REACTIONS OF ELECTRONICALLY EXCITED (A $^1\Pi$, $v' = 13$) $^{13}C^{16}O$ AND $^{12}C^{18}O$ MOLECULES WITH GROUND STATE CO(X $^1\Sigma^+$)[†]

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Summary

The 123.58 nm resonance radiation of krypton was used to excite selectively $^{13}C^{16}O$ and $^{12}C^{18}O$ to the A $^1\Pi$, $v' = 13$ state in a bath of $^{12}C^{16}O$. The excited isotopic molecules were shown to react with ground state CO yielding CO_2 and C_3O_2 products which were labelled with ^{13}C and ^{18}O. The isotopic composition of the C_3O_2 product showed that the reaction proceeded by the formation of a $(CO)_2$ intermediate which decomposed predominantly (64% - 88%) to carbon atoms and CO_2. Decomposition to oxygen atoms and C_2O radicals accounted for 12% - 36% of the total reaction. In addition, it was shown that each C—O bond of the $(CO)_2$ intermediate, one C—O bond corresponding to the CO molecule bearing the initial excitation and the other corresponding to the ground state CO, decomposed with equal probability. Therefore the $(CO)_2$ intermediate must have been sufficiently long lived to have allowed equilibration of the excitation which was initially located in only one of the two CO molecules.

1. Introduction

In previous studies [1 - 8] it has been shown that CO excited to the A $^1\Pi$ and A $^3\Pi$ states can react with ground state CO to yield CO_2 and C_3O_2 as final products. In the case of CO(A $^3\Pi$) the reaction has been shown [6, 7] to proceed via the formation of a $(CO)_2{}^*$ intermediate which decomposes to carbon atoms and CO_2:

$$CO^* + CO \rightarrow (CO)_2{}^* \rightarrow C + CO_2 \qquad (1)$$
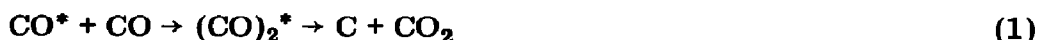
The carbon atoms subsequently combine with CO to give C_3O_2:

$$C + CO \rightarrow CCO \tag{2}$$

$$CCO + CO \rightarrow C_3O_2 \tag{3}$$

When CO is excited to the A $^1\Pi$, $v' = 13$ state a second reaction channel is also accessible energetically giving oxygen atoms and C_2O radicals:

$$CO^* + CO \rightarrow (CO)_2^* \rightarrow C_2O + O \tag{4}$$

There is no previous experimental evidence for reaction (4), which may occur via an OCCO intermediate structure, as opposed to reaction (1) which may occur via a COCO intermediate structure.

The relative contribution of reaction (4) can be determined by isotope selective excitation. (In the following discussion, in order to avoid confusion and also for brevity, ^{13}C and ^{18}O will be denoted by ¢ and ∅ respectively. C and O will be used to denote the most abundant isotopes, *i.e.* ^{12}C and ^{16}O.) For example, if C∅ is selectively excited in a bath of CO molecules, then the formation of carbon suboxide labelled with ^{18}O should be observed:

$$C\emptyset^* + CO \rightarrow (\emptyset CCO)^* \rightarrow \begin{cases} O + CC\emptyset \\ \emptyset + CCO \end{cases} \tag{5}$$
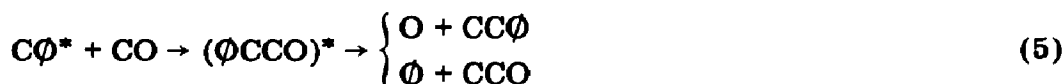
Reaction (4) can also be verified by selective excitation of ¢O. In the latter case the end carbon of C_3O_2 should be labelled with ^{13}C:

$$\text{¢}O^* + CO \rightarrow (OC\text{¢}O)^* \begin{cases} \rightarrow O + C\text{¢}O \\ \rightarrow O + \text{¢}CO \end{cases} \tag{6}$$
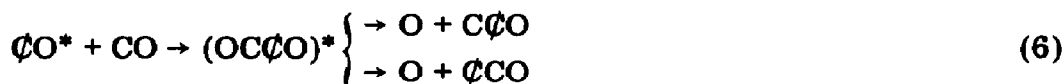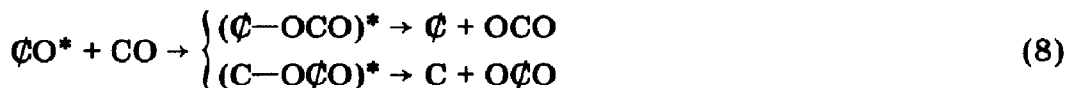
In each case labelling of the end CO in C_3O_2 as a result of reaction (4) must be in excess of that resulting from reactions (2) and (3) involving various isotopic forms of CO present in the reaction cell.

To observe reaction (4) by the isotopic composition of the C_3O_2 product, there must be a finite probability of decomposition of the C—O bond corresponding to the ground state CO. The decomposition pattern of the $(CO)_2^*$ intermediate should depend on its lifetime. This information can be obtained from the isotopic distribution of C_3O_2 relative to CO_2.

For example, if the intermediate were short lived one would expect preferential decomposition of the C—O bond corresponding to the CO molecule which was initially excited:

$$\text{¢}O^* + CO \rightarrow (\text{¢—OCO})^* \rightarrow \text{¢} + OCO \tag{7}$$

This is because the equilibrium internuclear separation of the A $^1\Pi$ state is 0.1235 nm [9] which is larger than that of the X $^1\Sigma^+$ state which is 0.1128 nm [9]. In addition, the A $^1\Pi$ state is in the present case excited vibrationally ($v' = 13$). Therefore the C_3O_2 should be more enriched in ^{13}C than the CO_2 is. In contrast, if the intermediate were sufficiently long lived for energy equilibration to occur prior to decomposition, the intermediate should decompose statistically

$$\text{¢O}^* + \text{CO} \rightarrow \begin{cases} (\text{¢—OCO})^* \rightarrow \text{¢} + \text{OCO} \\ (\text{C—O¢O})^* \rightarrow \text{C} + \text{O¢O} \end{cases} \tag{8}$$

giving CO_2 and C_3O_2 enriched equally with ^{13}C.

Finally, a more practical objective of this work was the determination of the final isotopic enrichment of ^{13}C and ^{18}O in the C_3O_2 and CO_2 products following selective excitation of ¢O and C¢ in natural isotopic abundance CO (1.1% ^{13}C and 0.2% ^{18}O). It has already been shown [10] that the relatively sharp and unreversed 123.58 nm resonance radiation of krypton excited only ¢O to the A $^1\Pi$, $v' = 13$ state, while a broader and more reversed resonance radiation excited both ¢O and C¢, but not CO, to the A $^1\Pi$, $v' = 13$ state.

2. Experimental details

The krypton resonance lamps employed in the present study have been described elsewhere [10]. Light source 1 was employed in exciting C¢ and light source 2 was employed in exciting ¢O. They were both excited with a 2450 Hz microwave generator using an Evenson cavity.

The irradiations were conducted in the reaction cell shown in Fig. 1. The cell, which was 37 cm long with an inside diameter of 1.85 cm, comprised one vertical arm of the thermosiphon circulating pump [11]. The other vertical arm passed through a Dewar flask which was filled with liquid nitrogen. Approximately 22 cm of this arm was in contact with liquid nitrogen. The inside diameters of the second arm and of the parallel tubing which connected it to the reaction cell were 1.0 cm.
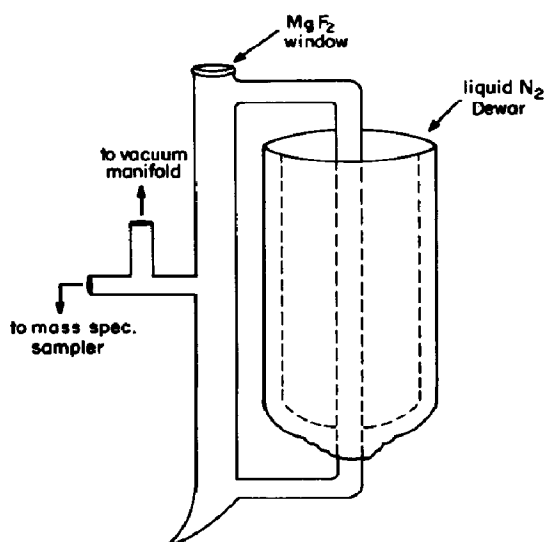

Fig. 1. The reaction cell and the thermosiphon circulating pump.

The total CO pressure was maintained constant at 6.7 ± 0.1 kPa in these experiments. The CO flow rate through the thermosiphon was approximately 0.5 cm^3 s^{-1} at 6.7 kPa [11]. This flow transferred the CO_2 and C_3O_2 products of the reaction into the liquid-nitrogen-cooled arm of the thermosiphon where they condensed. Irradiations ranged from 2 to 5 h. Following irradiation the non-condensibles were pumped off and the condensibles were transferred directly to the mass spectrometer for analysis. The mass spectrometer was an AEI series QUAD 250A quadrupole instrument.

The gases and the manufacturers' stated purities were as follows: Matheson research grade CO (99.99% minimum); Merck, Sharpe and Dohme ¢O (92 at.% ^{13}C); Stohler Isotope Chemicals C∅ (99 at.% ^{18}O). In order to minimize the condensible impurities, particularly CO_2, all gases were withdrawn for use while their storage bulbs were immersed in liquid nitrogen. The natural isotopic composition CO, before it was admitted to the reaction cell, was also passed through a trap filled with glass beads and immersed in liquid nitrogen. The isotopic composition of the reactants was determined with the mass spectrometer before each run.

3. Results and discussion

The isotopic enrichment data of the C_3O_2 and CO_2 products as a function of the ¢O/CO and C∅/CO reactant ratios are given in Table 1 and are plotted in Figs. 2 and 3. The abundance of the various C_3O_2, CO_2 and CCO isotopic species, relative to the corresponding unenriched (^{12}C and ^{16}O) species, were obtained from the relative intensities of the parent ions. Mass spectrometer ion currents were employed in this case, assuming that any isotopic effects in the fragmentation patterns and the mass spectrometer response were negligible.

The relative abundance of O¢CCO was calculated from

$$r_{O¢CCO} = 2 \frac{r_{69} + r_{70} + r_{71} - r_{41} - r_{42}}{1 + r_{41} + r_{42}} \tag{9}$$

where r represents the relative abundance of the ion indicated by the m/e number given as a subscript. Equation (9) is derived in Appendix A.

The CO_2 enrichment in both the ¢O and C∅ cases was diluted extensively with extraneous unenriched CO_2. Extraneous CO_2 arises primarily from CO_2 impurities in CO, and also from CO_2 formed during the reaction by the recombination of O atoms with CO. O atoms can be generated by the photolysis of O_2 which is also present as an impurity in CO. The extent of CO_2 dilution in the case of C∅ photolysis was more serious (no CO_2 enrichment was detected) than in the case of ¢O photolysis because of the substantially lower rate of excitation of C∅. In contrast, the C_3O_2 enrichment data were not affected by any dilution because C_3O_2 was formed only by the reaction under study.

TABLE 1

Isotopic enrichment data of the reaction of $\phi O(A\ ^1\Pi,\ v' = 13)$ and $C\phi(A\ ^1\Pi,\ v' = 13)$ with ground state $CO(X\ ^1\Sigma^+)$

$\phi O/CO$	C_3O_2 [a]			CCO [b]		$O\phi CCO$ [a]	ϕO_2 [c]
	$m/e = 69$	$m/e = 70$	$m/e = 71$	$m/e = 41$	$m/e = 42$		
0.0112	0.667	≈ 0	≈ 0	0.550	≈ 0	0.15	0.159
0.0239	0.701	0.057	≈ 0	0.587	≈ 0	0.21	0.222
0.0502	0.786	0.116	≈ 0	0.612	≈ 0	0.36	0.289
0.0898	0.934	0.162	≈ 0	0.729	0.078	0.32	0.235
0.117	1.043	0.240	≈ 0	0.803	0.107	0.39	0.276
0.148	1.122	0.319	≈ 0.052	0.873	0.145	0.47	0.414
0.295	1.665	0.770	0.158	1.232	0.351	0.78	0.426

$100C\phi/CO$	2.78	3.30	3.73	5.92	6.13	7.27	7.41	9.48	9.63	11.1	11.6	12.0	13.1
$OC_3\phi(m/e = 70)$ [d]	0.123	0.125	0.159	0.190	0.202	0.266	0.236	0.266	0.265	0.264	0.323	0.319	0.346

[a] Relative to C_3O_2 (m/e = 68).
[b] Relative to CCO (m/e = 40).
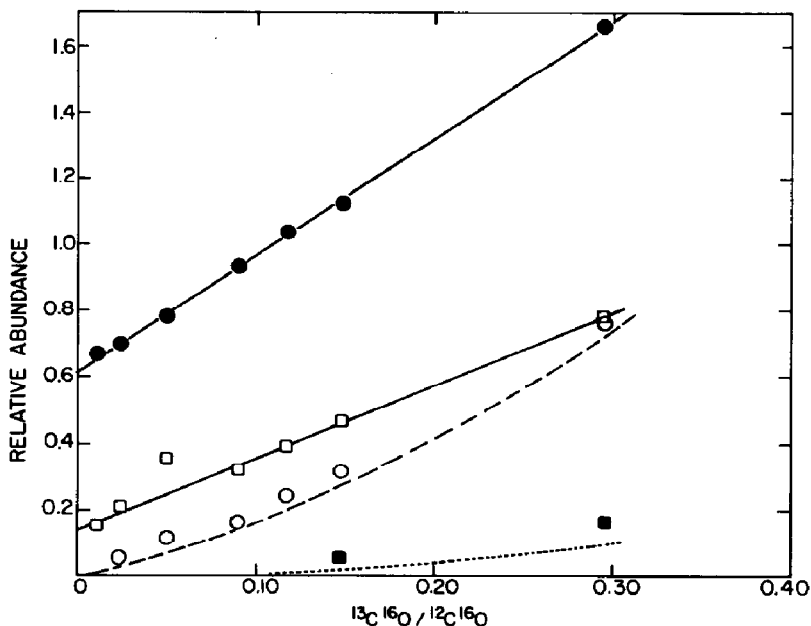[c] Relative to CO_2 (m/e = 44).
[d] Relative to C_3O_2 (m/e = 68).

Fig. 2. The relative ^{13}C isotope abundance of C_3O_2 vs. the ¢O/CO ratio: ●, ¢C_2O_2/OCCCO; □, OCC¢O/OCCCO; ○, O¢¢CO/OCCCO; ■, O¢¢¢O/OCCCO; — — —, r_{70} calculated from r_{69} on the basis of $r_{70} = 2r_{69}R - 3R^2$; — · — · —, r_{71} calculated from r_{69} on the basis of $r_{71} = r_{69}R^2 - 2R^3$. The above equations were derived assuming random reactions of the primary species with ¢O and CO.
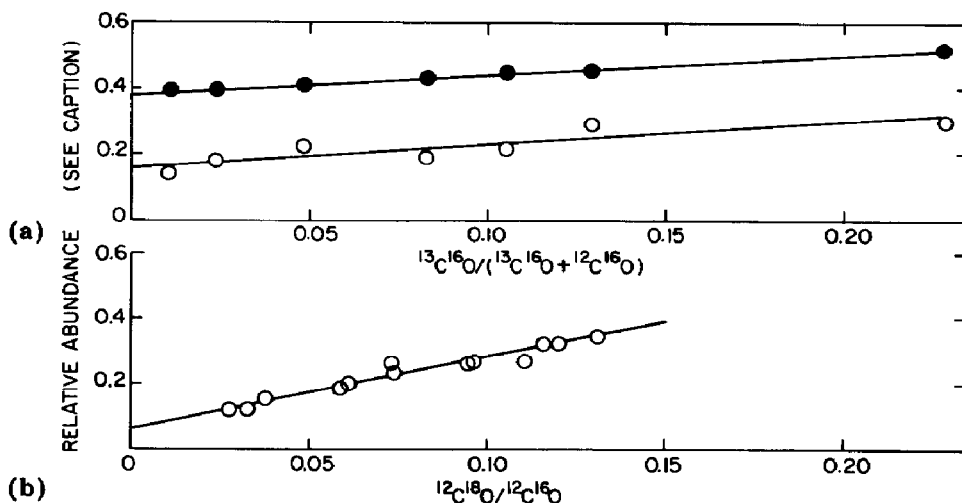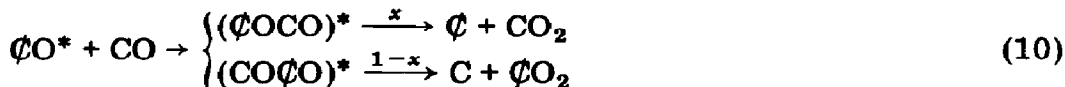

Fig. 3. (a) Equations (18) and (22) of the text (●) and eqns. (19) and (23) of the text (○); (b) the relative ^{18}O abundance of C_3O_2 vs. the C¢/CO ratio.

An inspection of the data of Table 1 shows that C_3O_2 is, for the most part, enriched with ^{13}C in its central carbon atom (cf. the second and seventh columns). Enrichment with ^{13}C and ^{18}O in the end carbon atoms is mainly a result of the statistical factor which is given by $2R$ where R is equal to the ¢O/CO or the C¢/CO ratio. The predominance of ^{13}C enrichment in the cen-
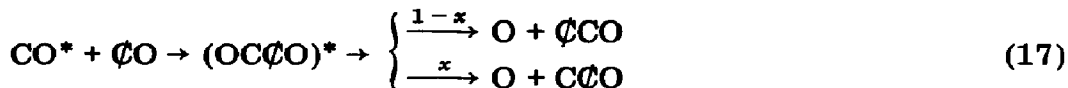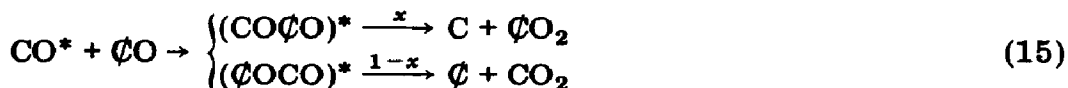
tral carbon atom of C_3O_2 shows that the primary reaction products of CO^* and CO are C atoms and CO_2. The small but finite ^{13}C and ^{18}O enrichment in the end carbon atoms of C_3O_2, beyond that which is accounted for by the statistical factor $2R$, shows that C_2O and O are also primary products.

The above observations can be treated more quantitatively with the aid of the following mechanism where electronic excitation is shown by an asterisk and the probability of decomposition of the C—O bond belonging to the CO molecule which is excited initially is denoted by x. The precursors of the C atoms and the C_2O radicals are assumed to be the $(COCO)^*$ and $(OCCO)^*$ intermediates respectively.

$$¢O^* + CO \rightarrow \begin{cases} (¢OCO)^* \xrightarrow{\ x\ } ¢ + CO_2 \\ (CO¢O)^* \xrightarrow{\ 1-x\ } C + ¢O_2 \end{cases} \tag{10}$$

$$¢O^* + ¢O \rightarrow (¢O¢O)^* \rightarrow ¢ + ¢O_2 \tag{11}$$

$$¢O^* + CO \rightarrow (O¢CO)^* \begin{cases} \xrightarrow{\ x\ } O + ¢CO \\ \xrightarrow{\ 1-x\ } O + C¢O \end{cases} \tag{12}$$

$$¢O^* + ¢O \rightarrow (O¢¢O)^* \rightarrow O + ¢¢O \tag{13}$$

Subsequent reactions of the above atoms and radicals with CO and ¢O to form labelled CO_2 and C_3O_2 are assumed to be proportional to the concentration of each species.

If any substantial concentration of CO^* existed, formed either directly or by energy transfer from $¢O^*$, then the corresponding reactions of CO^* must also be considered:

$$CO^* + CO \rightarrow (COCO)^* \rightarrow C + CO_2 \tag{14}$$

$$CO^* + ¢O \rightarrow \begin{cases} (CO¢O)^* \xrightarrow{\ x\ } C + ¢O_2 \\ (¢OCO)^* \xrightarrow{\ 1-x\ } ¢ + CO_2 \end{cases} \tag{15}$$

$$CO^* + CO \rightarrow (OCCO)^* \rightarrow O + C_2O \tag{16}$$

$$CO^* + ¢O \rightarrow (OC¢O)^* \rightarrow \begin{cases} \xrightarrow{\ 1-x\ } O + ¢CO \\ \xrightarrow{\ x\ } O + C¢O \end{cases} \tag{17}$$

A similar sequence of reaction steps (10) - (17) can also be written for the analogous case of $C\emptyset$.

Assuming that there are no significant isotopic effects in the rate constants of the above reactions, *i.e.* $k_{10} = k_{11} = k_{14} = k_{15} = k_I$ and $k_{12} = k_{13} = k_{16} = k_{17} = k_{II}$, the following equations can be derived:

$$\frac{r_{69} - 2R}{1 + r_{69} - 2R} = \frac{x + a}{1 + a} \frac{R^*}{1 + R^*} + \frac{1 - x}{1 + a} \frac{R}{1 + R} \tag{18}$$

$$\frac{r_{\cancel{C}O_2}}{1 + r_{\cancel{C}O_2}} = \frac{1-x}{1+a}\frac{R^*}{1+R^*} + \frac{x+a}{1+a}\frac{R}{1+R} \tag{19}$$

$$r_{O\cancel{C}CO} = 2R + \frac{a(1+R)(R^*-R)}{1 + R^* + \{(x+a)/(1-x)\}(1+R)} \tag{20}$$

$$r_{\cancel{\phi}CCO} = 2R + \frac{a(1-x)(1+R)(R^*-R)}{1 + R^* + a(1+R) + ax(R^*-R)} \tag{21}$$

where $a = k_{II}/k_I$ and $R^* = \cancel{C}O^*/CO^*$ for eqns. (18) - (20) and $R^* = C\cancel{\phi}^*/CO^*$ for eqn. (21).

The above equations are plotted in Figs. 2 and 3. A least-squares linear fit of the data gave the following equations:

$$\frac{r_{69} - 2R}{1 + r_{69} - R} = (0.382 \pm 0.005) + (0.588 \pm 0.0045)\frac{R}{1+R} \tag{22}$$

$$\frac{r_{\cancel{C}O_2}}{1 + r_{\cancel{C}O_2}} = (0.16 \pm 0.02) + (0.69 \pm 0.18)\frac{R}{1+R} \tag{23}$$

$$r_{O\cancel{C}CO} = (0.140 \pm 0.010) + (2.177 \pm 0.069)R \tag{24}$$

$$r_{\cancel{\phi}CCO} = (0.0666 \pm 0.0062) + (2.141 \pm 0.073)R \tag{25}$$

The error values in the above equations are equal to one standard deviation.

The ^{13}C enrichment data of CO_2 are minimum values in view of the dilution effects mentioned above. Also, the value of R^* is not known; it may vary with R and it may not be the same for $\cancel{C}O$ and $C\cancel{\phi}$ excitation. Thus an accurate determination of x and a is not possible. However, upper and lower limits can be established.

The variation in x and a as a function of R^*, determined from the intercepts of eqns. (18) and (20), is shown in Fig. 4. Assuming that $R^* \gg 1$, lower limits of 0.30 and 0.14 were determined for x and a respectively.

However, owing to the relatively large quenching cross section of the A $^1\Pi$, $v' = 13$ state by ground state CO [12] and the relatively low quantum yield (approximately 2×10^{-2}) of CO_2 and C_3O_2 product formation [8], significant concentrations of CO^* could be formed by energy transfer processes

$$\cancel{C}O^* + CO \rightarrow \cancel{C}O + CO^* \tag{26}$$

In previous energy transfer studies [12] no significant $CO(A$ $^1\Pi)$ fluorescence was observed when $\cancel{C}O$ or $C\cancel{\phi}$ was excited in the presence of CO. However, such fluorescence would not have been detected if CO were excited over a broad range of vibrational and rotational levels of the A $^1\Pi$ state or if CO were excited to any of the adjacent metastable states [13].
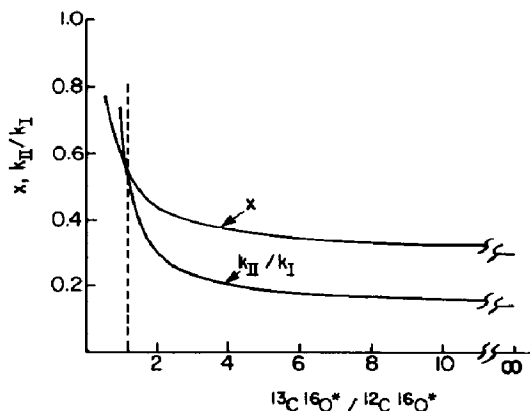
Fig. 4. The variation in x and k_{II}/k_I vs. the assumed $(\cancel{C}O)^*/(CO)^*$ ratio of the excited species: $---$, the minimum $(\cancel{C}O)^*/CO$ ratio obtained from ^{13}C enrichment in CO_2.

Upper limits for x and a can be established from the minimum R^* value for $\cancel{C}O$ excitation. The minimum R^* value was calculated from the sum of the intercepts of eqns. (18) and (19). The sum of these intercepts gave $R^*/(1 + R^*) \geqslant 0.54$, from which $R^* \geqslant 1.2$ was calculated. Thus, upper limits of 0.55 and 0.56 were determined for x and a respectively.

The present results $(0.30 < x < 0.55)$ are in line with the formation of a long-lived intermediate which decomposes statistically. Harteck and co-workers [6, 7] have concluded that the C—O bond bearing the initial excitation decomposed preferentially in reactions of $CO(a\ ^3\Pi)$ with ground state CO, suggesting a short-lived intermediate. However, it must be pointed out that the conclusions of Harteck and his colleagues [6, 7] were made solely on the basis of the higher ^{13}C enrichment in C_3O_2 relative to that in CO_2. It is therefore possible that, as in the present work, the CO_2 product was diluted with unenriched CO_2 which was present as an impurity in CO or was formed by the photolysis of oxygen impurities in CO.

Supporting evidence for the existence of long-lived $(CO)_2^*$ complexes, OCCO in this case, comes from the work of Bayes [14]. He observed that [18]O atoms react with CCO to produce equal amounts of CO and $C\cancel{O}$.

4. Conclusions

The present study has shown that $\cancel{C}O$ and $C\cancel{O}$ molecules excited to the $A\ ^1\Pi$, $v' = 13$ state react with ground state CO to yield isotopically enriched C_3O_2 and CO_2 products. Despite degradation of the initial isotopic selectivity by energy transfer and other isotope scrambling reactions, substantial isotopic enrichment in the C_3O_2 and CO_2 products can be obtained even with natural isotopic abundance CO. It was also shown that the reaction proceeds via long-lived $(CO)_2^*$ intermediates. Two reaction channels have been identified, one yielding carbon atoms and CO_2 and the other yielding C_2O and oxygen atoms.
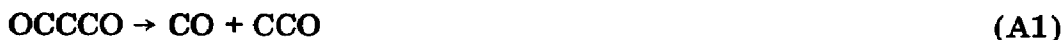
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Appendix A

Derivation of eqn. (9)

The relative abundance of the O¢CCO isotopic species, (eqn. (9)) of the text) can be obtained from the fragmentation patterns of the various isotopic species of C_3O_2, assuming no significant isotope effects, as follows:

$$OCCCO \rightarrow CO + CCO \tag{A1}$$

$$OC¢CO \rightarrow CO + ¢CO \tag{A2}$$

$$O¢CCO \rightarrow \begin{cases} ¢O + CCO \\ CO + C¢O \end{cases} \tag{A3}$$

$$O¢¢CO \rightarrow \begin{cases} ¢O + ¢CO \\ CO + ¢¢O \end{cases} \tag{A4}$$

$$O¢C¢O \rightarrow ¢O + C¢O \tag{A5}$$

$$O¢¢¢O \rightarrow ¢O + ¢¢O \tag{A6}$$

From the above decomposition pattern the abundance of the fragment with $m/e = 41$ relative to that of the fragment with $m/e = 40$ is

$$r_{41} = \frac{¢CO + C¢O}{CCO}$$

$$= \frac{OC¢CO + \frac{1}{2}O¢¢CO + \frac{1}{2}O¢CCO + O¢C¢O}{OCCCO + \frac{1}{2}O¢CCO} \tag{A7}$$

The abundance of the fragment with $m/e = 42$ relative to that of the fragment with $m/e = 40$ is

$$r_{42} = \frac{\cancel{C}\cancel{C}O}{CCO} = \frac{O\cancel{C}\cancel{C}O + \frac{1}{2}O\cancel{C}\cancel{C}CO}{OCCCO + \frac{1}{2}O\cancel{C}CCO} \tag{A8}$$

From the simultaneous solution of eqns. (A7) and (A8) the abundance $r_{O\cancel{C}CCO}$ of $O\cancel{C}CCO$ relative to that of $OCCCO$ is obtained in terms of observable quantities. This solution is given as eqn. (9) in the text.