γ-Radiation Induced Isotope Exchange in the Carbon Monoxide-Carbon Dioxide System

Studies in Silica vessels

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The behaviour of the isotopes ^{13}C, ^{14}C and ^{18}O in the $CO—CO_2$ system in silica vessels has been studied, and the usefulness of the system as a radiation dosimeter investigated. Each isotope has been employed under identical conditions. For the exchange of an oxygen atom between CO and CO_2 the established *G*-value of 4.2 has been confirmed. Apparent anomalies between results involving carbon- and oxygen-isotope labelling have been explained by a schematic initial reaction scheme involving participation of the silica :

$$C^{18}O^{18}O \rightsquigarrow C^{18}O + (^{18}O) \tag{1}$$

$$(^{18}O) + C^{16}O \rightarrow C^{16}O^{18}O \tag{2}$$

$$C^{18}O^{18}O + Si^{16}O^{16}O \rightarrow (C^{18}O + {}^{18}O)_{ads}.Si^{16}O^{16}O \rightsquigarrow (C^{18}O + {}^{16}O)_{ads}.Si^{16}O^{18}O \tag{3a}$$

$$(C^{18}O + {}^{16}O)_{ads}.Si^{16}O^{18}O \rightarrow Si^{16}O^{18}O + C^{18}O + (^{16}O) \tag{3b}$$

$$(^{16}O) + C^{16}O \rightarrow C^{16}O^{16}O \tag{4}$$

$$(^{16}O) + C^{18}O \rightarrow C^{16}O^{18}O \tag{5}$$

It was first established by Stranks [1] that isotope exchange occurred in $CO—CO_2$ mixtures under irradiation without any overall chemical change taking place. Since these intial experiments, the reaction :

$$^{14}CO + {}^{12}CO_2 = {}^{14}CO_2 + {}^{12}CO \tag{6}$$

has been studied in both directions, under the influence of γ-radiation,[2-6] protons,[7] and in the BEPO reactor.[2-3] The corresponding reactions with $C^{18}O^{18}O$ and with ^{13}CO,

$$C^{18}O^{18}O + C^{16}O \rightarrow C^{18}O + C^{16}O^{18}O \tag{7}$$

$$^{13}CO + {}^{12}CO_2(+O_2) \rightarrow {}^{13}CO_2 + {}^{12}CO \tag{8}$$

have been studied with γ- and with X-radiations.[8] The various results are collected in table 1, and are discussed by Anderson and Dominey.[9]

Different techniques and reaction conditions employed by the various workers may explain why conflicting results were obtained. Alternatively, higher *G*-values for exchange of ^{18}O compared with the exchange of ^{14}C might imply that reaction steps occur which can lead to an exchange of oxygen atoms without a corresponding exchange of carbon atoms. We have accordingly studied the ^{60}Co γ-radiolysis of the system using the three tracer atoms ^{13}C, ^{14}C and ^{18}O under identical conditions, and the effects of gas composition, pressure, cell shape, and surface. The systems $^{12}C^{16}O^{16}O + {}^{12}C^{18}O^{18}O$, $^{12}C^{18}O^{18}O + {}^{12}C^{16}O$, $^{13}C^{16}O + {}^{12}C^{16}O^{16}O$, $^{12}C^{16}O + {}^{13}C^{16}O^{16}O$, $^{12}C^{16}O + {}^{14}C^{16}O^{16}O$ and $^{14}C^{16}O + {}^{12}C^{16}O^{16}O$ have been examined,*

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* In no case was 100 % isotopic enrichment achieved. The use of these equations is a convenient shorthand ; all results are calculated for 100 % enrichment.

the first one in order to make allowance for its effects in the others. Thermal reactions, recently reviewed,[10] do not interfere under the experimental conditions used.

Our results support previous work with ^{13}C and ^{14}C and disagree with earlier ^{18}O work. Some preliminary results from ^{18}O work at these laboratories,[11] have been recalculated in the light of improvements in technique and are incorporated with the present results where appropriate.

TABLE 1

reaction	radiation	yield	ref.	remarks
$^{14}CO+^{12}CO_2\rightarrow$	γ	$G(^{14}CO_2)$ = 4.2 (±0.5)	3	vessels exposed to air before filling
$^{14}CO_2+^{12}CO$	BEPO	3.0 (±0.3)	3	vessels exposed to air before filling
	γ	4.4 (±0.4)	4	vessels exposed to air before filling
	γ	4.5 (±0.5)	5	
	protons	4.6 (±0.1)	7	
	γ	5.2 (±0.5)	6	vessels not exposed to air after baking at 800°C. Exposed vessels gave lower results.
$^{14}CO_2+^{12}CO\rightarrow$	γ	$G(^{14}CO)$ = 4.2 (±0.2)	2	vessels exposed to air before filling
$^{14}CO+^{12}CO_2$	BEPO	4.2 (±0.2)	2	vessels exposed to air before filling
	γ	5.2 (±0.4)	6	vessels not exposed to air after baking at 800°C. Exposed vessels gave similar results
$C^{18}O^{18}O+C^{16}O\rightarrow$	X	$G(C^{18}O)=8\text{-}11$	8	pressure dependent
$C^{18}O+C^{16}O^{18}O$		$G(C^{16}O^{18}O)=7\text{-}11$	8	
$^{13}CO+^{12}CO_2\rightarrow$ $^{13}CO_2+^{12}CO$	γ	$G(^{13}CO_2)=4$	8	

EXPERIMENTAL

A glass gas-handling system was designed with direct connections to an AEI MS2 mass spectrometer, and to a Perkin-Elmer Fractometer 451 gas chromatograph. This line was mercury free. Samples were sealed in silica cells (volume 3 ml) and irradiated in the BNL ^{60}Co γ-facility.[12]

Gases were kept prior to use for 24 h to ensure adequate mixing. The cells were previously baked at 500°C in air before evacuating (1.5×10^{-4} N m^{-2}) at 900°C for 24 h, and then filled with gas ($1.3\text{-}4.0\times10^{4}$ N m^{-2}). The CO_2 was frozen whilst sealing to avoid thermal exchange.

The cells were irradiated at a dose rate of 0.5-1.0 MRad h^{-1}, as measured by glucose solution dosimetry[13] and confirmed by calorimetry and the standard Fricke method. Since the vessel walls can increase the effective dose to a gaseous medium, an estimate of dose build-up effects and relative mass stopping powers was made. This showed that with a silica vessel of the dimensions used, any error from these effects was much less than the other experimental errors involved. This was further confirmed in some independent experiments[14] in which the dose measured by the Fricke method, after correction for the relative electron densities, was compared with that obtained using an ion chamber (2×10^{4} N m^{-2}

nitrogen) [2.44 (±0.12) and 2.50 (±0.12) MRad h^{-1} respectively] in the same irradiation position. Irradiations of $^{14}N_2/^{15}N_2$ mixtures in silica vessels using these results have yielded the expected results.

After irradiation, the cells were analyzed for total yield and product ratio (gas chromatograph) and isotopic ratios (mass spectrometer).

Major peaks were assigned as follows:

m/e
44 : $^{12}C^{16}O^{16}O$
45 : $^{13}C^{16}O^{16}O$
46 : $^{12}C^{16}O^{18}O$

m/e
47 : $^{13}C^{16}O^{18}O$
48 : $^{12}C^{18}O^{18}O$
49 : $^{13}C^{18}O^{18}O$

and after correction for cracking of CO_2 species,

28 : $^{12}C^{16}O$
29 : $^{13}C^{16}O$
30 : $^{12}C^{18}O$
31 : $^{13}C^{18}O$.

A peak at $m/e = 40$ corresponded to argon in a few experiments in which it was added as a standard to check that no loss of material occurred during irradiation, but otherwise its appearance together with a peak at $m/e = 32$ (O_2) was indicative of air contamination. Remarks made by Turnbull [15] regarding the interpretation of such mass spectra have been borne in mind, although it must be noted that his formulae apply only to samples in isotopic equilibrium. Shakhashiri and Gordon [16] quote similar formulae.

Samples containing ^{14}C were analyzed by gas scintillation counting, using an apparatus developed from one originally described by Feates [17] in which the gases were sampled by the chromatograph and the CO_2 was then frozen out with liquid nitrogen. A known quantity of each gas was counted in a 5 ml spiral anthracene cell using an EMI 6097S photomultiplier tube and Harwell 2000 Series counting equipment.

MATERIALS.—$C^{18}O^{18}O$ (97 %, Yeda Research Co.) was purified by freezing and pumping; $^{13}CO_2$ (61 %) was prepared from $Ba^{13}CO_3$ (BOC-Prochem) by reaction with $PbCl_2$.[18] Pure natural CO_2 was prepared from cylinder gas by a standard method.[19] SF_6 (BDH Ltd.), added as an electron scavenger at a concentration ~1 %, was purified by freezing and pumping, and CH_3NO_2, also used as an electron scavenger, was purified by vacuum distillation. All materials, including CO (BOC Grade X $^{12}C^{16}O$, BOC-Prochem $^{13}C^{16}O$ (61 %)) and Ar (BOC Grade X), were dried over P_2O_5 before use.

RESULTS

THE $C^{16}O^{16}O—C^{18}O^{18}O$ SYSTEM

We have been unable to reproduce using γ-radiation the rapid exchange reaction reported earlier [8] using X-radiation, in which a *G*-value $\sim 10^3$ was obtained. In an attempt to determine the reason for this, certain samples were deliberately contaminated with various materials which might have been present (mercury, stopcock grease, air, methane etc.), whilst other samples were rigorously purified from mercury (gold foil) and water (P_2O_5). No significant rapid exchange occurred in either case under γ-radiation, but the earlier work with X-radiation was readily confirmed.

Experiments on the slow γ-induced exchange reaction yielded a value for $G(C^{16}O^{18}O)$ of 2.8 ± 0.2 when corrected for a 50 : 50 mixture of $C^{16}O^{16}O$ and $C^{18}O^{18}O$ by the method of Dawes and Back.[20]

THE $C^{16}O—C^{18}O^{18}O$ SYSTEM

For each sample cell, the isotopic composition of the CO and CO_2, and the overall composition of the mixture, were determined after irradiation and compared with an unirradiated cell. The numbers of molecules of $C^{18}O$, $C^{16}O^{18}O$ and $C^{16}O^{16}O$ formed during the irradiation, and the numbers of $C^{18}O^{18}O$ and $C^{16}O$ molecules lost, were calculated, assuming that no overall loss of material occurred during irradiation. This was confirmed by gas chromatography and by adding a small amount (0.5 %) of argon as a control to one of the gas mixtures.

Sample pressure had no effect on the reaction; neither did packing the cells with silica wool. Use of a very large bulb in which the surface-to-volume ratio was decreased by a factor of 14, resulted in a decreased rate of $C^{16}O^{16}O$ production but little other change. The reaction was not significantly affected by the addition of small amounts of SF_6 or CH_3NO_2.

In order to compare directly the results of experiments with different initial compositions it was necessary to compare the change in the numbers of molecules of each species with radiation dose, instead of using the normal logarithmic notation.[21, 22] Correction factors have been applied to all yields (except for $C^{16}O^{16}O$) to compensate for changes in isotopic composition during irradiation, and to correct the initial isotopic purity of the CO_2 to 100 % $C^{18}O^{18}O$. Quoted *G*-values are thus initial values. No factor has been applied in the case of $C^{16}O^{16}O$ as it is a second stage product; this is discussed below. Gas-phase radiolysis of $C^{16}O$ is not significant at the dose used.[23, 24]

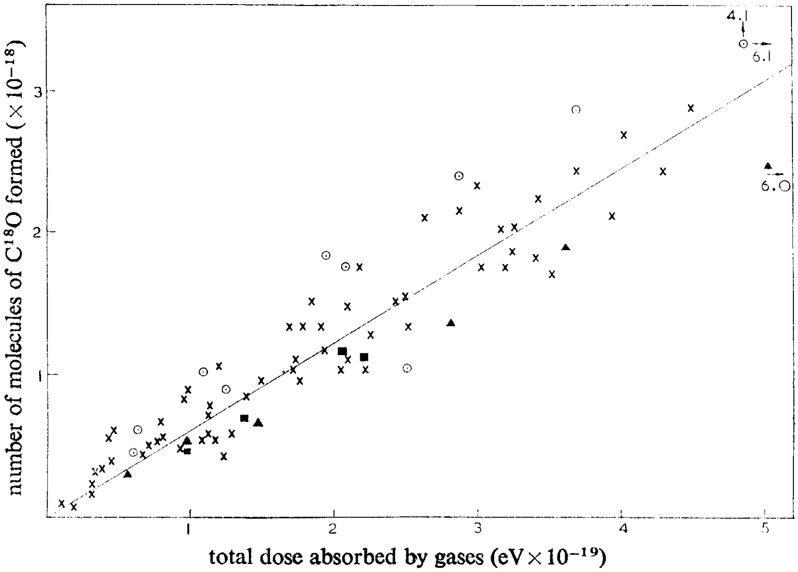

FIG. 1.—Production of $C^{18}O$. ⊙, Recalculated from ref. (11); ×, present work; ▲, 1 % SF_6 added; ■, 1 % CH_3NO_2 added.

Considered in terms of total dose absorbed by the gases, $C^{18}O$ formation and $C^{16}O$ and $C^{18}O^{18}O$ loss were independent of composition. High proportions of CO led to increases in $C^{16}O^{18}O$ formation (proportional to CO concentration) and decreases in $C^{16}O^{16}O$ formation.

Compositions in the range 10-55 % CO were employed. The results, incorporating the recalculated preliminary results of Dominey *et al.*[11] yield the following *G*-values:

$$G(C^{18}O) = 6.0\,(\pm 0.2) \quad G(-C^{18}O^{18}O) = 6.2\,(\pm 0.3)$$

$$G(-C^{16}O) = 7.0\,(\pm 0.3)$$

$$G(C^{16}O^{18}O) = 6.0 \rightarrow 4.2\ (50 \rightarrow 10\ \%\ CO)$$

$$G(C^{16}O^{16}O) = 0.7 \rightarrow 2.3\ (50 \rightarrow 10\ \%\ CO).$$

The errors represent one standard deviation from a plot of approximately 70 experimental points. Fig. 1 shows the plot for $C^{18}O$ formation.

THE ^{13}CO—$^{12}CO_2$ AND ^{12}CO—$^{13}CO_2$ SYSTEMS

Results for these systems have been treated in a similar fashion to those given above. Larger correction factors are involved because of the lower level of isotopic enrichment available, but the scatter is slightly less as the carbon isotope equilibrium is unaffected by reactions at the silica wall. Over the same composition and pressure ranges used in the $C^{18}O^{18}O$—$C^{16}O$ work, all *G*-values are constant and related to the total dose. Results are as follows:

		no. of results
^{13}CO loss in $^{13}CO + ^{12}CO_2$:	$G(-^{13}CO) = 4.2\,(\pm 0.2)$	40
$^{13}CO_2$ formation in $^{13}CO + ^{12}CO_2$:	$G(^{13}CO_2) = 4.5\,(\pm 0.2)$	
$^{13}CO_2$ loss in $^{12}CO + ^{13}CO_2$:	$G(-^{13}CO_2) = 4.1(\pm 0.2)$	30
^{13}CO formation in $^{12}CO + ^{13}CO_2$:	$G(^{13}CO) = 3.9(\pm 0.3)$	

Fig. 2 shows the plot for ^{13}CO formation in $^{12}CO + ^{13}CO_2$, and additionally demonstrates the lack of dependence on pressure and composition.

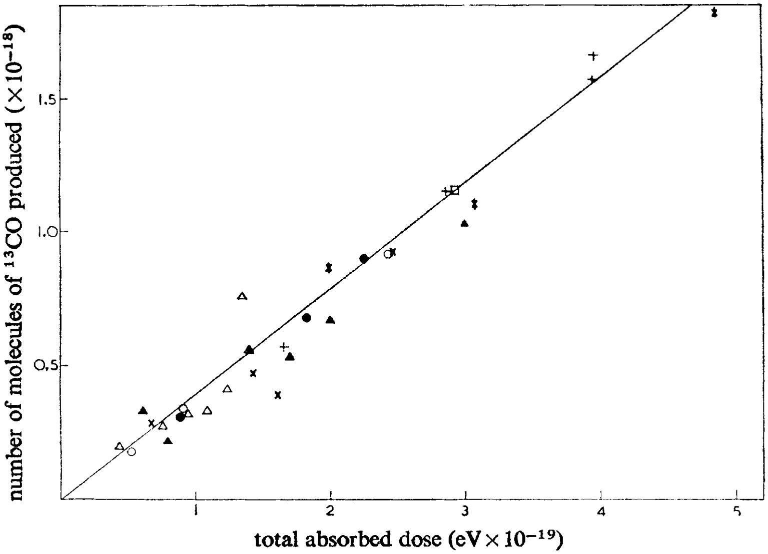

FIG. 2.—Production of ^{13}CO from $^{12}CO + ^{13}CO_2$. ×, 18.4 % CO; 1.68×10^4 N m^{-2}; +, 18.4 % CO; 3.10×10^4 N m^{-2}; ✱, 18.4 % CO; 5.49×10^4 N m^{-2}; ○, 27.5 % CO; 1.39×10^4 N m^{-2}; ●, 27.5 % CO; 2.43×10^4 N m^{-2}; □, 27.5 % CO; 4.33×10^4 N m^{-2}; △, various other compositions and pressures; ▲, 21.0 % CO; 1 % SF_6 added.

THE $^{13}C^{16}O$—$^{12}C^{18}O^{18}O$ SYSTEM

Results for this system have been included in the two previous sections, since the presence of ^{13}C has no effect on the ^{18}O distribution, and vice versa. Consideration of the ^{13}C distribution in the products of the $C^{16}O$—$C^{18}O^{18}O$ reaction throws light on the reaction mechanisms, particularly on the formation of $C^{16}O^{16}O$, which contained 61 % ^{13}C like the initial $C^{16}O$. This suggests that it was derived wholly from CO by an oxidation process which must be a wall reaction since the only other source of ^{16}O is the initial $C^{16}O^{16}O$ which is predominantly ^{12}C. Yields of $C^{16}O^{16}O$

are too great to be explained by gas-phase CO radiolysis,[23] although such radiolysis may have occurred on the walls.

The $C^{16}O^{18}O$ formed (as distinct from that initially present, which has 99 % ^{12}C) contained between 20-40 % ^{13}C, which suggests that only a proportion of the product was derived from CO: carbon from both CO and CO_2 must be used in $C^{16}O^{18}O$ formation, so at least two mechanisms occur simultaneously. A little ^{13}C appeared in the $C^{18}O^{18}O$ after radiolysis, presumably by the reverse of the reaction forming $C^{16}O^{18}O$.

THE ^{14}CO—$^{12}CO_2$ AND ^{12}CO—$^{14}CO_2$ SYSTEMS

The results of these studies have been calculated using relations of the type [21, 22]

$$(^{12}CO\text{—}^{14}CO_2): \; G(^{14}CO) = \frac{-(\%CO)(100-\%CO)\times 2.303\times\log_{10}(1-f)}{100\times D} \tag{9}$$

D = dose absorbed (total) in eV molecule^{-1}; f = fraction of the exchange which has occurred, i.e., $f = 100/\%CO \times$ fraction of activity found in the CO. The composition range 0.5–10 % CO was examined—typical results are shown in fig. 3. The mean values of both $G(^{14}CO)$ and $G(^{14}CO_2)$ from all 32 experiments each are 4.2 (±0.2). There are no variations due to composition or total pressure.

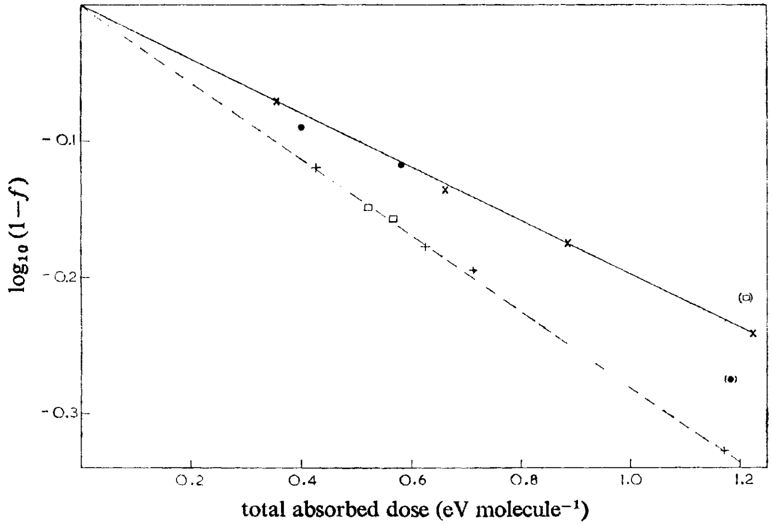

FIG. 3.—Production of ^{14}CO from $^{12}CO+^{14}CO_2$. ×, 4.51×10^4 N m^{-2}; ●, 2.51×10^4 N m^{-2}; 10.3 % CO; $G(^{14}CO) = 4.22$ —; +, 1.97×10^4 N m^{-2}; □, 1.09×10^4 N m^{-2}; 6.9 % CO; $G(^{14}CO) = 4.16$ ---

DISCUSSION

We have not attempted to study the actual active species responsible for the efficient reoxidation of CO which results in the exchange, but have tried to establish the actual physical pathways involved, in order to resolve the existing anomalies in the literature. In the mechanism outlined here these species will be represented by (O); the possible identity of this species is reviewed below.

No rapid chain reaction was detected in the γ-radiolysis of $C^{16}O^{16}O$—$C^{18}O^{18}O$, whilst the observations of Anbar and Perlstein [8] using X-radiation have been confirmed. Whilst the possibility of an inhibitor or chain initiator as impurity in the gases cannot be entirely ruled out, every conceivable precaution was taken to purify our gases. Each set of workers used $C^{18}O^{18}O$ from the same source. Calculations based on the different radiation energies, mass absorption coefficients and dosimetry techniques are unable to explain this curious difference. X-radiation may activate the cell surface in some way, allowing a chain reaction to be initiated; there was no possibility that a discharge was excited in the gas in our experiments.

We may reconcile all the remaining observations by considering the ^{13}C distribution in the products of the $^{13}C^{16}O—^{12}C^{18}O^{18}O$ reaction, and also the fact that whilst carbon isotope balance in the gas-phase was maintained during irradiation, oxygen isotope balance was not. A small percentage of ^{18}O was lost to the wall and replaced by ^{16}O, and the ^{18}O was successfully recovered from certain cells packed with silica wool by re-irradiating them in the presence of $C^{16}O^{16}O$. We pointed out earlier that $C^{16}O^{16}O$ production comes about by reaction of $C^{16}O$ with a ^{16}O atom whose source must be the wall. CO absorbed on alumina during irradiation yields some CO_2 on desorption.[25] Since $G(C^{16}O^{16}O)$ decreases as [CO] increases, the reaction:

$$C^{16}O+(^{16}O)_{wall}\rightarrow C^{16}O^{16}O \tag{10}$$

cannot occur, and we propose instead that ^{18}O atoms exchange with ^{16}O atoms from the silica wall. We further suggest that this process takes place with a G-value of about 2. It would be undetected with C-isotope work if oxygen atoms or active species absorbed directly, whilst if dissociative absorption of CO_2 occurred, the effect would remain undetected with ^{14}C because of the low enrichment, and would be equal to about 1 standard deviation in the ^{13}C results for the same reason. If we subtract the " G-exchange " value of 4.2 from the ^{18}O results (i.e., for $C^{18}O^{18}O+C^{16}O\rightarrow C^{16}O^{18}O+C^{18}O$, all G-values equal 4.2) the following yields remain:

$G(-C^{18}O^{18}O)$ and $G(C^{18}O)$: $\simeq 2$

$G(-C^{16}O)$: $\simeq 2.8$

$G(C^{16}O^{18}O)$: $\simeq 1.8-0$ for $50\rightarrow 10$ % CO.

$G(C^{16}O^{16}O)$: $\simeq 0.7-2.3$ for $50\rightarrow 10$ % CO.

$G(^{16}O)$: $\simeq 2$ (from wall, where $[^{16}O]\gg[^{18}O]$).

Making allowance for the probable errors in these numbers, all the products may be accounted for on a total dose absorbed basis by five schematic reaction steps:

$$^{12}C^{18}O^{18}O\rightsquigarrow {}^{12}C^{18}O+(^{18}O) \tag{1}$$

$$(^{18}O)+{}^{13}C^{16}O\rightarrow {}^{13}C^{16}O^{18}O \tag{2}$$

$$^{12}C^{18}O^{18}O+Si^{16}O^{16}O\rightarrow(^{12}C^{18}O+{}^{18}O)_{ads.}Si^{16}O^{16}O\rightsquigarrow (^{12}C^{18}O+{}^{16}O)_{ads.}Si^{16}O^{18}O \tag{3a}$$

$$(^{12}C^{18}O+{}^{16}O)_{ads.}Si^{16}O^{18}O\rightarrow Si^{16}O^{18}O+{}^{12}C^{18}O+(^{16}O) \tag{3b}$$

$$(^{16}O)+{}^{13}C^{16}O\rightarrow {}^{13}C^{16}O^{16}O \tag{4}$$

$$(^{16}O)+{}^{12}C^{18}O\rightarrow {}^{12}C^{16}O^{18}O \tag{5}$$

At higher concentrations of CO, more surface adsorption sites are occupied by this CO and hence (3*a*) cannot occur so readily. This results in a lower concentration of (^{16}O) and so (2) becomes favoured relative to (4). Thus one obtains proportionally more $C^{16}O^{18}O$ than $C^{16}O^{16}O$. This hypothesis is consistent with the observation of Marsh and Wright [23] that no wall-oxidation occurred in their CO-radiolysis study. The proportion of $^{12}C^{16}O^{18}O$ to $^{13}C^{16}O^{18}O$ increased at low CO concentrations and higher doses, and this is to be expected from the reaction scheme since relatively more $^{12}C^{18}O$ is available under such conditions to react with (^{16}O) (5), and more sites are available to facilitate (^{16}O) production.

Mention must be made of a gas-phase reaction sequence which could lead to a similar isotopic distribution. Verdurmen[26] found that singlet oxygen atoms can exchange with the O-atom in CO without deactivation. Thus, we could write a sequence of reactions comprising (1), (11) and (4):

$$(^{18}O\ \text{singlet}) + {}^{13}C^{16}O \rightarrow {}^{13}C^{18}O + (^{16}O\ \text{singlet}) \tag{11}$$

which give the overall stoichiometry (12):

$$^{12}C^{18}O^{18}O + 2\,^{13}C^{16}O \rightarrow {}^{12}C^{18}O + {}^{13}C^{18}O + {}^{13}C^{16}O^{16}O \tag{12}$$

We would therefore predict that $G(C^{18}O)$ (both carbon isotopes) should lie between $2G(-C^{18}O^{18}O)$ (8.4, from (12)) and $G(-C^{18}O^{18}O)$ (4.2, from (1)-(2)) if the two schemes are in competition. However, there is a difference of 2.0 between $G(-C^{18}O^{18}O)$ and $G(-{}^{13}CO_2)$ which cannot be accounted for by this gas phase mechanism. Furthermore the observed loss of ^{18}O to the wall shows that a sequence involving the wall must be responsible for at least 80 % of the observed reaction.

The identity of the species we write as (O) has been the subject of considerable speculation. It cannot be the ground state oxygen atom $O(^3P)$ since this would react too slowly with CO to account for the apparent radiation stability of CO_2.[27] Many other species than singlet O-atoms (e.g., CO_3, CO_4^-, O_2^+, O_2^-, O^- etc.) have been considered by various authors. Whilst conclusive identification remains impossible at present, there is mounting evidence that more than one species is involved, and that one of them is derived from molecular oxygen.

Enhancement of the exchange yield by O_2 occurs at both low[3, 4] and high[7, 19] dose rates, although more complex effects are observed under the latter conditions. With pure CO_2, a steady state concentration of molecular oxygen proportional to (dose rate)$^{\frac{1}{2}}$ is formed. Under high dose rates, it is possible that greater interaction between different active species occurs than at low dose rates, possibly between the two different types of active species proposed by Best *et al.*[28] in a recent study of the graphite-CO_2 reaction. Our species (O) may be identified with their " B " species, deactivated by CO, which is thought to be O^-; they propose also a neutral or positively charged "A" species derived from, and deactivated by, CO_2 but not significantly by CO under our conditions (singlet O-atoms would fill this requirement). Lack of an effect on the addition of SF_6 or CH_3NO_2 does not rule out the participation of negative ion species if they form directly from CO_2.

Use of the exchange reaction as a gas-phase dosimeter has been suggested. The greater accuracy of gas scintillation counting in comparison with mass spectrometry means that the ^{14}C reaction ($^{14}CO + {}^{12}CO_2$) may be used with reasonable accuracy under the conditions of our study. It is necessary to limit the temperature to 200°C or below because recent experiments have indicated that the silica surface may be activated by irradiation at higher temperatures and allow a thermal or chain process to occur below the expected[29] temperature of 630°C.

CONCLUSION

The rate of isotope exchange in the CO—CO_2 system in silica bulbs is given by $G(\text{exchange}) = 4.2 \pm 0.2$. Correction must be made to this figure if oxygen isotopes are employed in observing the exchange because of exchange of oxygen atoms with the surface. Only the ^{14}CO—$^{12}CO_2$ system is suitable as a chemical dosimeter in silica vessels. We also conclude that the fast chain exchange reaction between $C^{16}O^{16}O$ and $C^{18}O^{18}O$ occurs only under X-irradiation whilst under γ-irradiation a slow exchange reaction with $G(C^{16}O^{18}O) \simeq 2.8$ occurs.

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