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Formation of *trans*-M(O)$_2$(CO)$_4$ (M = Mo and W): Intermediates in the Photooxidation of Matrix-Isolated M(CO)$_6$

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Photolysis of Mo(CO)$_6$ or W(CO)$_6$, isolated in O$_2$-doped Ar or CH$_4$ matrices at 10 K, produces IR and Raman spectroscopic evidence for formation of two oxo carbonyl species, A and B. The observed isotopic shifts in IR and Raman bands (natural-abundance Mo isotopes, and ^{13}CO and ^{18}O$_2$ substitution) are used to show that B is a *trans*-dioxo metal tetracarbonyl species, M(O)$_2$(CO)$_4$, with a linear O=M=O group. The mechanism of photooxidation is briefly discussed.

Introduction

There is considerable mechanistic interest in the oxidation of transition-metal species by dioxygen. One approach is to study the addition of O$_2$ to coordinatively unsaturated transition-metal centers. Matrix isolation has played a significant role in these experiments because it is particularly easy to generate the unsaturated metal centers in matrices.[2] Thus, cocondensation of metal atoms with O$_2$ has produced evidence for all of the more probable types of MO$_x$ complexes:

$$M + O_2 \xrightarrow[\text{Ar, 12 K}]{\text{cocondense}} MO_x$$
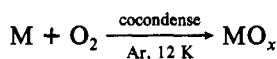
Examples include **1**,[3a] **2**,[3b] **3**,[3c] and **4**.[3d]
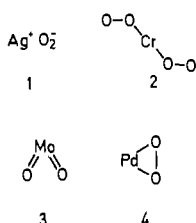
An alternative approach is the UV photolysis of transition-metal carbonyls in the presence of oxygen. This method has been used to generate peroxo complexes that were detected by ESR.[4]

Recently we described[5,6] how photolysis of matrix-isolated Cr(CO)$_6$ in the presence of O$_2$ produced, inter alia, "chromyl carbonyl", Cr(O)$_2$(CO)$_2$ (**5**). The IR spectra not only showed

5
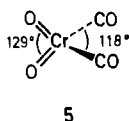
clearly that the O—O bond had been cleaved but also provided

estimates of the OC—Cr—CO and O=Cr=O bond angles (**5**). The molecule was interesting because it was the first example of a Cr(IV) carbonyl compound, yet it appeared to be one of the more stable products formed during the photooxidation of Cr(CO)$_6$. Although several other products were detected, they proved to be more difficult to characterize and the proposed oxidation mechanism[5] was necessarily somewhat tentative.

Those experiments[5,6] with Cr(CO)$_6$ prompted us to study the photooxidation of matrix-isolated Mo(CO)$_6$ and W(CO)$_6$. The behavior of Mo and W was anticipated to be different from that of Cr, since Mo and W dioxo compounds are generally more stable than the corresponding Cr complexes (e.g. [Mo(O)$_2$(CN)$_4$]$^{4-}$ and [W(O)$_2$(CN)$_4$]$^{4-}$ are stable at room temperature).[7] These systems are also of interest because oxidized Mo and W carbonyl species are proposed intermediates in the formation of olefin metathesis catalysts.[8] A more practical consideration is that Mo has seven relatively abundant isotopes,[9] which have played an important role in the IR characterization of other matrix-isolated Mo/oxide species.[3c,10]

Our experiments have been most successful and have provided spectroscopic evidence for a number of oxidized Mo and W species significantly different from those observed in the analogous reactions of Cr(CO)$_6$. In this paper we describe the characterization of the previously unknown complexes *trans*-dioxotetracarbonylmolybdenum and -tungsten (**6**). We

6

show that the extensive IR and Raman data provide a considerable amount of structural information about these complexes. Finally, we discuss briefly how these species may be formed from the parent hexacarbonyl and discuss possible reasons for their apparent stability. A fuller discussion of the complete photooxidation processes of Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$ will be presented elsewhere.[11]

(1) (a) University of Nottingham. (b) University of Oxford.
(2) Downs, A. J.; Hawkins, M. *Adv. Infrared Raman Spectrosc.* **1983**, *10*, 1–109. Moskovits, M.; Ozin, G. A., Eds. "Cryochemistry"; Wiley-Interscience: New York, 1976. Turner, J. J.; Poliakoff, M. *ACS Symp. Ser.* **1983**, *No. 211*, 35.
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(9) The relative abundances of the seven most commonly occurring isotopes of molybdenum are as follows: ^{92}Mo, 14.8%; ^{94}Mo, 9.3%; ^{95}Mo, 15.9%; ^{96}Mo, 16.7%; ^{97}Mo, 9.6%; ^{98}Mo, 24.1%; ^{100}Mo, 9.6%. From: Weast, R. C.; Astle, M. J., Eds. "CRC Handbook of Chemistry and Physics", 64th ed.; CRC Press: Boca Raton, FL, 1983.
(10) Levason, W.; Narayanaswamy, R.; Ogden, J. S.; Rest, A. J.; Turff, J. W. *J. Chem. Soc., Dalton Trans.* **1982**, 2009.
(11) Almond, M. J.; Crayston, J. A.; Downs, A. J.; Poliakoff, M.; Turner, J. J., to be submitted for publication.
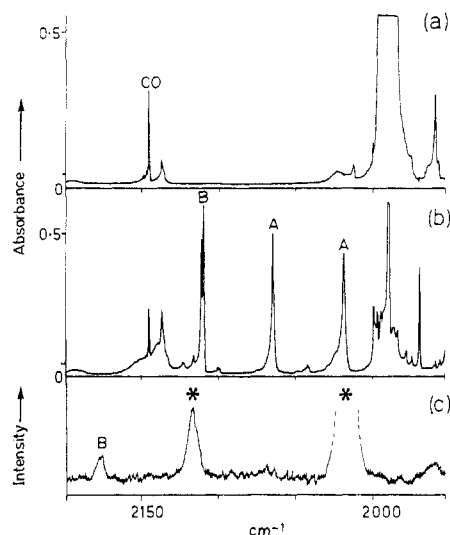
Figure 1. IR absorption and Raman spectra of the CO-stretching region illustrating UV photolysis of $Mo(CO)_6$ in a CH_4 matrix doped with O_2 (dilution $Mo(CO)_6:O_2:CH_4 \approx 1:200:2000$) at 20 K: (a) IR spectrum after spray-on; (b) IR spectrum showing appearance of bands due to A and B after 4-min unfiltered UV photolysis of $Mo(CO)_6$ followed by 30-min irradiation with $\lambda = 403$ nm (note that the CO absorption band contour broadens after photolysis); (c) Raman spectrum showing a single band due to B. Bands marked with asterisks are due to residual hexacarbonyl. This spectrum was obtained after photolysis steps similar to those preceding spectrum b (i.e., successive 30 min duration photolyses at 312, 435, and 363 nm).

Experimental Section

The IR experiments with $Mo(CO)_6$ were performed at Nottingham. The IR experiments with $W(CO)_6$ and all of the Raman experiments were performed at Oxford. Both laboratories use Air Products Displex CS202 closed-cycle refrigerators, which have been described previously,[6,12] and matrices were produced by pulsed deposition.

Nottingham. All IR spectra were run on a Nicolet 7199 FTIR interferometer with 32K data collection (0.5-cm^{-1} resolution, 0.1-cm^{-1} accuracy) and three degrees of zero-filling in the Fourier transform. A Philips HPK-125 W medium-pressure Hg arc was used for UV photolysis, with a Pyrex filter ($\lambda > 320$ nm) or Balzer's interference filters (band-pass ca. 20 nm) when appropriate. Matrix gases (Messer Griesheim, purity ≥99.998%), ^{13}CO and $^{18}O_2$ (BOC Prochem), and $Mo(CO)_6$ (BDH) were used without further purification. Force constant calculations were carried out on an Apple 2 computer.[13]

Oxford. IR spectra were recorded on a Perkin-Elmer Model 580A spectrophotometer (0.5-cm^{-1} resolution and accuracy). Raman spectra were excited at 5145 Å by means of a Spectra-Physics Model 165 Ar$^+$ laser and recorded on a Spex Ramalog 5 spectrometer (typically 5–6-cm^{-1} resolution and accuracy). The optical arrangements used for measuring Raman spectra of matrices have been described previously.[6,14] The Hg arc and optical filters were the same as those used at Nottingham, although the focusing optics were somewhat different. Matrix gases (BOC grade X), $^{18}O_2$ and ^{13}CO (BOC Prochem), $Mo(CO)_6$ (Ralph N. Emmanuel), and $W(CO)_6$ (Koch Light) were used without further purification.

Results

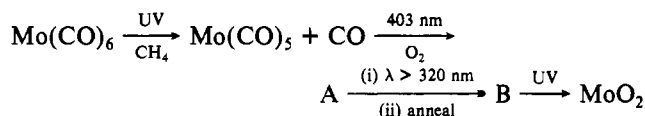UV photolysis of $Mo(CO)_6$ or $W(CO)_6$ in CH_4 or Ar matrices doped with O_2 initially produces $M(CO)_5$ and CO. Further photolysis with an unfiltered Hg arc produces two mixed-carbonyl–oxygen species, A and B, and increasing quantities of CO and CO_2. Prolonged photolysis yields as final products MO_2 and MO_3, the IR spectra of which are already known.[3c,15] The various stages of the oxidation can be at least

Table I. Wavenumbers^a (cm^{-1}) of C–O-Stretching Bands Observed after UV Photolysis of a Matrix Containing $M(CO)_6$ ($M = Mo, W$) and O_2

Mo			W	
R^b	IR^b	assignt	R^b	IR^c
2120	d	$M(CO)_6$ a_{1g}	2122	d
2020	d	$M(CO)_6$ e_g	2013	d
d	1988	$M(CO)_6$ t_{1u}	d	1986
e	1968	$M(CO)_5$ e	e	1970
e	1927	$M(CO)_5$ a_1	e	1931
2070	2064	A	2060	2054
2012	2015	A	2010	2008
2175	d	B	2160	d
d	2110	B	d	2096

^{a} For error limits, refer to Experimental Section. ^{b} Conditions: CH_4/O_2 matrix; dilution $M(CO)_6:O_2:CH_4 \approx 1:200:2000$. ^{c} Conditions: Ar/O_2 matrix; dilution $W(CO)_6:O_2:Ar \approx 1:100:2000$. ^{d} Inactive or not observed. ^{e} Raman bands of $M(CO)_5$ were not observed because of its extreme photosensitivity to the visible radiation used to excite the scattering ($\lambda = 514$ nm).

partially separated by using different filters to limit the wavelengths of the photolyzing radiation. Thus, for $Mo(CO)_6$ in CH_4/O_2 matrices, an approximate reaction sequence[16] is

$$Mo(CO)_6 \xrightarrow[CH_4]{UV} Mo(CO)_5 + CO \xrightarrow[O_2]{403 \text{ nm}}$$

$$A \xrightarrow[(ii) \text{ anneal}]{(i) \lambda > 320 \text{ nm}} B \xrightarrow{UV} MoO_2$$

We shall now present vibrational spectra which show that B is $trans$-$Mo(O)_2(CO)_4$ (**6**).

Product B: ν_{C-O} **Region.** Figure 1a shows the C–O-stretching region of the IR spectrum of $Mo(CO)_6$ after deposition in a CH_4 (+10% O_2) matrix. Figure 1b shows the IR spectrum of the *same* matrix after photolysis, at the stage when the yield of B is at a maximum. It can be seen that A has *two* IR absorptions, marked A, in this region, while B has only one band, marked B. Figure 1c shows the Raman spectrum measured in a similar but separate experiment, showing the Raman band assigned to B. This Raman band shows the same growth and decay behavior as the IR band due to B during the various stages of the photooxidation. It is clear from these spectra that (i) both A and B must be due to oxidized species since their IR absorptions are at higher frequency[5] than those of $Mo(CO)_6$, (ii) B must contain at least *two* CO groups since it has noncoincident IR and Raman bands, (iii) B *could* be centrosymmetric because of this noncoincidence, and (iv) the spectra are consistent with linear $M(CO)_2$ (**7**), planar $M(CO)_3$ (**8**), and $M(CO)_4$ (**9**) moieties.[17]
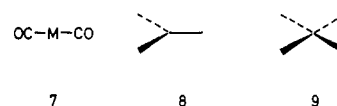

The frequencies of bands observed in the ν_{C-O} region are summarized in Table I.

We can determine the number of CO groups in product B by photolysis of $Mo(CO)_6$ partially enriched with ^{13}CO. Isotopic enrichment is the most widely used technique for characterizing matrix-isolated metal carbonyls,[18] e.g. $Cr(O)_2(CO)_2$.[5] It is now becoming clear that the technique works

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(13) (a) Perutz, R. N.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262. (b) Perutz, R. N. Ph.D. Thesis, University of Cambridge, 1974.
(14) Burdett, J. K.; Downs, A. J.; Gaskill, G. P.; Graham, M. A.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 523.
(15) Green, D. W.; Ervin, K. M. *J. Mol. Spectrosc.* **1981**, *89*, 145.

(16) This scheme is by no means comprehensive. CO_2 is also produced as is at least one additional metal carbonyl species with a ν_{C-O} IR band at 1998 cm^{-1} (for W).
(17) A D_{4h} $M(CO)_4$ species has *two* Raman-active C–O stretching vibrations, a_{1g} and b_{1g}. Thus, we must postulate that the b_{1g} band was not observed, a not unreasonable assumption in view of the rather weak Raman scattering of B.
(18) Burdett, J. K.; Poliakoff, M.; Turner, J. J.; Dubost, H. *Adv. Infrared Raman Spectrosc.* **1976**, *2*, 1–52.
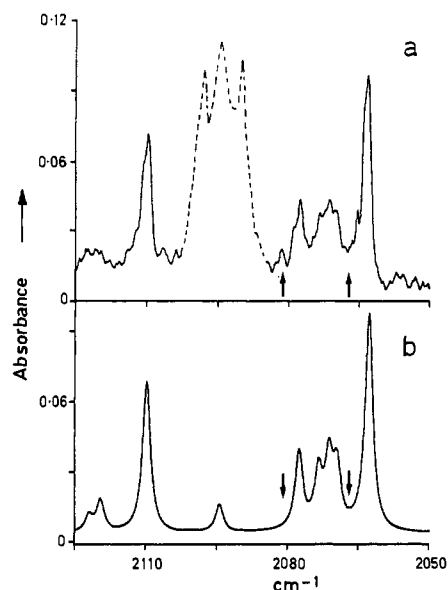
Figure 2. (a) IR absorption spectrum of approximately 55% ^{13}CO-enriched B in a CH$_4$ matrix doped with O$_2$. (b) Spectrum predicted (Lorentzian bands, fwhm = 4 cm^{-1}) for a planar M(CO)$_4$ moiety of D_{4h} symmetry. The broad band due to photoejected ^{13}CO at 2095 cm^{-1} (dotted line) obscures part of the spectrum. Thus, only the region between the two arrows is shown in subsequent spectra (Figure 3).
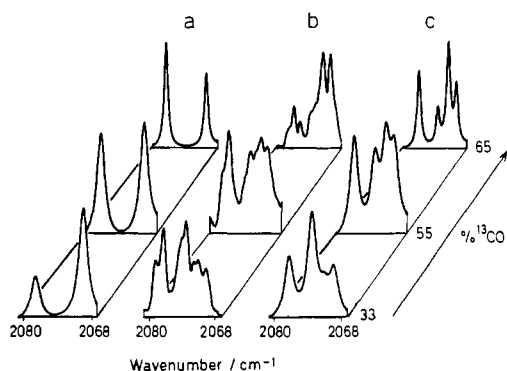
Figure 3. Stacked plot showing the differences between the IR absorption spectra predicted for D_{4h} (**9**) and D_{3h} (**8**) structures of Mo(O)$_2$(CO)$_4$, upon 33%, 55%, and 65% ^{13}CO enrichment: (a) predicted spectra for the D_{3h} M(CO)$_3$ moiety with optimized force constants; (b) observed spectra after photooxidation of ^{13}CO-enriched Mo(CO)$_6$; (c) predicted spectra for D_{4h} M(CO)$_4$ with force constants as in Table II.

extremely well for relatively symmetrical molecules but can produce ambiguous results for molecules with low symmetry.[19] We will show that product B has high symmetry so that these limitations do not apply here.

Figure 2a shows the IR spectrum obtained by photooxidation of Mo(CO)$_6$ containing 55% ^{13}CO.[20] There are at least four bands assignable to B, which immediately shows that B must contain more than *two* CO groups, since a dicarbonyl species would give rise to only three bands with intensities approximately in the ratio 1:2:1 (cf. Cr(O)$_2$(CO)$_2$).[5] The observed spectrum is similar to that predicted for a D_{4h} M-(CO)$_4$ moiety[21] (**9**; see Figure 2b). Unfortunately part of the
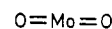
(19) Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *Inorg. Chem.* **1983**, *22*, 3259.

(20) Mo(CO)$_6$ was enriched by UV photolysis in the gas phase in the presence of ^{12}CO/^{13}CO mixtures at a total pressure of ca. 5 torr. For details see: Perutz, R. N.; Turner, J. J. *Inorg. Chem.* **1975**, *14*, 262.

(21) The predicted frequencies and relative intensities of the bands in this region are identical for D_{4h} and C_{4v} M(CO)$_4$ moieties, since the G matrices are diagonal and carry no bond angle information. A C_{4v} species should, however, have an IR-active a$_1$ vibration, although for a near-planar structure the band will be weak.

Table II. Observed and Calculated Wavenumbers (cm^{-1}) for the Carbonyl Stretching Modes of Different Mo(O)$_2$(^{12}CO)$_x$(^{13}CO)$_{4-x}$ Species in a CH$_4$/O$_2$ Matrix at 20 K[g]

obsd[a]	calcd[f]	mode	molecule
2175.0[b]	2174.9	a$_{1g}$	Mo(^{12}CO)$_4$ (D_{4h})
e	2127.4	b$_{2g}$	
2110.0	2109.6	e$_u$	
d	2167.8	a$_1$	Mo(^{12}CO)$_3$(^{13}CO) (C_{2v})
2123.0	2122.7	a$_1$	
2110.0	2109.6	b$_2$	
2073.4	2073.9	a$_1$	
d	2158.6	a$_1$	*cis*-Mo(^{12}CO)$_2$(^{13}CO)$_2$ (C_{2v})
2119.0	2120.1	b$_2$	
2077.6	2078.2	a$_1$	
2069.9	2069.7	b$_2$	
e	2160.8	a$_g$	*trans*-Mo(^{12}CO)$_2$(^{13}CO)$_2$ (D_{2h})
2110.0	2109.6	b$_{2u}$	
e	2093.6	a$_g$	
2063.4	2062.6	b$_{1u}$	
c	2148.4	a$_1$	Mo(^{12}CO)(^{13}CO)$_3$ (C_{2v})
c	2096.6	a$_1$	
2071.3	2071.5	a$_1$	
2063.4	2062.6	b$_2$	
e	2126.4	a$_{1g}$	Mo(^{13}CO)$_4$ (D_{4h})
e	2080.0	b$_{2g}$	
2063.4	2062.6	e$_u$	

[a] IR frequencies; for error estimates refer to Experimental Section. [b] Raman band. [c] Not observed, predicted to be overlapped or obscured by bands of Mo(CO)$_6$ or uncoordinated ^{12}CO and ^{13}CO. [d] Not observed, predicted to be weak. [e] IR-inactive band. [f] Each frequency was entered only once into the least-squares refinement. [g] Nine frequencies, root-mean-square error 0.39 cm^{-1}, maximum error 1.1 cm^{-1}. Force constants (N m^{-1}): k_{CO} = 1833.74, k_{cis} = 20.66, k_{trans} = 35.85.

observed spectrum is obscured by the broad absorption of the uncoordinated ^{13}CO produced during photolysis. This ^{13}CO absorption could be masking additional bands due to B. Thus, it is difficult to use this *single* spectrum to eliminate the possibility that B contains an M(CO)$_3$ moiety (**8**). This possibility can be eliminated, however, by comparing the spectra obtained by photooxidation of samples of Mo(CO)$_6$ with 33%, 55%, and 65% ^{13}CO enrichment. These are illustrated in Figure 3, which, it should be noted, covers only part of the spectral region included in Figure 2. For all three experiments, the spectra predicted for a D_{3h} M(CO)$_3$ fragment (Figure 3a) are quite different from the observed spectra (Figure 3b). On the other hand, there is a striking agreement between the observed spectra and those predicted for a D_{4h} M(CO)$_4$ moiety (Figure 3c). Table II summarizes the observed and calculated frequencies for Mo(^{12}CO)$_{4-x}$(^{13}C)$_x$ species. A similar spectrum is observed upon ^{13}CO enrichment of the tungsten analogue, although some of the bands are overlapped by bands due to A and uncoordinated ^{13}CO.

Thus, the ^{13}CO enrichment experiments confirm that B contains a planar or near-planar[21] Mo(CO)$_4$ moiety (**9**). We now present vibrational spectra in the region 700–900 cm^{-1} which indicate that B also contains a linear O=M=O group (**10**).
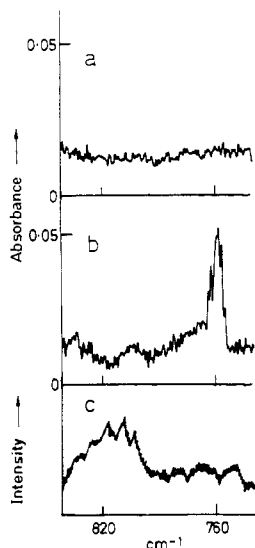
$$O=Mo=O$$

10

Product B: ν_{M-O} Region. Figure 4a shows that the IR spectrum of Mo(CO)$_6$ isolated in a CH$_4$ (+10% O$_2$) matrix has no absorptions in the region 740–840 cm^{-1}. During photooxidation, a broad IR absorption centered at 757 cm^{-1} (Figure 4b) grows in and decays at the same rate as the carbonyl absorption of B. Thus, the two IR bands must be due to the same compound. Similarly, a broad feature at 820 cm^{-1} in the Raman spectrum (Figure 4c) can be assigned to

Figure 4. The 740–840-cm^{-1} regions of the IR absorption and Raman spectra during photooxidation of $Mo(CO)_6$ in a CH_4 matrix containing 10% O_2 showing bands due to product B: (a) IR spectrum before photolysis; (b) IR spectrum after UV photolysis followed by irradiation with $\lambda = 403$ nm and $\lambda > 320$ nm; (c) corresponding *Raman* spectrum obtained after a photolysis sequence similar to that preceding (b) (30 min, $\lambda = 312$ nm; 30 min, $\lambda = 435$ nm; 30 min, $\lambda = 363$ nm).

Table III. Wavenumbers^a (cm^{-1}) of Bands Observed in the Region 700–950 cm^{-1} after UV Photolysis of a Matrix Containing $M(CO)_6$ and Oxygen

| Mo			W	
IR^b	R^b	assign	IR^c	R^b
954	*d*	A	914	*d*
d	820	B a_{1g}	*d*	850
758	*d*	B a_{2u}	751	*d*
945	*d*	MoO_2 ν_1 $(a_1)^e$		
900	*d*	MoO_2 ν_3 $(b_1)^e$		
913	*d*	MoO_3 ν_3 $(e')^{e,f}$	*d*	

^{a} For error limits, refer to Experimental Section. ^{b} Conditions: CH_4/O_2 matrix; dilution $M(CO)_6:O_2:CH_4 \approx 1:200:2000$. ^{c} Conditions: Ar/O_2 matrix; dilution $W(CO)_6:O_2:Ar \sim 1:100:2000$. ^{d} Not observed or inactive. ^{e} Reference 3c. ^{f} Reference 15.

B (see Table III). Both the IR and Raman bands shift when the experiment is repeated with $^{18}O_2$, indicating that B indeed contains oxygen. Although the Raman spectrum was necessarily recorded under adverse conditions (i.e., low laser power to avoid photolysis of the sample, and hence wide monochromator slits), it is clear that the IR and Raman bands of B are not coincident, again supporting the possibility of a centrosymmetric structure.

The IR absorption of B appears broad in Figure 4, but it actually consists of seven relatively sharp bands (Figure 5b, Table IV). These bands have the correct relative intensities for the naturally occurring isotopes[9] of Mo. The presence of this isotopic splitting means that the absorption is due to an Mo=O vibration and thus the O=O bond of the O_2 must have been broken during the photooxidation. The separation, 7.3 cm^{-1}, between the bands assigned to ^{92}Mo and ^{100}Mo is much larger than that predicted for a single Mo=O group, 4.5 cm^{-1} (Figure 5a), but approaches that of a linear O=Mo=O moiety, 8.0 cm^{-1} (Figure 5c). We can prove that B contains only *two* oxygen atoms by photooxidation of $Mo(CO)_6$ in a matrix containing a mixture of unscrambled $^{16}O_2$ and $^{18}O_2$ (i.e., no $^{16}O^{18}O$) (Figure 6). There are only two absorptions (both split by Mo isotopes) due to $Mo^{16}O_2$ and $Mo^{18}O_2$. A molecule containing three or more oxygen atoms would necessarily give rise to additional bands due to mixed $^{16}O/^{18}O$ species. The
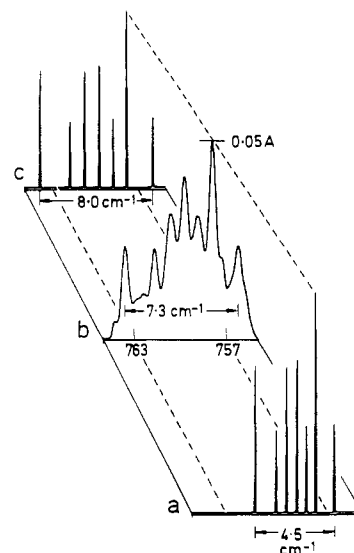
Figure 5. Observed and calculated Mo isotope structure in the IR absorption spectra of monooxo and dioxo species isolated in an O_2-doped CH_4 matrix at 20 K: (a) calculated isotope frequency pattern for a monooxo species assuming the Mo=O group to be a simple harmonic oscillator; (b) observed molybdenum isotope structure for the 757-cm^{-1} band of B; (c) isotope pattern for a linear dioxo species calculated by using eq 2 with $\theta_1/2 = 90°$. The calculated spectra are depicted as stick plots with heights given by the relative natural abundances of the molybdenum isotopes.[9]
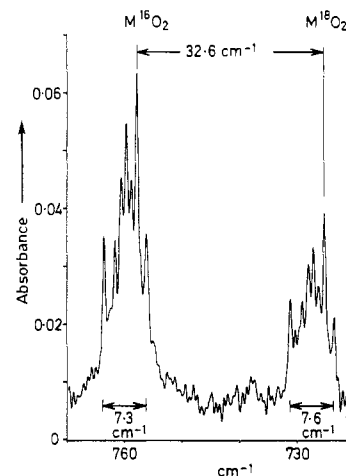
Figure 6. The 780–720-cm^{-1} region of the IR absorption spectrum obtained after photooxidation of a CH_4 matrix containing $Mo(CO)_6$ and doped with both $^{16}O_2$ and $^{18}O_2$. The two bands are assigned to $\nu_{as}(^{16}O=Mo=^{16}O)$ and $\nu_{as}(^{18}O=Mo=^{18}O)$. Both clearly exhibit molybdenum isotope structure.

Table IV. Wavenumbers (cm^{-1}) of the Antisymmetric OMO Stretching Vibration of Different Isotopomers of *trans*-$Mo(O)_2(CO)_4$ in $CH_4 + 10\%$ O_2 Matrices at 20 K

	$M^{16}O_2$	$M^{18}O_2$	$\Delta\nu^a$
^{92}Mo	763.6	731.2	32.4
^{94}Mo	761.7	729.2	32.5
^{95}Mo	760.6	728.1	32.5
^{96}Mo	759.7	727.3	32.4
^{97}Mo	758.9	726.4	32.5
^{98}Mo	757.9	725.3	32.6
^{100}Mo	756.3	723.6	32.7
$\Delta\nu^b$	7.3	7.6	

^{a} Wavenumber difference, $\nu(^{16}O_2) - \nu(^{18}O_2)$. ^{b} Maximum isotopic shift, $\nu(^{92}$Mo$) - \nu(^{100}$Mo$)$.

absence of any bands assignable to $^{16}OMo^{18}O$ in Figure 6 has considerable implications for the mechanism of the photooxidation, as noted below.

Table V. Comparison of the Observed and Calculated Shifts (cm^{-1}) on ^{18}O Substitution for the Linear O=M=O Antisymmetric and Symmetric Modes for the Isoelectronic Molecules Mo(O)$_2$(CO)$_4$, W(O)$_2$(CO)$_4$, and [Re(O)$_2$(CN)$_4$]$^{3-}$

	Mo(O)$_2$(CO)$_4$^{a}	W(O)$_2$(CO)$_4$^{a}	[Re(O)$_2$(CN)$_4$]$^{3-b}$
	Antisymmetric (IR)		
^{16}O$_2$	757.9	751.0	775.0
^{18}O$_2$	725.3	714.0	737.0
$\Delta\nu_{obsd}$ − $\Delta\nu_{calcd}$^{c}	0.2	0.5	−0.3
	Symmetric (Raman)		
^{16}O$_2$	820	850	879
^{18}O$_2$	775	805^d	832
$\Delta\nu_{obsd}$ − $\Delta\nu_{calcd}$^{e}	−2	−4	−3

^{a} This work; Mo frequencies given for ^{98}Mo. ^{b} Reference 24. ^{c} $\Delta\nu_{calcd}$ for the antisymmetric stretching fundamental is obtained from eq 1 with $\theta_u/2 = 90°$. Thus $R_1 = [m(^{16}O)[m(M) + 2(m(^{18}O))]]/[m(^{18}O)[m(M) + 2(m(^{16}O))]]$. ^{d} Reference 6. ^{e} For a linear O=M=O unit, the shift of the symmetric stretch on ^{18}O$_2$ substitution is obtained from the expression $\nu(^{16}O)/\nu(^{18}O) = [m(^{18}O)/m(^{16}O)]^{1/2}$ (Herzberg, G. "Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand: Princeton, NJ, 1945; p 187).

Thus, B contains *four* CO groups and *two* O atoms, i.e., Mo(O)$_2$(CO)$_4$. Since the IR absorption at 757 cm^{-1} shows isotopic splitting by Mo isotopes and since it is not coincident with the Raman band at 820 cm^{-1}, it must be due to an antisymmetric O=Mo=O stretching vibration. Its position is close to that expected for a *trans*-dioxo species, and this is supported by the IR and Raman frequencies of W(O)$_2$(CO)$_4$, which lie close to those of the isoelectronic and *stable* d^2 anion^{22} [Re(O)$_2$(CN)$_4$]$^{3-}$ (Table V). These analogies can be confirmed by a more quantitative analysis of the IR spectra of Mo(O)$_2$(CO)$_4$.

The isotopic shift in the frequency of bands in the M–O stretching region (Table IV), unlike those in the C–O stretching region, can be used to estimate bond angles. For the *harmonic* triatomic oscillator O=M=O, isotopic frequencies can be used to calculate an accurate value of the bond angle, but since the observed frequencies are necessarily anharmonic, the frequency shifts between different isotopomers give different calculated values of the bond angle.^{23,24} Thus, the frequencies $\nu(^{16}O_2)$ and $\nu(^{18}O_2)$ for the isotopic substitution
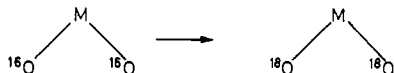
give an upper limit θ_u for the bond angle (eq 1), where $m(X)$

$$\sin\frac{\theta_u}{2} = \left[\frac{m(M)[m(^{16}O) - (m(^{18}O))R_1]}{2(m(^{16}O))(m(^{18}O))(R_1 - 1)}\right]^{1/2} \quad (1)$$

is the atomic mass of the appropriate atom and $R_1 = [\nu(^{18}O_2)/\nu(^{16}O_2)]^2$. Similarly, the isotopic substitution
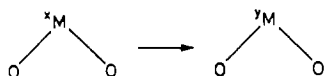
gives a lower limit, θ_1 (eq 2), where $R_2 = [\nu(^yM)/\nu(^xM)]^2$.

$$\sin\frac{\theta_1}{2} = \left[\frac{(m(^xM))(m(^yM))(1 - R_2)}{2(m(O))[R_2(m(^yM)) - m(^xM)]}\right]^{1/2} \quad (2)$$

(22) Howard-Lock, H. E.; Lock, C. J. L.; Turner, G. *Spectrochim. Acta, Part A* **1982**, *38A*, 1283.
(23) Allavena, M.; Rysnik, R.; White, D.; Calder, V.; Mann, D. E. *J. Chem. Phys.* **1969**, *50*, 3399. Maillard, D.; Allavena, M.; Perchard, J. P. *Spectrochim. Acta, Part A* **1975**, *31A*, 1523.
(24) For a recent example of the use of these formulas see: Green, D. W.; McDermott, D. P.; Bergman, A. *J. Mol. Spectrosc.* **1983**, *98*, 111.

Unfortunately, the calculated values of θ become increasingly sensitive to the precise value of the isotopic shift as the O=M=O molecule approaches linearity.^{18}

These equations apply rigorously only to *isolated* MO$_2$ species but appear also to give realistic bond angles for more complicated molecules (e.g., Mo(O)$_2$Br$_2$,^{10} Cr(O)$_2$(CO)$_2$,^{5} etc.).

Applying eq 1 and 2 to the frequencies of the bands in Figure 6, we obtain values^{25} for Mo(O)$_2$(CO)$_4$:

$$\theta_1 = 145^{+8}_{-7}° \qquad \theta_u = 168^{+5}_{-3}°$$

These values are consistent with our interpretation that B contains a linear O=M=O moiety, particularly if we consider that an isotopic shift only 0.2 cm^{-1} larger than the observed value gives $\theta_u = 180°$ (Table V). If this linear O=Mo=O group (10) is combined with the planar Mo(CO)$_4$ unit (9) already deduced from the ^{13}CO-enrichment experiments, we have the *trans*-dioxo octahedral structure (6) for product B.

Structure of A. At present it is not possible to assign an unambiguous structure to A. It must contain at least two CO groups as it has two ν_{C-O} IR absorptions. After photooxidation of ^{13}CO-enriched Mo(CO)$_6$, part of the spectrum due to A is unfortunately obscured by residual absorptions of unoxidized Mo(CO)$_6$. Nevertheless, it is clear from these spectra that A contains three or more CO groups.^{26} A probably contains an O$_2$ unit as it has an IR band at 954 cm^{-1}. Unfortunately, the IR band of the Mo compound at 954 cm^{-1} has no apparent Mo isotopic splitting, so we cannot easily distinguish between dioxo and peroxo groups. The most plausible structures for A are the Mo(O)$_2$(CO)$_3$ (11) and MoO$_2$(CO)$_4$ (12) species,
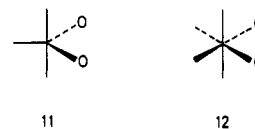
but experiments aimed at a more definite identification are still under way.^{11} IR bands similar to those of A are also observed^6 in the photooxidation of matrix-isolated Cr(CO)$_6$, presumably due to an intermediate in the formation of Cr(O)$_2$(CO)$_2$. Thus, the tricarbonyl structure (11) for A is attractive on mechanistic grounds as it could be a common precursor to both Cr(O)$_2$(CO)$_2$ and Mo(O)$_2$(CO)$_4$:
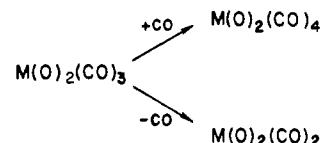

Discussion

Unlike Cr(O)$_2$(CO)$_2$, the major photooxidation product of matrix-isolated Cr(CO)$_6$, both Mo(O)$_2$(CO)$_4$ and W(O)$_2$(CO)$_4$ are coordinatively saturated 18-electron compounds, which could conceivably be stable near room temperature. The metals are presumably in a +IV oxidation state with a d^2 electronic configuration. Simple molecular orbital arguments predict that the trans isomer of d^2 M(O)$_2$(CO)$_4$ should be more stable than the cis isomer. The HOMO of the trans isomer (13) is stabilized by π interaction with four CO groups while the HOMO of the cis isomer (14) is stabilized by π interaction

(25) The standard errors of the bond angles were estimated by calculating bond angles for all possible isotopic shifts.
(26) It may be possible to avoid this problem of overlapping bands by carrying out the photooxidation experiments with a precursor like W(CO)$_5$·py as an alternative to W(CO)$_6$. The ν_{C-O} bands of W(CO)$_5$·py lie to lower frequency than those of W(CO)$_6$, and near-UV photolysis has been shown to lead to formation of W(CO)$_5$; see: Boxhoorn, G.; Oskam, A.; McHugh, T. M.; Rest, A. J. *Inorg. Chim. Acta* **1980**, *44*, L1.

13   14
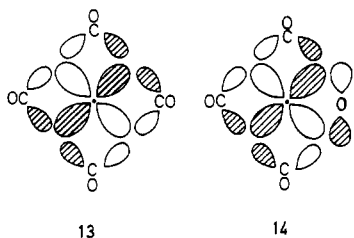
with only three CO groups and is *destabilized* by π interaction with the O atom. However, the relative stability of the trans isomer in our photooxidation experiments should not be taken as conclusive evidence for thermodynamic stability. It could merely be the result of fortuitously poor overlap between the emission of the Hg arc and the absorption bands of the trans isomer.

A detailed discussion of how $M(O)_2(CO)_4$ is formed from matrix-isolated $M(CO)_6$ must clearly await positive identification of the various intermediates, particularly A. Nevertheless, some conclusions can already be drawn about the mechanism. In the experiment where $M(CO)_6$ was photooxidized by a mixture of $^{16}O_2$ and $^{18}O_2$, *no* bands due to $M^{16}O^{18}O(CO)_4$ were observed (see Figure 6). This means that both O atoms in the $M(O)_2(CO)_4$ molecule must originate from the *same* O_2 molecule. However, the experiments also show that CO_2 is produced before significant quantities of $M(O)_2(CO)_4$ are observed. These two observations can be rationalized by assuming either (a) that formation of $M(O)_2(CO)_4$ requires *two* molecules of O_2, with some carbonyl-containing intermediate X

$$M(CO)_6 + O_2 \rightarrow X + 2CO_2$$

$$X + O_2 \rightarrow M(O)_2(CO)_4$$
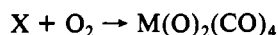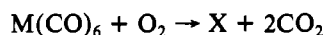
or (b) that formation of CO_2 and $M(O)_2(CO)_4$ are alternative pathways
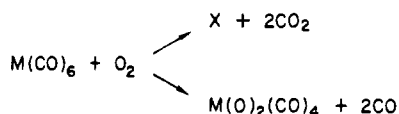
However, the first explanation seems less likely after an experiment in which the ratio of O_2 to CH_4 was reduced from 1:10 to 1:100 and the ratio of photogenerated CO_2 to $M(O)_2(CO)_4$ appeared to be unchanged. Thus, formation of $M(O)_2(CO)_4$ from $M(CO)_6$ probably involves only one molecule of O_2.

$M(O)_2(CO)_4$ is destroyed by further UV photolysis, eventually producing metal oxide species, but it is not yet clear whether this loss of CO is caused by excitation of d → d or O → M charge-transfer transitions.

Conclusions

Our experiments have shown that photooxidation of $M(CO)_6$ proceeds via the formally 18e compound *trans*-$M(O)_2(CO)_4$. Recent experiments, particularly in liquefied noble gases, have shown that coordinatively saturated compounds, first prepared in matrices at 20 K, are often much more stable than originally supposed. Thus, $Cr(CO)_5N_2$, formed by photolysis of $Cr(CO)_6$ in the presence of N_2, is stable at −35 °C in liquid xenon solution.[27] The possibility that $Mo(O)_2(CO)_4$ and $W(O)_2(CO)_4$ are stable at temperatures substantially higher than 20 K should therefore be given serious consideration.

Registry No. $Mo(CO)_4$, 44780-98-5; $Mo(^{12}CO)_3(^{13}CO)$, 91444-03-0; *cis*-$Mo(^{12}CO)_2(^{13}CO)_2$, 91444-00-7; *trans*-$Mo(^{12}CO)_2(^{13}CO)_2$, 91547-49-8; $Mo(^{12}CO)(^{13}CO)_3$, 91444-01-8; $Mo(^{13}CO)_4$, 91444-02-9; $Mo(O)_2(CO)_4$, 91444-04-1; $W(O)_2(CO)_4$, 91444-05-2; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; O_2, 7782-44-7; $^{18}O_2$, 32767-18-3; ^{13}CO, 1641-69-6.

(27) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B., II; Graham, M. A. *Inorg. Chem.* **1983**, *22*, 911.