08 | 16.16 | 12.38 |
| | Total $CO_2$, $\times 10^{-5}$ mol. | 21.48 | 21.52 | 21.58 | 21.64 | 16.41 |
| | Normal $CO_2$ : Labeled $CO_2$ | 3.10 | 2.98 | 2.93 | 2.95 | 3.08 |
| After the irradiation | $CO_2$ (%) | (88.6)[c] | 86.6 | 86.3 | 86.6 | 86.7 |
| | COO* (%) | (9.5) | 12.7 | 12.4 | 13.0 | 12.4 |
| | $CO_2$* (%) | (1.90) | 0.11 | 0.84 | 0.45 | 0.94 |

N. B. a) Isotopic composition of the carbon dioxide used ($CO_2$ : COO* : $CO_2$* = 51.1 : 39.9 : 8.5)
b) The value corrected for the energy absorption by glass wool in the reaction vessels.
c) Percentages in parentheses are those of the blank.

both cases was $0.88\times10^5$ rad/sec. and $0.55\times10^5$ rad/sec., respectively.

First, mean $G(-CO_2^*)$ value was estimated to be $0.3_7$ from No. 1, 2 and 3. In the case where glass wool was contained in the ampoule, the $G(-CO_2^*)$ value was calculated to be $0.3_5$ using the dose rate corrected for the energy absorbed by the glass wool. Since $G(-CO_2^*)$ was not altered by the addition of the glass wool, it may be reasonable to regard the effect of the wall of the vessel negligible to the reaction.

However, the result observed after 3 hr. irradiation (No. 3) should be eliminated from the data for discussion, because the isotopic equilibrium may have been completed at that time and the isotopic composition of this system was not changed by further irradiation. Therefore, it is more reasonable to calculate the $G$-value of the exchange reaction of oxygen atoms between carbon dioxide molecules by the following equation,

$$G_{\mathrm{corr}}(-CO_2^*)=\frac{([CO_2^*]_0-[CO_2^*]_\infty)k\times N_A}{I\cdot W\cdot 6.25\times10^{11}}$$

where $I$ is the dose rate in rads/hr., and $W$ is the amount of carbon dioxide in grams. The $G$ value calculated by this equation was $1.7_2$. In the discussion $G_{\mathrm{corr}}(-CO_2^*)$ will be used hereafter.

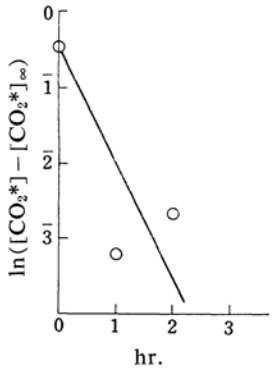


Fig. 2. Irradiation time vs. $\ln([CO_2^*]-[CO_2^*]_\infty)$. $k=1.5\ \mathrm{hr}^{-1}$

**Total $G$ Value of the Exchange Reaction.** — The apparent $G$ values calculated above correspond to the exchange reaction a between $CO_2$* and $CO_2$. However, there are several similar reactions b—f in this system, which are not observed because of the situation that the species of the reactant and the product are the same.

$$CO_2^*+CO_2 \rightarrow COO^*+COO^* \quad (a)$$
$$CO_2^*+COO^* \rightarrow COO^*+CO_2^* \quad (b)$$
$$CO_2^*+CO_2^* \rightarrow CO_2^*+CO_2^* \quad (c)$$
$$COO^*+CO_2 \rightarrow COO^*+CO_2 \quad (d)$$
$$COO^*+COO^* \rightarrow COO^*+COO^* \quad (e)$$
$$CO_2+CO_2 \rightarrow CO_2+CO_2 \quad (f)$$

Fraction of the reaction a to all the reactions is calculated by

$$\frac{l\cdot n}{l\cdot n+l\cdot m+m\cdot n+\frac{l^2}{2}+\frac{m^2}{2}+\frac{n^2}{2}}=\frac{l\cdot n}{\frac{1}{2}(l+m+n)^2}$$

where $l$, $m$ and $n$ are the initial molar fractions of $CO_2$*, COO* and $CO_2$, respectively. Thus, the total $G$ value of carbon dioxide $G_{\mathrm{total}}^{\mathrm{exc}}$ in such a kind of exchange reaction is given by

$$G_{\mathrm{total}}^{\mathrm{exc}}=G_{\mathrm{corr}}(-CO_2^*)\cdot\frac{1}{2\cdot l\cdot n} \quad (2)$$

Since $2\cdot l\cdot n$ equals to $0.033_7$, $G_{\mathrm{total}}^{\mathrm{exc}}$ was calculated to be 51 using the $G_{\mathrm{corr}}(-CO_2^*)$ value of $1.7_2$.

**Comparison of the $G$ Value of the Radiation-Induced Exchange Reaction with That of Radiolysis.**—Harteck et al.[3] reported a rather small $G^{\mathrm{dec}}$ value (0.005) for the radiolysis of carbon dioxide at 1 atm. and concluded that

this small value was resulted from the simultaneous backward reaction induced by radiation. This conclusion was based on the fact that the $G^{dec}$ value increased to $8.5\pm1$ when nitrogen dioxide ($NO_2$) was added as inhibitor to the backward reaction[3]. In our experiment, the forward and backward reactions under irradiation may give rise to exchange reaction of oxygen atoms between carbon dioxide molecules as actually shown by the present experiment. Therefore the $G^{exc}_{total}$ must correspond to Harteck's $G^{dec}$ in which the contribution of the backward reaction was eliminated. However, since the $G^{exc}_{total}$ is determined to be 51, it is larger to some extent than $G^{dec}$ of Harteck (8.5). This discrepancy may be attributed to the fact that the nitrogen dioxide added in Harteck's experiment may have some roles other than as an inhibitor of the backward reaction, whereas the samples in our experiment did not contain any impurities.

## Summary

Oxygen exchange of carbon dioxide induced by $\beta$-ray irradiation has been investigated by use of oxygen isotope O*. From the decrease of O* amount, the apparent and total values of the exchange reaction, $G_{corr}(-CO_2^*)$ and $G^{exc}_{total}$, have been calculated to be $1.7_2$ and 51, respectively. The latter value 51 would be equivalent to the forward reaction, but has been shown to be larger than the corresponding value (8.5) in Harteck's experiment.

Appreciation is expressed to Mr. Yohta Nakai for his collaborations in operation of the Van de Graaff accelerator and also to Dr. Yasushi Kobayashi and Mr. Masashi Takahashi for their preparation of heavy carbon dioxide.

*Department of Chemistry*
*Faculty of Science*
*Osaka University*
*Nakanoshima, Kita-ku, Osaka* (*K. H.*)

*Osaka Laboratory*
*Japanese Association for*
*Radiation Research on Polymers*
*Neyagawa City, Osaka* (*K. H., H. T. & M. H.*)