686. *Radiolysis of Carbon Dioxide.*

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The radiolysis of carbon dioxide in the presence of sulphur dioxide and nitrogen dioxide as scavengers has been studied by using the Harwell nuclear reactor, BEPO, and two different sources of γ-radiation. The measured G value for carbon monoxide production is 3·51($\pm$0·23) for γ-radiation. Possible reasons for the discrepancy between this value and previous data are discussed. Uncertainties in the methods of dosimetry used for reactor radiation are discussed and it is concluded that G(CO) for reactor radiation agrees with the value for γ-radiation within the limits of these uncertainties.

The apparent stability of carbon dioxide to high-energy radiation is well established [1-4] and is attributed to a very efficient recombination process initiated either by carbon atoms [3] or by oxygen [5] produced in the initial radiolysis. While it was shown in very early radiation-chemical studies that the presence of mercury- or phosphorus-containing impurities [6] or the addition of hydrogen or methane [7] resulted in carbon monoxide production, there is little recorded work on quantitative measurements of the initial yield of carbon monoxide from the radiolysis of carbon dioxide in the presence of oxygen-atom scavengers in the gas phase. Harteck and Dondes [3,4] give G(CO) = 8·5 ($\pm$ 1) for a variety of radiations having used nitrogen dioxide as an oxygen-atom scavenger; Steinberg [8] gives a value of G(CO) = 4·5 ($\pm$ 0·4) for ^{60}Co γ-radiation with the same scavenger. In view of this discrepancy and of the importance of carbon dioxide radiolysis in nuclear reactor technology we have measured the decomposition of carbon dioxide in the presence of both sulphur dioxide and nitrogen dioxide, using γ-radiation from both a ^{60}Co source and an irradiated fuel-rod assembly (T.I.G. pond), and mixed n,γ-radiation from two positions in the Harwell nuclear reactor BEPO.

Results

Dosimetry.—The Fricke dosimeter was used for ^{60}Co γ-radiation, and ionisation-chamber measurements were used for the spent fuel-rod assembly. Dosimetry in nuclear reactors is difficult owing to the complex nature of the radiation and the different modes of energy absorption which predominate for different materials. The principal components of reactor radiation are γ-radiation with various quantum energies, and neutrons whose energies range in a continuous spectrum from a fraction of an electron-volt to several million electron-volts. Non-fissile materials irradiated in a reactor absorb energy from γ-rays, from the elastic scattering

[1] Wourtzel, *Le Radium*, 1919, **11**, 346.
[2] Lind, " The Chemical Effects of alpha Particles and Electrons," Chemical Catalog Co., New York, 1929.
[3] Harteck and Dondes, *J. Chem. Phys.*, 1955, **23**, 902.
[4] Harteck and Dondes, *J. Chem. Phys.*, 1957, **26**, 1727.
[5] Hirschfelder and Taylor, *J. Chem. Phys.*, 1938, **6**, 783.
[6] Cameron and Ramsay, *J.*, 1908, **93**, 966.
[7] Lind and Bardwell, *J. Amer. Chem. Soc.*, 1925, **47**, 2675.
[8] Steinberg, Brookhaven National Laboratory Research Report, No. BNL 665, March, 1961.

of fast neutrons, and from nuclear processes induced by neutron capture, but the relative importance of each of these processes depends critically on the material being irradiated. While the energy absorbed by condensed media in BEPO has been measured accurately by calorimetry,[9] the direct application of these results to the radiolysis of gases inevitably overestimates the amount of energy absorbed, because of the uncompensated loss of recoil atoms and electrons to the walls of the vessel. Thus radiation-chemical yields in gases that are calculated directly from the calorimetric data will be minimum values. We have attempted to estimate a correction by comparing the yields of nitrogen from the radiolysis of nitrous oxide in the reactor (calculated from the calorimetric work) with those obtained for γ-radiation where the dosimetry is more precise.

With ^{60}Co γ-radiation at a dose rate of $1\cdot9 \times 10^{17}$ ev g.$^{-1}$ min.$^{-1}$ the mean of 8 determinations gave $G(N_2) = 10\cdot35$ ($\pm$ 0·44) from the radiolysis of nitrous oxide, while the dose–yield curves were linear up to 0·15% conversion, *i.e.*, up to doses of $1\cdot8 \times 10^{20}$ ev g.$^{-1}$. This value agrees with the value of $G(N_2) = 10\cdot5$ ($\pm$ 0·7) obtained by Hearne and Hummel [10] for measurements under comparable conditions and is close to the value 11·0 ($\pm$ 0·4) which they give for the average of all their irradiations, weighted in favour of the determinations with tritium β-radiation. Our irradiations were carried out in cylindrical glass cells of about 3 cm. diameter and at a gas pressure of 50 cm. (Hg.) so that our conditions corresponded to those shown by the above authors to be essentially free from " wall effects."

When nitrous oxide at one atmosphere pressure was irradiated in the T.I.G. pond in bulbs identical with those used for the study of mixtures of carbon dioxide and nitrogen dioxide the mean of three determinations was $G(N_2) = 8\cdot6$ ($\pm$0·3). These irradiations were carried out at doses between 1 and $2\cdot8 \times 10^{21}$ ev g.$^{-1}$, corresponding to about 2% decomposition. It has been shown by Hearne and Hummel [10] and by Steinberg [11] that for doses above about 10^{19}—10^{20} ev g.$^{-1}$ the integral yield of nitrogen is no longer independent of dose and the value $G(N_2) = 8\cdot6$ agrees well with other work in the same dose range.[11–13]

One obtains $G(N_2) = 7\cdot0$ ($\pm$ 0·4) by calculation from the calorimetric data for BEPO at doses equivalent to those used with γ-radiation in the T.I.G. pond where $G(N_2) = 8\cdot6$ ($\pm$ 0·3). Since the value of $G(N_2)$ appears to be well established for γ-radiation, the lower yield obtained for BEPO suggests that, in the absence of LET effects, the direct application of our calorimetric data to energy absorbed in a gas may lead to G values which are too low by 8·6 ($\pm$0·3)/7·0 ($\pm$0·4) = 1·23 ($\pm$0·12).

Radiolysis of Carbon Dioxide.—Yields of carbon monoxide from the irradiation of carbon dioxide in the presence of nitrogen dioxide and sulphur dioxide are given in the Table; where sufficient results have been obtained, the standard deviation is quoted. For all γ-sources the mean value of $G(CO)$ is 3·51 $\pm$ 0·23. The yield of carbon monoxide shows no systematic variation with dose rate from $3\cdot6 \times 10^{15}$ ev g.$^{-1}$ min.$^{-1}$ to $9\cdot4 \times 10^{17}$ ev g.$^{-1}$ min.$^{-1}$ for γ-radiation, with nitrogen dioxide concentrations ranging from 2·4% to 13·1%, or with sulphur dioxide concentrations ranging from 2·5% to 8·0%. With nitrogen dioxide as scavenger the oxygen yields were somewhat erratic, but corresponded approximately to half the carbon monoxide yield, while with sulphur dioxide no oxygen was detected. Presumably the sulphur trioxide formed by the capture of oxygen atoms is stable at low concentrations and remains in the condensable gases during analysis.

The mean yield for experiments within the dose rate range 0·9—$1\cdot7 \times 10^{18}$ ev g.$^{-1}$ min.$^{-1}$ in the Harwell reactor BEPO is $G(CO) = 2\cdot49$ ($\pm$0·18), calculated from calorimetric data. If this value is corrected by the amount indicated by the nitrous oxide dosimetry, we obtain 3·06 ($\pm$0·3).

In the absence of oxygen-atom scavengers we confirm the apparent stability of carbon dioxide under high-energy radiation. At a dose rate of $2\cdot95 \times 10^{16}$ ev g.$^{-1}$ min.$^{-1}$ with ^{60}Co γ-radiation, exposure of pure carbon dioxide for periods 100 times greater than those used in the presence of scavengers produced a steady-state concentration of carbon monoxide less than 0·01%.

[9] Anderson and Waite, Harwell Research Report, No. A.E.R.E. C/R2253, 1960; Linacre and Thomas, unpublished work, A.E.R.E., Harwell.
[10] Hearne and Hummel, *Radiation Res.*, 1961, **15**, 254.
[11] Steinberg, Brookhaven Research Report, No. BNL 612, 1960.
[12] Dolle, 2nd U.N. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1958, A Conf./15/P1214.
[13] Dimitriev *et al.*, *Zhur. priklad. Khim.*, 1960, **33**, 808; *Zhur. fiz. Khim.*, 1961, **35**, 727.

Carbon monoxide yields from the radiolysis of carbon dioxide.

Dose rate $\times 10^{-16}$ (ev g.$^{-1}$ min.$^{-1}$)	Scavenger	Scavenger concn. (% by vol.)	G'(CO) *	G(CO)
^{60}Co-γ:				
2·95	SO_2	2·5	3·08 ± 0·18	3·18 ± 0·19
,,	,,	3·93	3·56 ± 0·07	3·70 ± 0·07
,,	,,	8·0	3·24 ± 0·19	3·52 ± 0·20
0·36	SO_2	4·1	3·09 ± 0·21	3·23 ± 0·22
19·1	,,	4·0	3·76 ± 0·24	3·92 ± 0·25
2·95	NO_2	2·38	3·58 ± 0·34	3·68 ± 0·35
,,	,,	4·7	3·31 ± 0·11	3·47 ± 0·11
γ's from irradiated fuel rods (T.I.G. pond):				
94	NO_2	4·6	3·35	3·51
,,	,,	5·5	3·40	3·59
,,	,,	13·1	2·88	3·27
		Mean value for γ-radiation		3·51 (± 0·23)
Reactor radiation (BEPO):				
Expt. hole E3/3				
93·2	NO_2	4·7	2·48	2·74
102	,,	7·0	1·96	2·28
96·2	,,	4·6	2·12	2·33
Expt. hole E6				
149	,,	4·3	2·39	2·58
158	,,	6·4	2·33	2·61
165	,,	3·9	2·24	2·40
		Mean value for reactor radiation †		2·49 (±0·18)

* G'(CO) calculated from total energy absorption. G(CO) calculated from energy absorbed in CO_2 alone. † Calculated directly from calorimetric data.

Discussion

The G values for carbon monoxide production reported here are all significantly lower than those reported by Harteck and Dondes [3,4] for radon α-particles, for fission-fragment irradiation, and for reactor radiation, but are much closer to the value of 4·5 (±0·4) reported by Steinberg [8] for ^{60}Co γ-radiation in the presence of 0·5—5% nitrogen dioxide and at total pressures from 4 to 54 atm. The irradiation cells used by Steinberg were constructed of nickel with a stainless-steel filling-tube, whereas the bulbs used in the present work were of silica or Pyrex glass. This difference may be responsible for the slightly different results obtained. Steinberg [8] showed that G(CO) was lower at 270° than at 26°, which may be due to the thermal oxidation of carbon monoxide by nitrogen dioxide. Moreover, the decomposition yield for the radiolysis of nitrogen dioxide itself increases markedly above 200°.[13] Both these effects will result in a decreasing yield of carbon monoxide with increasing temperature above 200° but are unlikely to affect G(CO) below this temperature. Steinberg does not report any measurements between 26° and 270° where both our work and that of Harteck and Dondes (reactor radiation, 140°; fission-fragment recoils, 70°; Rn α-particles, room temperature) was carried out. However, it is unlikely that the lower value of G(CO) obtained for reactor irradiation at 60° compared with that for γ-radiation at 20° in the present work is due to the difference in temperature of irradiation.

In all previous work except that of Steinberg,[8] who used vapour-phase chromatography for analysis, no direct measurement was made of the carbon monoxide yield, only the pressure of non-condensable gases being measured. It is possible that the proportions of non-condensable gas assumed to be carbon monoxide and oxygen may be incorrect or may be influenced by traces of air as an unsuspected contaminant.

Steinberg suggests that the difference between his radiolysis yield and those given by

Harteck and Dondes may be due to an LET effect, but such a large effect of ionisation density in a gas-phase reaction would be surprising. While present methods for gas dosimetry in nuclear reactors lack the precision which has been achieved for simple radiation sources, our results indicate that the difference in the radiolysis yield for carbon monoxide production for γ-radiation [$G(CO) = 3{\cdot}51$ ($\pm$ 0·23)] and for reactor radiation in BEPO [$G(CO) = 3{\cdot}06$ ($\pm$ 0·3), corrected for the nitrous oxide dosimeter] is within the uncertainty of reactor dosimetry. Moreover, this difference is much too small to explain the difference between the results of Steinberg and those of Harteck and Dondes. In addition, preliminary measurements of the radiolysis of carbon dioxide with ~1 Mev protons [14] indicate that $G(CO)$ is not increased beyond the value obtained for γ-radiation. A close examination of Harteck and Dondes's data shows that their yields of carbon monoxide from carbon dioxide are not unequivocally established. In their work with reactor radiation [3] no direct dosimetry was carried out. They assumed that the energy absorbed by the carbon dioxide was proportional to the ratio of the mass of gas irradiated to the mass of the entire reactor muliplied by the total thermal energy output of the reactor, making a calculated allowance for the distribution of fission energy. Such a calculation must be subject to large uncertainties, so that the wide discrepancy between their value of $G(CO) = 8$—9 and our present value of about 3 based on direct dosimetry in BEPO is perhaps not surprising. Their yield of carbon monoxide from the decomposition of carbon dioxide with fission-fragment radiation is also subject to uncertainties in the dosimetry. The quoted value [4] of "$G(-CO_2)$ approaching 8 at a dose of 10^9R" is based on a value for the nitrous oxide dosimeter of $G(-N_2O) = 12$. In their paper on nitrous oxide dosimetry Harteck and Dondes [15] do not state how they estimated the energy absorption to derive this G value for fission-fragment radiation, while later work by Steinberg [11] shows that $G(-N_2O)$ decreases with increasing dose and at a dose of 10^9 R he finds $G(-N_2O) = 9{\cdot}0$. In the absence of LET effects, and on the assumption that Harteck and Dondes were indeed comparing the decomposition of carbon dioxide and nitrous oxide at a total dose of 10^9R, the use of Steinberg's value for the nitrous oxide dosimeter would lower Harteck and Dondes's value for $G(CO)$ to about 5·5 for fission-fragment radiations. The yield for carbon monoxide production in the work of Harteck and Dondes with radon α-particles appears to be unequivocal, but in view of the conflicting results now available from Steinberg and from the present work it seems important to repeat this work with direct measurement of the carbon monoxide and oxygen yields by gas-chromatography.

That the G value for the primary step in the radiolysis of carbon dioxide is about 3 has been confirmed by experiments on the radiation-induced exchange of ^{14}C between ^{14}CO and unlabelled carbon dioxide.[16]

Experimental

Materials.—Cylinder carbon dioxide (Distillers Co., Hammersmith) was purified by passage over copper oxide wire at 800° to oxidise carbon monoxide and other reducing impurities, *e.g.*, hydrogen, then over copper dispersed on kieselguhr at 180° to remove oxygen. Water vapour was removed by drying at −78° and the gas finally purified by vacuum-distillation at liquid-nitrogen temperature, the non-condensable gases being removed and only the middle part of the distillate accepted.

$^{14}CO_2$ was prepared by oxidising ^{14}CO (obtained from the Radiochemical Centre, Amersham) over copper oxide.

Sulphur dioxide from a syphon (A. Boake Roberts & Co.) was dried over phosphorus pentoxide, condensed at −78°, and distilled *in vacuo*, only the middle fraction being accepted.

[14] Anderson and Best, unpublished work.
[15] Harteck and Dondes, *Nucleonics*, 1956, **14**, No. 3, 66.
[16] Dominey, unpublished work.

Nitrogen dioxide was prepared by thermal decomposition of lead nitrate and purified by fractional distillation.

Anæsthetic-grade nitrous oxide from a cylinder (British Oxygen Co.) was dried at −78° and distilled *in vacuo* at liquid-nitrogen temperature.

Gas Handling.—The bulbs in which gases were irradiated were fitted with diaphragm-type break-seals at one end and several cm. of capillary tubing at the other. They were thoroughly cleaned with chromic acid, washed with distilled water, and dried before use. The bulbs used for the experiments in the ^{60}Co γ-sources were made of Pyrex glass with volumes of 60—70 ml., except for the work at low dose rate where a smaller bulb had to be used. In the experiments in the T.I.G. pond and in the reactor, BEPO, silica bulbs were used with volumes of 13—15 ml.

For the experiments with the ^{60}Co γ-radiation sources the gases were handled completely in the absence of mercury before radiolysis, gas pressures being measured with a glass spiral gauge used as a null instrument with an external mercury manometer. Mixtures were made in a 1-l. bulb with a cold finger attached, measured quantities of the gases being condensed successively into the cold finger and the mixtures allowed to expand into a manifold where 6 bulbs could be filled simultaneously to a total pressure of 40—50 cm. (Hg). The bulbs were connected to a manifold *via* stop-cocks; after equilibration, the stop-cocks were closed, the gas mixtures frozen, and the bulbs sealed off. The silica bulbs used for irradiations in BEPO and the T.I.G. pond were filled by a different technique: the required amount of nitrogen dioxide, measured with a silicone oil manometer, was condensed into the bulb. $^{14}CO_2$ of known specific activity was measured with a mercury manometer and then condensed into the bulb. A trap cooled to −78° was interposed between the manometer and the bulb in an attempt to exclude mercury from the bulb. The total pressure in the bulb was about 30 cm. (Hg). The gases were frozen in liquid nitrogen before sealing was done at a constriction drawn in the capillary tubing.

Bulbs were filled with nitrous oxide by similar techniques.

Extreme care was taken to ensure that a " Tesla " spark coil used to test the leak tightness of fused joints was not brought into contact with any of the individual gases or gas mixtures. Preliminary tests had shown that exposure of a mixture of carbon dioxide and nitrogen dioxide for a few seconds was sufficient to produce carbon monoxide concentrations as high as 0·05%, which was the same magnitude as that produced in the highest dose studies with ^{60}Co γ-radiation.

Analysis.—After irradiation the gases were transferred to a vacuum-system through the break-seals by conventional vacuum techniques. In the experiments with the ^{60}Co γ-sources the gases not condensable at liquid-nitrogen temperature were analysed in a Perkin–Elmer vapour-phase fractometer. Helium was used as the carrier gas at a flow rate of 60 ml. min.$^{-1}$ with a 2-m. column of Perkin–Elmer column material " I " at 30°. Under these conditions the carbon monoxide and the oxygen peak were well separated. Calibrations were carried out before and after each batch of analyses.

In the experiments in which $^{14}CO_2$ was used, inactive carbon monoxide was added as carrier to the irradiated gas. After separation from the $^{14}CO_2$ by distillation at liquid-nitrogen temperature the carbon monoxide fraction was mixed with unlabelled carbon dioxide and then re-distilled. This process was carried out 4 times to remove all traces of $^{14}CO_2$, and the carbon monoxide was then oxidised over copper oxide to carbon dioxide. This was converted into barium carbonate which was counted under a thin end-window G.M. tube. In this way the proportion of carbon dioxide converted into carbon monoxide during radiolysis was determined by comparing the ratio of the ^{14}CO activity after radiolysis with the initial $^{14}CO_2$ activity.

Irradiations and Dosimetry.—Two positions in a 300-c ^{60}Co γ-radiation source and one position in a 1-c ^{60}Co source gave a range of doses from $3{\cdot}6 \times 10^{15}$ to $1{\cdot}9 \times 10^{17}$ ev g.$^{-1}$ min.$^{-1}$ in carbon dioxide. Under these conditions the total dose received by the gas samples was restricted so that the decomposition of carbon dioxide did not exceed 0·05%. Dose rates were measured with the Fricke dosimeter, the ferric ion concentration being measured spectrophotometrically at a wavelength of 3020 Å where the molar extinction coefficient is 2178 at 25° and the temperature coefficient 0·7% per °c. $G(Fe^{3+})$ is taken [17] as 15·6 and the doses in carbon dioxide were corrected for the difference in electron density between the carbon dioxide and 0·8N-sulphuric acid.

Irradiations in the T.I.G. pond were carried out at a dose rate of ~1 Mrad per hr.

[17] Hochanadel and Ghormley, *J. Chem. Phys.*, 1953, **21**, 880.

($9{\cdot}4 \times 10^{17}$ ev g.$^{-1}$ min.$^{-1}$ in carbon dioxide) measured with an ionisation chamber calibrated against the Fricke dosimeter.[18]

The irradiations in BEPO were carried out in the pneumatic-tube device in experimental hole E3/3 and in a vertical self-serve apparatus in experimental hole E6. In both positions the samples could be loaded and unloaded with the reactor operating. Thermal-neutron doses were monitored by measuring the activity developed in a cobalt wire attached to the samples. The wires were counted against a standard in a position of reproducible geometry below an end-window G.M. counter-tube. The energy absorbed in the gas phase was then calculated by using the calorimetric values determined for condensed materials,[9] which relate the thermal-neutron dose to the energy absorbed. The irradiation times in both T.I.G. pond and BEPO were such that up to 1·7% of the carbon dioxide was decomposed. The temperature of irradiation was about 20° in both the ^{60}Co γ-sources and the T.I.G. pond; in the reactor experiments the irradiation temperature was about 60° in both experimental holes used.

We are indebted to Dr. C. B. Amphlett and to Mr. J. Wright for helpful discussions.

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[*Received, February 19th,* 1962.]

[18] Clark, Price, and Rogers, Harwell Research Report No. A.E.R.E., R-3665, 1961.