Journal of Organometallic Chemistry, 444 (1993) 199–202

JOM 23050

Formation of $(\eta^2\text{-}O_2)Co(CO)$ and $(\eta^2\text{-}O_2)Co(CO)_2$ by photolysis of $Co_2(CO)_8$ in dioxygen matrices at 20 K

Matthew J. Almond and Rachel H. Orrin

Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading, RG6 2AD (UK)

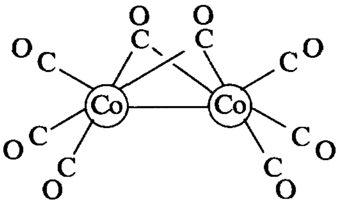
(Received May 21, 1992)

Abstract

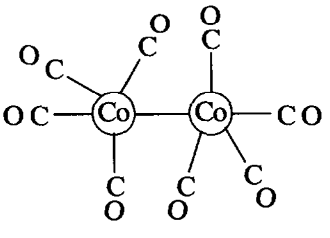
UV irradiation of $Co_2(CO)_8$ in a pure O_2 matrix generates the oxocarbonyl intermediates $(\eta^2\text{-}O_2)Co(CO)_3$ and $(\eta^2\text{-}O_2)Co(CO)_2$, which have been identified by IR spectroscopy including isotopic substitution with ^{18}O. These species are the same as those made previously by cocondensation of Co atoms with CO/O_2 mixtures.

1. Introduction

There is considerable current interest in the formation of organometallic compounds where the metal atom is in a high oxidation state [1,2]. We have recently used the technique of matrix isolation to stabilise a number of oxocarbonyl species of this type [3–8] that are produced by photolysis of a binary metal carbonyl in the presence of dioxygen. Thus more-or-less complete schemes for the photo-oxidation of the mononuclear binary carbonyls $M(CO)_6$ (M = Cr, Mo or W) [3,4] and $Fe(CO)_5$ [8] have been proposed. The matrix photochemistry of the binuclear carbonyls remains less well explored. We recently demonstrated that the final photo-oxidation products of $Mn_2(CO)_{10}$ [5] and $Re_2(CO)_{10}$ [6] in low-temperature matrices are Mn_2O_7 and Re_2O_7, respectively. In the case of $Re_2(CO)_{10}$ we also discovered two oxocarbonyl intermediates, both of which appeared to contain only one metal centre [6]. We have now turned our attention to the photo-oxidation of the molecule $Co_2(CO)_8$, a system which is likely to be extremely complicated. There is the usual competition between M–CO and M–M bond rupture that is a feature of the photochemistry of all binuclear carbonyl species [9,10]. Furthermore, three separate isomers of $Co_2(CO)_8$ have been identified in low-temperature matrices [11]. Of these, the first (**I**) shows two CO bridges, the second (**II**) has the metal centres linked by Co–Co bonding and has no CO bridges, while the third, whose structure has not been determined, appears likewise to have no bridging CO groups.



I



II

Although there are no reports concerning the photooxidation of this molecule, its matrix photochemistry has been quite extensively explored. Thus the interconversion of the three isomers [11] and their photolysis to yield $Co_2(CO)_7$ and $Co(CO)_4$ [9] have been investigated. There have also been a number of papers devoted to the chemistry of matrix-isolated cobalt atoms [12–15]. Thus Co atoms react at 10–12 K with CO to

---

Correspondence to: Dr. M.J. Almond.

0022-328X/93/$6.00

yield a range of mononuclear binary cobalt carbonyls $Co(CO)_n$ ($n = 1$–4) [12], and with CO/O_2 mixtures to form the oxocarbonyl species $(\eta^1\text{-}O_2)Co(CO)_4$ and $(\eta^2\text{-}O_2)Co(CO)_n$ ($n = 1$–3) [13]. It was our principal intention, in the work now described, to determine whether or not oxocarbonyl molecules of the type formed by the reaction of Co atoms with CO/O_2 mixtures could also be generated by the photooxidation of $Co_2(CO)_8$. At the same time we hoped to learn something about the mechanism of the photooxidation process.

2. Experimental section

$Co_2(CO)_8$ (Aldrich) was stored in n-hexane to stabilize it, and fresh samples were separated from the hexane on a vacuum line prior to use. $^{16}O_2$ (99.999% purity) and Ar (99.99% purity) were used as supplied by Aldrich. $^{18}O_2$ (97.7 at.%) was used as supplied by Merck, Sharp and Dohme. The apparatus and experimental procedures used for the matrix work were as described elsewhere [8,16].

3. Results

The condensate formed by deposition at 20 K of $Co_2(CO)_8$ vapour with O_2 in the approximate ratio 1:500 showed an IR spectrum in agreement with that previously observed by Brown and Sweany [11] and which they assigned to three isomers of the molecule $Co_2(CO)_8$. There was no sign of the superoxo species $(\eta^1\text{-}O_2)Co(CO)_4$ [13,17] whose ESR spectrum was seen by Symons *et al.* [17] when $Co_2(CO)_8$ vapour was frozen on to a cold finger at 77 K in the presence of O_2. The failure to detect this radical by IR spectroscopy under these conditions (under which its concentration is expected to be very low) probably reflects the much greater sensitivity of ESR over IR spectroscopy towards radicals. We invariably noted some decomposition of the $Co_2(CO)_8$ during spray-on as evidenced by the presence of CO [18] and CO_2 [19] within the matrix and a film of metallic cobalt inside the spray-on tube.

When the condensate is subjected to photolysis using either 337 nm or broad-band UV radiation the IR absorptions of $Co_2(CO)_8$ decay. Bands due to free CO [18] and CO_2 [19] increase in intensity while absorptions at 2123, 2066, 2063, 1966, 1957 and 1945 cm^{-1} assigned to the molecule $Co_2(CO)_7$ which has no bridging CO groups, [9] appear and grow. There is no sign of any mononuclear binary cobalt carbonyl *i.e.* $Co(CO)_n$ ($n = 1$–4) [9,12,20,21]. However, absorptions are seen in the $\nu(CO)$ region of the IR spectrum at 2081, 2046 and 2027 cm^{-1} (see Fig. 1) and also grow upon photolysis. These belong to no known binary carbonyl of cobalt. Rather they may be identified with the peroxo species $(\eta^2\text{-}O_2)Co(CO)_3$ (**A**) and $(\eta^2\text{-}O_2)Co(CO)_2$ (**B**) which have been previously prepared in low-temperature matrices by the reaction of Co atoms with CO/O_2 mixtures [13] and which are reported to show $\nu(CO)$ vibrations at: **A**, $-2086/2076$ and $2050/2046$ cm^{-1}; **B**, $-2035/2020$ cm^{-1} [22*]. Inspection of the 1000–900 cm^{-1} region of our spectrum shows the growth of broad features centred at 940 and 950 cm^{-1} (see Fig. 2) which may also be assigned to **A** and **B**, respectively [13].

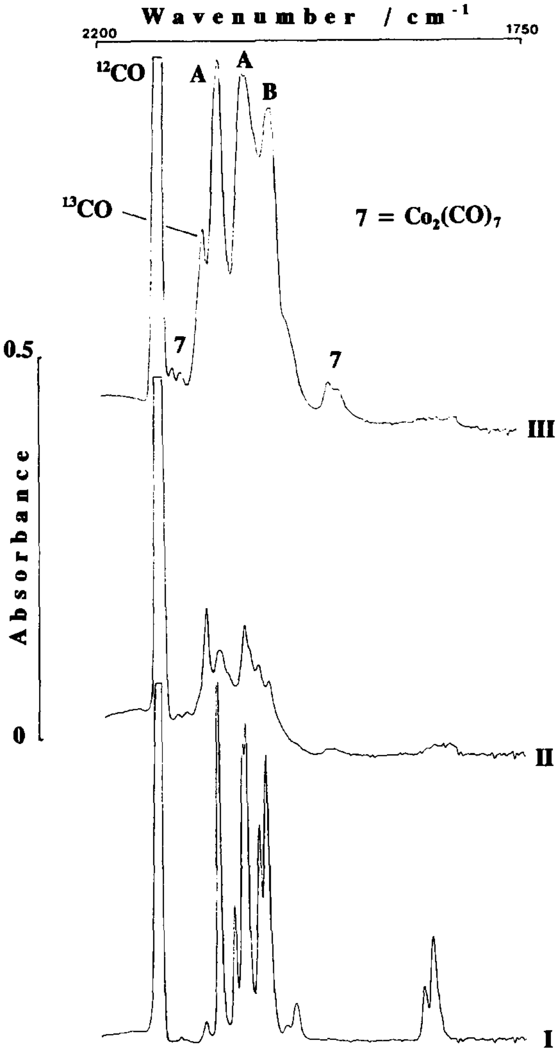


Fig. 1. Infrared absorption spectra (2200–1750 cm^{-1}) of O_2 matrices containing $Co_2(CO)_8$. I, after deposition of a *ca.* 1 : 2500 $Co_2(CO)_8 : O_2$ mixture, II, as I but after broad-band UV–Vis photolysis for 150 min; III, After broad-band UV-visible photolysis for 150 min of a *ca.* 1:500 $Co_2(CO)_8 : O_2$ mixture. The higher concentration of $Co_2(CO)_8$ builds up a higher concentration of **A** and **B**.

---

[*] Reference number with an asterisk indicates a note in the list of references

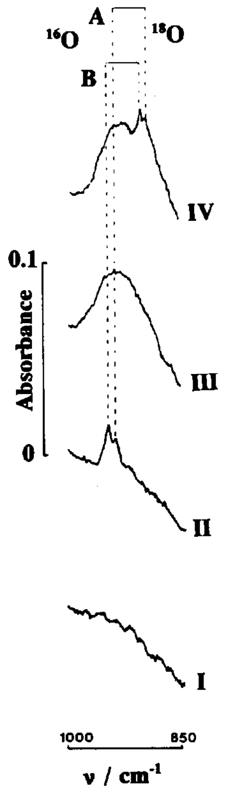


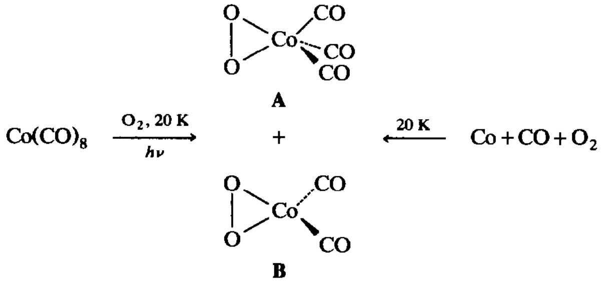
Fig. 2. Infrared absorption spectra (1000–800 cm^{-1}) of O_2 matrices containing $Co_2(CO)_8$. I 1:500 $Co_2(CO)_8$:$^{16}O_2$ after deposition; II, 1:500 $Co_2(CO)_8$:$^{16}O_2$ after broad-band UV-visible photolysis for 150 min; III, 1:500 $Co_2(CO)_8$:$^{18}O_2$ after deposition; IV 1:500 $Co_2(CO)_8$:$^{18}O_2$ after broad-band UV–VIS photolysis for 150 min. The broad feature around 920 cm^{-1} in the background of spectra III and IV is due to an interference effect from the thin layer of matrix upon the spectroscopic window.

In order to confirm our assignment of these features we carried out a series of experiments involving: (i) variation of the concentration of O_2 within the matrix by dilution with Ar in the ratio Ar:O_2 = 80:20; (ii) variation of the concentration of $Co_2(CO)_8$ within the matrix to a $Co_2(CO)_8$:O_2 ratio of *ca.* 1:2500; (iii) replacing $^{16}O_2$ by $^{18}O_2$. On reducing the concentration either of $Co_2(CO)_8$ or of O_2 we found that the bands assigned to **A** and **B** were substantially reduced in intensity. This result implies that **A** and **B** are products of a reaction between $Co_2(CO)_8$ and O_2. Upon substitution of $^{16}O_2$ by $^{18}O_2$ the band of **B** at 950 cm^{-1} shifted to 897 cm^{-1}, while the ^{18}O-isotopomer of **A** was seen as a rather indistinct shoulder at *ca.* 888 cm^{-1} (see Fig. 2). These isotope shifts of 53 and 52 cm^{-1} match, within experimental error, the calculated shift of 54 cm^{-1} for the ν(O–O) vibration of **A** or **B**. They are also more or less consistent with the previously reported ^{16}O–^{18}O shifts for $(\eta^2\text{-}O_2)Co(CO)_3$ and $(\eta^2\text{-}O_2)Co(CO)_2$ [12,23*].

4. Discussion

Our results are of interest because they show that the same oxocarbonyl products may be produced by a "breaking-down" reaction *i.e.* the photolysis of $Co_2(CO)_8$ in the presence of O_2 as by a "building-up" reaction *i.e.* the reaction of Co atoms with a CO/O_2 mixture (Scheme 1). In a similar vein binary carbonyls such as $Co(CO)_4$ have been generated by a variety of thermal and photochemical routes [9,12,20,21], but to our knowledge this is the first occasion upon which an oxocarbonyl intermediate has been prepared by two such different routes. These results imply that there is some intrinsic thermodynamic stability associated with **A** and **B**, and that their presence at reasonably high concentrations within the matrix is not solely a result of other factors, *e.g.* a fortuitous lack of overlap between their absorption bands and the output of the photolysis source.

We may compare briefly the outcome of these experiments on $Co_2(CO)_8$ with those of the photooxidation of other binary metal carbonyls. Peroxo species similar to **A** and **B** are formed on photolysis of various mononuclear carbonyls. Thus $M(CO)_6$ (M = Cr, Mo or W) yield $(\eta^2\text{-}O_2)M(CO)_4$ [3,4] while $Fe(CO)_5$ [8] gives rise to $(\eta^2\text{-}O_2)Fe(CO)_4$. There is also a precedent for the formation of mononuclear oxocarbonyls from binuclear carbonyl precursors. On photooxidation by O_2, $Re_2(CO)_{10}$ gives rise to an oxocarbonyl intermediate which is believed to be $O{=}Re(CO)_5$, formed by breaking a Re–Re bond [6]. Our results imply that, like $Re_2(CO)_{10}$, $Co_2(CO)_8$ is photooxidised *via* a mechanism that involves separation of the two metal centres. Although binuclear fragments predominate in the electron-impact mass spectrum of $Co_2(CO)_8$, our findings are in keeping with the estimated low metal–metal bond energy in the Co–Co bonded form of $Co_2(CO)_8$ (**II**) [25,26] and the observation that the CO-bridged form of the molecule (**I**) is readily converted into **II** in low-temperature matrices upon UV irradiation [11]. Thus a possible mechanism of the reaction is dissociation of $Co_2(CO)_8$ to form $Co(CO)_4$ radicals, which then



Scheme 1.

TABLE 1. Bands observed upon the photooxidation of $Co_2(CO)_8$ in O_2 matrices at 20 K

ν (cm^{-1}) [a,b]	Origin	Ref.
2340 (vs)	CO_2	19
2140 (vs)	CO	18
2122 (wm)	$Co_2(CO)_7$	9
2081 (m)	$(O_2)Co(CO)_3$	12
2066 (m)	$Co_2(CO)_7$	9
2063 (m)	$Co_2(CO)_7$	9
2052 (s)	$Co_2(CO)_7$	9
2046 (ms, sh)	$(O_2)Co(CO)_3$	12
2027 (s)	$(O_2)Co(CO)_2$	12
1966 (m)	$Co_2(CO)_7$	9
1957 (m)	$Co_2(CO)_7$	9
1945 (sh) (wm)	$Co_2(CO)_7$	9
950 (w)	$(O_2)Co(CO)_2$	12
940 (w)	$(O_2)Co(CO)_3$	12
660 (vs)	CO_2	19

[a] ±1 cm^{-1}. [b] s strong, m medium, w weak, v very, sh shoulder.

TABLE 2. Behaviour of bands assigned to ν(O–O) vibrations of **A** and **B** upon ^{18}O-substitution

$\nu(^{16}O)$ (cm^{-1}) [a]	$\nu(^{18}O)$ (cm^{-1}) [a]	$\Delta\nu_{obs}$ (cm^{-1}) [b]	$\Delta\nu_{calc}$ (cm^{-1})	$R\nu_{obs}$ [c]	$R\nu_{calc}$	Origin
950	897	53	54	0.944	0.943	ν(O–O) **B**
940	888	53	54	0.945	0.943	ν(O–O) **A**

[a] ±1 cm^{-1}. [b] $\Delta\nu = (\nu\ ^{16}O - \nu\ ^{18}O)$; ±2 cm^{-1}. [c] $R\nu = (\nu^{16}\ O/\nu^{18}O)$; ±0.002.

react with O_2 to generate (via loss of CO) the observed peroxo-species $(\eta^2\text{-}O_2)Co(CO)_n$ ($n = 2$ or 3)

$$\begin{tikzcd} Co_2(CO)_8 \arrow[d, "h\nu"'] & \\ Co(CO)_4 + O_2 \arrow[r] & (\eta^2\text{-}O_2)Co(CO)_n + (4-n)CO \end{tikzcd}$$

There was no sign in our experiments of $Co(CO)_4$, even at low O_2 concentrations. This result is consistent with the failure to observe $Re(CO)_5$ radicals upon photo-oxidation of matrix-isolated $Re_2(CO)_{10}$ [6] even though peroxo-rhenium carbonyl species that appeared to be derived from $Re(CO)_5$ were seen in this system.

Acknowledgment

We thank the Research Board of the University of Reading for providing a studentship for R.H.O.

References and notes

1 W. A. Herrmann, W. Wagner, U. N. Flessner, U. Volkhardt and H. Komber, *Angew. Chem., Int. Ed. Engl., 30* (1991) 1636; W. A. Herrmann, R. W. Fischer and D. W. Marz, *Angew. Int. Ed. Engl., 30* (1991) 1638 W. A. Herrmann and M. Wang, *Angew. Chem. Int. Ed. Engl., 30* (1991) 1641; W. A. Herrmann, R. W. Albach and J. Behm, *J. Chem. Soc., Chem. Commun.,* (1991) 367; W. A. Herrmann, C. Romao, R. W. Fisher, P. Kiprof and C. M. de Bellephon, *Angew. Chem., Int. Ed. Engl., 30* (1991) 185.

2 F. Bottomley, J. Chen, S. M. MacIntosh and R. C. Thompson, *Organometallics, 10* (1991) 906; F. Bottomley, E. C. Ferris and P. S. White, *Organometallics, 9* (1990) 1166; F. Bottomley and S. Karslioglu, *Organometallics, 11* (1992) 326.

3 J. A. Crayston, M. J. Almond, A. J. Downs, M. Poliakoff and J. J. Turner, *Inorg. Chem., 23* (1984) 3051.

4 M. J. Almond, J. A. Crayston, A. J. Downs, M. Poliakoff and J. J. Turner, *Inorg. Chem., 25* (1986) 19.

5 M. J. Almond, *J. Mol. Struct., 172* (1988) 157.

6 M. J. Almond and R. H. Orrin, *J. Chem. Soc., Dalton Trans.,* (1992) 1229.

7 M. J. Almond, and R. H. Orrin, *Polyhedron, 11* (1992) 2157.

8 M. Fanfarillo, H. E. Cribb, A. J. Downs, T. Greene and M. J. Almond, *Inorg. Chem., 31* (1992) 2962; M. Fanfarillo, A. J. Downs, T. Greene and M. J. Almond, *Inorg. Chem., 31* (1992) 2973.

9 R. L. Sweany and T. L. Brown, *Inorg. Chem., 16* (1977) 421.

10 See also, for example, T. Kobayashi, H. Ohtani, H. Noda, S. Teratoni, H. Yamazaki and K. Yasufuku, *Organometallics, 5* (1986) 110.

11 R. L. Sweany and T. L. Brown, *Inorg. Chem., 16* (1977) 415.

12 A. J. L. Hanlan, H. Huber, E. Kundig, B. McGarvey and G. A. Ozin, *J. Am. Chem. Soc., 97* (1975) 7054.

13 G. A. Ozin, A. J. L. Hanlan and W. J. Power, *Inorg. Chem., 18* (1979) 2390.

14 G. A. Ozin and A. J. L. Hanlan, *Inorg. Chem., 18* (1979) 1781.

15 G. A. Ozin and A. Vander Voet, *Can. J. Chem., 51* (1973) 637.

16 M. J. Almond and M. Hahne, *J. Chem. Soc., Dalton Trans.,* (1988) 2255.

17 S. A. Fieldhouse, B. W. Fullam, G. W. Neilson and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.,* (1974) 567.

18 H. Dubost, *Chem. Phys., 12* (1976) 139.

19 L. Fredin, B. Nelander and G. Ribbegard, *J. Mol. Spectrosc., 53* (1974) 410.

20 O. Crichton, M. Poliakoff, A. J. Rest and J. J. Turner, *J. Chem. Soc., Dalton Trans.,* (1973) 1321.

21 R. L. Sweany, *Inorg. Chem., 19* (1980) 3512.

22 These doublets are reported to arise as a result of matrix splittings (see ref. 13).

23 In fact these previously reported $^{156}O-^{18}O$ shifts of 62 cm^{-1} for $(\eta^2\text{-}O_2)Co(CO)_3$ and of 59 cm^{-1} for $(\eta^2\text{-}O_2)Co(CO)_2$ seem rather large for ν(O–O) of an η^2-coordinated O_2 unit.

24 B. F. G. Johnson, J. Lewis, I. G. Williams and J. M. Wilson, *J. Chem. Soc. A,* (1967) 341.

25 D. R. Bidinosti and N. S. McIntyre, *J. Chem. Soc., Chem. Commun.,* (1967) 1.

26 P. J. Gardner, A. Cartner, R. G. Cunninghame and B. H. Robinson, *J. Chem. Soc., Dalton Trans.,* (1976) 2582.