

The most likely alternative to our previously suggested internal flip mechanism for the $\alpha \rightarrow \beta$ interconversion would be a process in which one or both of the ligands would break at least one of their M–P bonds. It seems to us that for any process of the latter type, two predictions could be made. (1) It would not proceed cleanly in the solid state. (2) If such a process occurred in solution, it is likely that the presence of a large excess of dppe would affect the rate of isomerization, probably in the sense of retarding it. On the other hand, for the internal flip mechanism, isomerization would be possible in the solid state, and in solution the presence of excess dppe should have no influence on the rate. Experimental tests have been carried out relating to both of these points.

When green α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$ was heated under static vacuum at 250 °C it was converted completely and without decomposition to brown β - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$, as monitored by the color change and by the infrared spectrum (Figure 1) of the product after 2 days of heating. If dissociation and recombination of dppe ligands were required for isomerization to occur, it seems extremely unlikely that such a clean, quantitative conversion would occur. The fact that isomerization occurs by a flip mechanism in the solid does not, of course, require that this be the only mechanism for isomerization in solution.

In CH_2Cl_2 solution, as shown in Figures 6 and 7, the first-order conversion of the α - to the β -isomer and the approach to equilibrium are quantitatively the same in the presence of a 20-fold molar excess of dppe and in the absence of any added dppe. Clearly, any mechanism entailing the initial dissociation of an entire dppe molecule is ruled out. In addition, it would seem unlikely that even a process in which only one end of one dppe or only one Cl^- ligand would have to come adrift to initiate the process could fail to be retarded by the presence of so much dppe in the environment, since the vacancy created by this initial dissociation would be promptly filled by a dppe molecule to give either $\text{Mo}_2\text{Cl}_4(\text{dppe})_3$ or $\text{Mo}_2\text{Cl}_3(\text{dppe})_3$, which would be unable to contribute to the isomerization process.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Registry No. α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2 \cdot \text{OC}_4\text{H}_8$, 99531-95-0; α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$, 64490-77-3.

Supplementary Material Available: Tables of displacement parameters, structure factors, and complete bond lengths and angles (14 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England, and Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England

Peroxo and Dioxo Metal Carbonyl Intermediates in the Photooxidation of Matrix-Isolated $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) in the Presence of Dioxygen: A Vibrational Spectroscopic Study Using ^{18}O

Matthew J. Almond,^{1a} Joseph A. Crayston,^{1b,c} Anthony J. Downs,^{*1a} Martyn Poliakoff,^{*1b} and James J. Turner^{*1b}

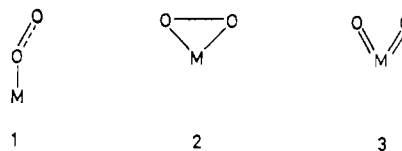
Received June 5, 1985

The photolysis of $\text{M}(\text{CO})_6$ molecules ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) isolated in O_2 -doped Ar or CH_4 matrices at 10–20 K has been monitored by reference to the IR, Raman, and UV-visible spectra of the matrices. These spectra indicate that the oxidation of $\text{M}(\text{CO})_6$ to binary oxide molecules like MO_2 ($\text{M} = \text{Cr}, \text{Mo}$) and MO_3 ($\text{M} = \text{Mo}, \text{W}$) proceeds via four oxo-carbonyl intermediates, A–D. B has already been shown to be a *trans*-dioxo metal tetracarbonyl, $\text{M}(\text{O})_2(\text{CO})_4$ ($\text{M} = \text{Mo}, \text{W}$). Isotopic enrichment with ^{18}O indicates that (i) A is a peroxo-metal species, $(\eta^2\text{-O}_2)\text{M}(\text{CO})_x$, where x is probably 4 and the molecular symmetry C_{2v} , (ii) C is a dioxo metal carbonyl, $\text{M}(\text{O})_2(\text{CO})_y$, where y is probably 3, and (iii) D is a dioxo metal dicarbonyl, $\text{M}(\text{O})_2(\text{CO})_2$ (the Cr version of which has been characterized previously). Hence we propose a unified reaction scheme for the matrix photooxidation of all three metal hexacarbonyls. Differences in behavior stem in part from differences in the photolability of the intermediates, but the intermediate $\text{Cr}(\text{O})_2(\text{CO})_2$, D, is favored under conditions where Mo and W favor the 18e species *trans*- $\text{M}(\text{O})_2(\text{CO})_4$, B.

Introduction

There is intense interest in finding transition-metal catalysts for the selective oxidation of organic substrates.² One of the few successful autoxidation processes is the epoxidation of ethylene catalyzed by Ag. For a selective catalyst, it is desirable that both dioxygen and the substrate should bind reversibly to the transition-metal center so that oxidation of the substrate can take place. In order to probe the types of *unstable* dioxygen complexes that may be active catalytic intermediates, coordinatively unsaturated metal complexes have been allowed to react with dioxygen and the products immobilized in low-temperature matrices. For example, matrix cocondensation of metal atoms³ with O_2 gives rise to molecules that may emulate some of the different types of active centers created by adsorption of O_2 on a metal surface. Matrix experiments have also revealed a wide range of metal– O_2 interactions in the adducts that O_2 forms with metalloporphyrins.⁴

Such matrix products derived from thermal reactions of O_2 are typically metal–dioxygen complexes involving either η^1 coordination (superoxo, 1) or η^2 coordination (peroxo, 2) of the O_2 ligand.



A different picture emerges from sputtering experiments involving matrix trapping of the species generated when a stream of dioxygen enters the discharge region of a hollow metal cathode: the IR spectra of these species suggest that they are not metal–dioxygen compounds but that the O–O bond has been ruptured to form binary metal oxide molecules, e.g., 3.⁵

Unfortunately, partial aggregation of the unsaturated metal centers is an unavoidable complication in many of these cocondensation experiments. Hence we have favored a different technique for generating the metal centers that overcomes this problem. Our technique involves UV photolysis of a metal car-

(1) (a) University of Oxford. (b) University of Nottingham. (c) Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

(2) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

(3) (a) Huber, H.; Klotzbücher, W.; Ozin, G. A.; Vander Voet, A. *Can. J. Chem.* **1973**, *51*, 2722. (b) Tevault, D. E.; Smardzewski, R. R.; Urban, M. W.; Nakamoto, K. *J. Chem. Phys.* **1982**, *77*, 577.

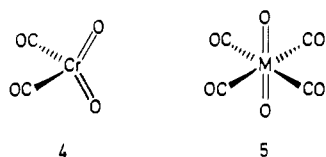
(4) Watanabe, T.; Ama, T.; Nakamoto, K. *J. Phys. Chem.* **1984**, *88*, 440.
(5) Green, D. W.; Ervin, K. M. *J. Mol. Spectrosc.* **1981**, *89*, 145.

Table I. Wavenumbers (cm^{-1}) of $\nu(\text{C—O})$ IR and Raman Bands of O_2 -Containing Metal Carbonyl Intermediates^f

intermediate	$\text{Cr}^{a,b}$		Mo^b		W	
	IR	IR	R	IR ^c	R ^b	
A	2128 vw 2062.1 m, sh 2027.5 ms 2007.4 m	2133 w 2064.2 ms 2016.3 ms 1996 m	<i>d</i> 2060 m 2008 w, sh <i>d</i>	<i>d</i> 2053 m 2007 m <i>d</i>	<i>d</i> 2058 m 2006 ms <i>d</i>	
$\text{M}(\text{O})_2(\text{CO})_4$ (B)	<i>d</i> <i>d</i>	<i>e</i> 2110.05	2175 <i>e</i>	<i>e</i> 2096	2160 <i>e</i>	
C	2108 w 2050 m	2106 w 2025 m	<i>a</i> <i>a</i>	2091 m 1998 m	<i>a</i> <i>a</i>	
$\text{M}(\text{O})_2(\text{CO})_2$ (D)	<i>a</i> ₁ <i>b</i> ₁	2123 m, br 2041 m, br	<i>d</i> <i>d</i>	2112 m, br 2018 m, br	2115 sh <i>d</i>	

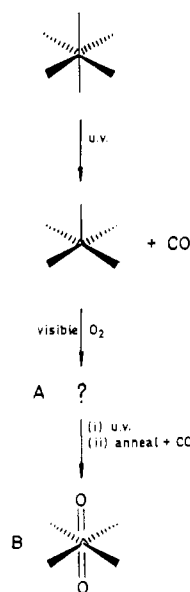
^a Raman spectra of these species could not be obtained because of photosensitivity under the exciting radiation. ^b CH_4/O_2 matrix; IR bands $\pm 0.5 \text{ cm}^{-1}$, Raman bands $\pm 5 \text{ cm}^{-1}$. ^c Ar/O_2 matrix. ^d Not observed due to weakness or overlap with other bands. ^e Inactive. ^f Abbreviations: w, weak; m, medium; s, strong; sh, shoulder, br, broad.

bonyl complex isolated in an O_2 -doped matrix. In this way we generate a 16-electron fragment which may then react with O_2 . Thus, we have shown that UV photolysis of $\text{Cr}(\text{CO})_6$ in the presence of O_2 gives rise to $\text{Cr}(\text{O})_2(\text{CO})_2$ (4) as the major product,⁶ while similar photolysis of $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ produces⁷ several species including the *trans*-dioxo metal tetracarbonyl $\text{M}(\text{O})_2(\text{CO})_4$ ($\text{M} = \text{Mo}, \text{W}$; 5).



These oxo-metal species are of interest because they may be akin to those involved in the Mo-SiO_2 heterogeneous catalysts used in olefin epoxidation⁸ and metathesis reactions.² The $\text{M}(\text{O})_2(\text{CO})_4$ species are coordinatively saturated compounds, and we have alluded⁷ to the possibility that they may survive in the liquid phase at temperatures substantially higher than 20 K. Since the submission of our earlier manuscript,⁷ there have been reports that oxo metal carbonyl anions of the type $[\text{M}(\text{CO})_x(\text{O})_y]^-$ exist in the gas phase⁹ and that O_2 reacts with $(\eta^5\text{-Me}_5\text{C}_5)\text{Re}(\text{CO})_2$ - (THF) to form the curious trioxo complex $(\eta^5\text{-Me}_5\text{C}_5)\text{Re}(\text{O})_3$.¹⁰ WO has recently been detected as one of the products arising from UV flash photolysis of a gaseous $\text{W}(\text{CO})_6\text{-O}_2$ mixture.¹¹

Our earlier experiments^{6,7} did not provide a detailed understanding of the mechanism of photooxidation. In the absence of further information, we rationalized our results on the basis of Scheme I. In this paper we describe new results derived from experiments aimed at a fuller elucidation of the steps of the reaction. In particular, we have concentrated on determining when the cleavage of the O—O bond occurs. Our strategy has involved three stages: (i) narrow-band UV-vis photolysis combined with a careful study of the $\nu(\text{C—O})$ region of the IR spectrum of assess the number of the intermediates appearing in the photooxidation process; (ii) a study of the relatively weak absorptions in the region $1000\text{--}700 \text{ cm}^{-1}$ that develop with photolysis and that are associated with coordinated oxygen to determine their assignment to the different intermediates; (iii) the use of $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ to find out how the oxygen is bonded in each intermediate. In this way we have observed that the peroxo-metal complex $(\eta^2\text{-O}_2)\text{M}(\text{CO})_x$

Scheme I

($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; x is probably 4) is formed initially and that UV photolysis results in rupture of the O—O bond to produce dioxo metal carbonyls $\text{O}_2\text{M}(\text{CO})_y$ ($y = 2\text{--}4$). Finally we propose a unified reaction scheme for all three metals.

Experimental Section

The experiments were carried out in accordance with procedures described elsewhere.^{7,12,13} Although the spectra illustrated in this paper were all recorded at Nottingham on a Nicolet 7199 FTIR interferometer (32K data points, 256K transform points, and 0.5-cm^{-1} resolution), most of the IR spectra relating to the photooxidation of $\text{W}(\text{CO})_6$ were recorded at Oxford on a Perkin-Elmer Model 580A dispersive spectrophotometer (0.5-cm^{-1} resolution and accuracy). All the Raman studies were carried out at Oxford, the spectra being excited at 5145 \AA by means of a Spectra-Physics Model 165 Ar^+ laser and recorded on a Spex Ramalog 5 spectrometer (typically $2\text{--}6\text{-cm}^{-1}$ resolution and accuracy). UV-vis spectra were recorded on Perkin-Elmer Lambda 5 (Nottingham) and Perkin-Elmer 330 (Oxford) spectrophotometers.

Matrix gases (Messer Griesheim or BOC Grade X), ^{13}CO and $^{18}\text{O}_2$ (BOC Prochem), $\text{Cr}(\text{CO})_6$ (BDH or Ventron Alfa Products), $\text{Mo}(\text{CO})_6$ (BDH or Ralph N. Emmanuel), and $\text{W}(\text{CO})_6$ (Koch-Light) were used without further purification. The isotopically scrambled O_2 was prepared by using a new procedure developed by Appelman¹⁴ and taking advantage of the fact that the fluoroxy sulfate anion, SO_4F^- , transfers one oxygen atom quantitatively to H_2O to form H_2O_2 and subsequently oxidizes the H_2O_2 to O_2 .

- (6) Poliakoff, M.; Smith, K. P.; Turner, J. J.; Wilkinson, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 651.
 (7) Crayston, J. A.; Almond, M. J.; Downs, A. J.; Poliakoff, M.; Turner, J. J. *Inorg. Chem.* **1984**, *23*, 3051.
 (8) Iwasawa, Y.; Nakamura, T.; Takamatsu, K.; Ogasawara, S. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 939.
 (9) Lane, K.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 2719.
 (10) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313.
 (11) Samoilova, A. N.; Efremov, Yu. M.; Gurvich, L. V. *J. Mol. Spectrosc.* **1981**, *86*, 1.

- (12) Crayston, J. A. Ph.D. Thesis, University of Nottingham, 1984.
 (13) Almond, M. J. D.Phil. Thesis, University of Oxford, 1984.
 (14) Appelman, E. H., unpublished results. Appelman, E. H.; Basile, L. J.; Thompson, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 3384.

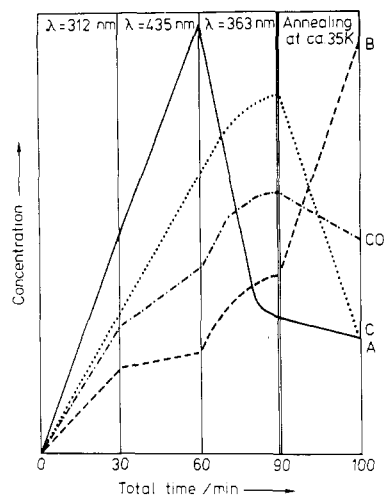


Figure 1. Plots showing changes in the concentrations of the species A, B, C, and free CO during photolysis at different wavelengths and annealing of $\text{W}(\text{CO})_6$ isolated in a CH_4 matrix doped with O_2 at 20 K. The concentrations were deduced from integrated IR absorbance measurements made on spectra recorded at 0, 30, 60, 70, 80, 90, and 100 min. The wavenumbers (cm^{-1}) of the bands used to estimate the concentrations were as follows: A, 2053; B, 2096; C, 1998; CO, 2140.

Table II. Wavenumbers (cm^{-1}) of the Low-Frequency Bands of A^a

	Cr	Mo	W
$^{16}\text{O}_2$	995.2	954	914
$^{16}\text{O}^{18}\text{O}$	<i>b</i> (966.0)	929.1 (927.1)	899 ^c (888.2)
$^{18}\text{O}_2$	<i>b</i> (937.1)	899 (899.4)	<i>b</i> (861.7)
$\Delta(^{16}\text{O}_2, ^{18}\text{O}_2)$	- (56.9)	55 (54.6)	- (52.3)
ρ^d	- (0.98)	0.91 (0.98)	- (0.99)

^a Calculated frequencies in parentheses. Calculations are based on a diatomic harmonic oscillator. ^b Predicted to lie beneath strong MO_2 bands. ^c Tentative assignment. ^d Asymmetry parameter as defined in the text (eq 2).

Results and Discussion

Observation of New Intermediates in the Matrix Photooxidation of $M(\text{CO})_6$. Our previous experiments⁷ with Mo and W demonstrated two successive intermediates A and B. By using more selective and controlled photolysis and annealing, we have now found another oxygen-containing intermediate, C.¹⁵ The three intermediates are formed and decay in the sequence $\text{A} \rightarrow \text{C} \rightarrow \text{B}$ (see Figure 1). In addition we have also found a fourth intermediate, D, which is also formed from C and which, for Mo and W, has IR bands with frequencies and relative intensities similar to those of $\text{Cr}(\text{O})_2(\text{CO})_2$. A similar, careful study of the photooxidation of matrix-isolated $\text{Cr}(\text{CO})_6$ has revealed the formation of Cr analogues of the intermediates A and C. All $\nu(\text{C}-\text{O})$ data are collected in Table I. Before considering these $\nu(\text{C}-\text{O})$ bands of A, C, and D in any detail, we examine the low-frequency region of the spectra to determine in which intermediates the O—O bond has been cleaved.

Low-Frequency Region (750–1100 cm^{-1}). (i) **IR Spectrum of A.** The data for the Cr, Mo, and W versions of A are given in Table II. The Mo version has given the fullest results, and so we discuss these in some detail. The IR spectrum in Figure 2a was measured after irradiation of $\text{Mo}(\text{CO})_6$ isolated in a CH_4 matrix containing $^{16}\text{O}_2$ and $^{18}\text{O}_2$ in roughly equimolar proportions. The band at 954 cm^{-1} associated with A (Table II) shifts on ^{18}O substitution to 899 cm^{-1} and so must arise from the motion of at least one oxygen atom. A similar experiment using a mixture of all three isotopomers, in the approximate proportions $^{16}\text{O}_2 : ^{16}\text{O}^{18}\text{O} : ^{18}\text{O}_2 = 1:2:1$, gave an IR spectrum (Figure 2b, Table II) including the symmetrical triplet $954, 929, \text{ and } 899 \text{ cm}^{-1}$. Such

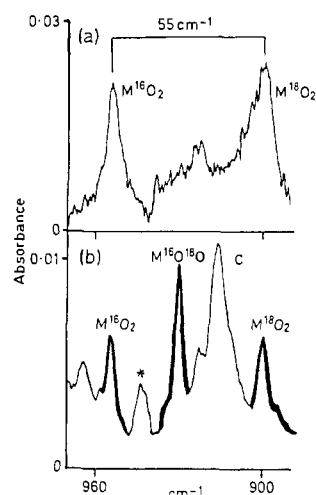


Figure 2. ^{18}O isotopic spectra of the low-frequency IR band due to intermediate A(Mo): (a) photolysis (2 min, unfiltered Hg arc) of $\text{Mo}(\text{CO})_6$ in a CH_4 matrix containing $\sim 1:1$ $^{16}\text{O}_2 : ^{18}\text{O}_2$; (b) photolysis of $\text{Mo}(\text{CO})_6$ in a matrix containing $^{16}\text{O}_2 : ^{16}\text{O}^{18}\text{O} : ^{18}\text{O}_2$ in the approximate ratio 1:2:1. Other bands are due to MoO_2 (*) and C.

Table III. Wavenumbers (cm^{-1}) of O—O and M=O Stretching Vibrations of MO_2 Species with Asymmetry Parameters, ρ

	$\nu(\text{O}-\text{O})$			ρ	ref
	$^{16}\text{O}_2$	$^{16}\text{O}^{18}\text{O}$	$^{18}\text{O}_2$		
	Peroxo $\nu(\text{O}-\text{O})$				
$\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}(\text{O}_2)^a$	858	834	810	1.00	<i>c</i>
$\text{Ni}(t\text{-BuNC})_2(\text{O}_2)^a$	898	873	848	1.00	17
$\text{Pt}(\text{PPh}_3)_2(\text{O}_2)^a$	828	805.5	782	0.98	<i>d</i>
LiO_2^b	1097	1067	1035	0.97	23
NiO_2^b	966	940	914	1.00	3a
$\text{Fe}(\text{TPP})\text{O}_2^b$	1195	1162	1122	0.97	4
	Dioxo $\nu(\text{M}=\text{O})$				
MoO_2 ($\theta = 110^\circ$) ^b	905.6	875.5	864.6	1.47	23
WO_2 ($\theta = 119^\circ$) ^b	937.2	901.2	899.8	1.52	5
SnO_2 (linear) ^b	863.1	847.2	824.7	0.83	<i>e</i>
CeO_2 ($\theta = 146^\circ$) ^b	736.8	714.8	708.3	1.71	<i>f</i>
UO_2 (linear) ^b	776.1	771.1	737.1	0.23	22

^a Room temperature. ^b Matrix. ^c Horn, R. W.; Weissberger, E.; Collman, J. P. *Inorg. Chem.* **1970**, *9*, 2367. ^d Andrews, L. *J. Chem. Phys.* **1969**, *50*, 4288. ^e Bos, A.; Ogden, J. S. *J. Phys. Chem.* **1973**, *77*, 1513. ^f Gabelnick, S. D.; Reedy, G. T.; Chasanov, M. G. *J. Chem. Phys.* **1974**, *60*, 1167.

a pattern argues that the vibration involves *two* equivalent O atoms and rules out the possibility that the absorption originates in the M=O stretching mode of a monooxo-molybdenum group. Similarly the $^{16}\text{O}_2$ - $^{18}\text{O}_2$ isotopic shift of 55 cm^{-1} is substantially in excess of that predicted ($\sim 45 \text{ cm}^{-1}$) for an isolated M=O oscillator. The presence of two equivalent O atoms in A is consistent with the results described in our earlier papers^{6,7} relating to the species that arise from the reaction of a single molecule of O_2 with a group VI (6)³³ metal center; it is consistent too with O_2 concentration studies.¹³ As we have pointed out elsewhere,^{6,7} the absence of a $\nu(^{16}\text{O}^{18}\text{O})$ band in the $^{16}\text{O}_2$ - $^{18}\text{O}_2$ experiment (Figure 2a) implies that O_2 is neither dissociating prior to coordination at the metal center nor undergoing scrambling with another O_2 molecule once it is coordinated.

There are three possible models for the MO_2 moiety in A: (a) a superoxo-metal unit, $(\eta^1\text{-O}_2)\text{M}$, as in 1; (b) a peroxo-metal unit, $(\eta^2\text{-O}_2)\text{M}$, as in 2; (c) a dioxo-metal unit, $\text{O}=\text{M}=\text{O}$, as in 6.



(15) Although C is an intermediate in the conversion of A to B, we have chosen not to reflect this sequence by relabeling the three intermediates alphabetically. Instead, we use labels consistent with those adopted in our previous paper.⁷

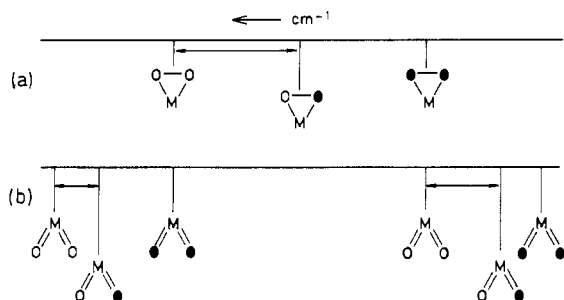


Figure 3. Predicted ^{18}O isotopic splitting patterns in the IR spectra of (a) the $\nu(\text{O}-\text{O})$ band of a dioxygen complex and (b) the $\nu_{\text{as}}(\text{M}=\text{O})$ and $\nu_{\text{as}}(\text{M}=\text{O})$ bands of a bent dioxometal complex, assuming a scrambled 1:2:1 $^{16}\text{O}_2$: $^{16}\text{O}^{18}\text{O}$: $^{18}\text{O}_2$ mixture (O = ^{16}O , ● = ^{18}O). The horizontal arrows in (a) and (b) indicate that $\Delta\nu(^{16}\text{O}_2 - ^{16}\text{O}^{18}\text{O})$ wavenumber spacing which is equal to the $\Delta\nu(^{18}\text{O}_2 - ^{16}\text{O}^{18}\text{O})$ spacing in (a) but not in (b).

Table III summarizes $^{16}\text{O}_2$ and $^{18}\text{O}_2$ data for a number of established compounds containing MO_2 moieties. The table shows that superoxo-metal units are characterized by a $\nu(^{16}\text{O}-^{16}\text{O})$ stretching frequency in the range 1200–1050 cm^{-1} and peroxy-metal units by a frequency in the range 950–800 cm^{-1} , whereas dioxo-metal units are characterized by $\text{M}=\text{O}$ stretching frequencies in the range 1000–750 cm^{-1} . In principle, it should also be possible to distinguish between a *side-on*-bonded species such as **2** and an *end-on*-bonded species such as **1** on the basis of whether $\text{M}^{16}\text{O}^{18}\text{O}$ exhibits one or two distinct O—O stretching modes: in practice, the difference in energy between the two modes of the *end-on*-bonded species may be too small to be detected.¹⁶ A dioxo-metal unit should have two infrared-active $\text{M}=\text{O}$ stretching modes unless it is linear (cf. **5**), although in practice the symmetric stretching mode is usually only weak in infrared absorption. It follows that the $^{16}\text{O}_2$ band of A at 954 cm^{-1} is most probably due to a peroxy-metal, **2**, or a dioxo-metal group, **6**. Substitution with ^{18}O provides two criteria for distinguishing between a band due to O—O stretching, $\nu(\text{O}-\text{O})$, as in **2**, and one due to antisymmetric $\text{M}=\text{O}$ stretching, $\nu_{\text{as}}(\text{M}=\text{O})$, as in **6**.

(a) First, if one supposes that the observed band is due to $\nu_{\text{as}}(\text{M}=\text{O})$ of a dioxo-metal species, then the $\nu(^{18}\text{O}_2)/\nu(^{16}\text{O}_2)$ ratio, R , allows an estimate of an *upper* limit, θ_u , to the O—M—O bond angle (eq 1). The upper limit to the bond angle calculated in

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

this way for the Mo version of A is an *unlikely* 20°, effectively eliminating the dioxo possibility. By contrast, the $\nu(^{18}\text{O}_2)/\nu(^{16}\text{O}_2)$ ratio for $\nu(\text{O}=\text{O})$ of a peroxy-metal group can be predicted well by neglecting coupling with $\nu(\text{M}-\text{O})$ and treating the O—O ligand as a diatomic oscillator^{12,17} (Table III). This predicted ratio is 0.9428, close to the observed value of 0.942 for the Mo version of A.

(b) Second, we derive crucial support for the presence of a peroxy group in A from the observation that the $\nu(^{16}\text{O}-^{18}\text{O})$ band is *symmetrically* disposed between $\nu(^{16}\text{O}_2)$ and $\nu(^{18}\text{O}_2)$ (Figure 2b) as predicted by a simple harmonic model. A useful measure of the asymmetry of the $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}/^{18}\text{O}_2$ band pattern is the *asymmetry parameter*, ρ , defined by eq 2. A symmetrical pattern

$$\rho = \frac{2[\nu(^{16}\text{O}^{18}\text{O}) - \nu(^{18}\text{O}_2)]}{\nu(^{16}\text{O}_2) - \nu(^{18}\text{O}_2)} \quad (2)$$

has $\rho = 1$. As can be seen from Table III, ρ is close to unity for typical dioxygen complexes. This behavior contrasts with the

Table IV. Trends in O—O Stretching Frequency (cm^{-1}) and O—O Bond Length (\AA) for Transition-Metal Complexes

Cr, Mo, W			
	$\nu(\text{O}-\text{O})$		$\nu(\text{O}-\text{O})$
$\text{Cr}(\text{O}_2)(\text{CO})_4$	995.2	$\text{W}(\text{O}_2)(\text{CO})_4$	914.0
$\text{Mo}(\text{O}_2)(\text{CO})_4$	954.0		
Co, Rh, Ir ^{b,c}			
	$L'_2 = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$		$L' = \text{AsMePh}_2$
	$\nu(\text{O}-\text{O})$	$d(\text{O}-\text{O})$	$\nu(\text{O}-\text{O})$
$[\text{CoL}'_4(\text{O}_2)]^+$	909	1.42	<i>c</i>
$[\text{RhL}'_4(\text{O}_2)]^+$	<i>c</i>	1.42	852
$[\text{IrL}'_4(\text{O}_2)]^+$	845	1.63	838
Ni, Pd, Pt ^b			
	$L = \text{PPh}_3$		$L = t\text{-BuNC}$
	$\nu(\text{O}-\text{O})$	$d(\text{O}-\text{O})$	$\nu(\text{O}-\text{O})$
$\text{NiL}_2(\text{O}_2)$	<i>c</i>		893
$\text{PdL}_2(\text{O}_2)$	875	1.37	893
$\text{PtL}_2(\text{O}_2)$	822	1.43	<i>c</i>

^a This work. ^b Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235. ^c Obscured or too weak to be observed.

unsymmetrical $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}/^{18}\text{O}_2$ pattern with $\rho \neq 1$ generally observed for the $\nu_{\text{as}}(\text{M}=\text{O})$ mode of dioxo complexes (Table III). The reasons for the unsymmetrical pattern are illustrated in Figure 3. Irrespective of whether the two oxygen atoms form a peroxy-**(2)** or a dioxo-metal group **(6)**, introduction of $^{16}\text{O}^{18}\text{O}$ lowers the local symmetry from C_{2v} to C_s and allows mixing between modes previously belonging to different symmetry classes. In the case of the peroxy structure, this coupling is likely to be relatively small since the other modes are energetically well removed from $\nu(\text{O}-\text{O})$ and so $\nu(^{16}\text{O}-^{18}\text{O})$ is almost exactly halfway between $\nu(^{16}\text{O}-^{16}\text{O})$ and $\nu(^{18}\text{O}-^{18}\text{O})$ (Figure 3a). In a dioxo-metal group, however, there is likely to be substantial coupling between the two $\text{M}-\text{O}$ stretching fundamentals of $\text{M}^{16}\text{O}^{18}\text{O}$ so that $\nu(\text{M}=\text{O})$ appears at energies significantly shifted from the mean values $1/2[\nu_{\text{s}}(\text{M}=\text{O}) + \nu_{\text{s}}(\text{M}=\text{O})]$ and $1/2[\nu_{\text{as}}(\text{M}=\text{O}) + \nu_{\text{as}}(\text{M}=\text{O})]$ derived from the symmetrical C_{2v} species M^{16}O_2 and M^{18}O_2 . Where the positions of both $\nu(\text{M}=\text{O})$ modes have been located, it is evident that the coupling has the effect of causing mutual repulsion between the modes of $\text{M}^{16}\text{O}^{18}\text{O}$ (Figure 3b).

Our experiments have shown that the $\nu(^{16}\text{O}-^{18}\text{O})$ band of A(Mo) (Figure 2b, Table II) corresponds to $\rho = 0.98$, lending persuasive support to the view that A is a peroxy-metal **(2)** and not a dioxo-metal **(6)** derivative. It was unfortunate therefore that IR bands due to other species masked one or more of the $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ bands associated with the Cr and W versions of A. However, the results with $^{16}\text{O}_2$ imply that $\nu(\text{O}-\text{O})$ of A decreases in the order $\text{Cr} > \text{Mo} > \text{W}$. A similar trend is displayed by those few peroxy systems that permit a group comparison by allowing the ligand environment to be held constant while the metal is changed (Table IV). Since there must be some mixing between $\nu(\text{O}-\text{O})$ and $\nu(\text{M}-\text{O})$, part of this trend may be due to the effect of increased metal mass on the G-matrix elements. It is likely, however, that the trend reflects also changes in O—O bond length (Table IV), which depend in turn on the degree of charge transfer to dioxygen.^{4,18}

Thus, we conclude that the addition of O_2 to the unsaturated d^6 center gives as the first identifiable species A, a peroxy metal carbonyl. Such a product is not totally unprecedented. For example, the major product formed on cocondensation of Co atoms with $\text{CO}-\text{O}_2$ mixtures is believed to be a peroxy cobalt carbonyl complex, tentatively formulated as $(\text{O}_2)\text{Co}(\text{CO})_4$.¹⁹

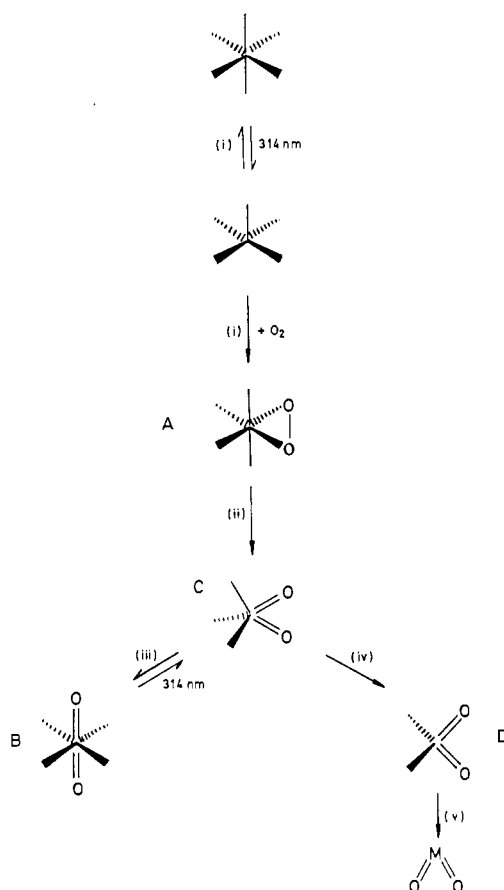
(ii) **IR Spectrum of C.** The changes in the low-frequency region of the IR spectrum accompanying the generation of intermediate

(16) See for example: Darling, J. H.; Garton-Sprenger, M. B.; Ogden, J. S. *Faraday Symp. Chem. Soc.* **1973**, *8*, 75. A similar problem arises with group VI-dinitrogen derivatives: Burdett, J. K.; Downs, A. J.; Gaskill, G. P.; Graham, M. A.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 523.

(17) Nakamura, A.; Tatsuno, Y.; Yamamoto, M.; Otsuka, S. *J. Am. Chem. Soc.* **1971**, *93*, 6052.

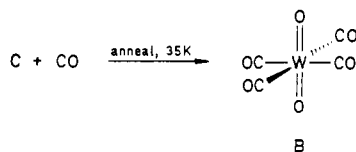
(18) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1.

(19) Ozin, G. A.; Lee Hanlan, A. J.; Power, W. J. *Inorg. Chem.* **1979**, *18*, 2390.

Scheme II^a

^a Legend: (i) Cr, 544 nm; Mo, 403 nm; W, 435 nm. (ii) Cr, W, 367 nm; Mo, 314 nm. (iii) Mo and W only; Mo, 403 nm or anneal at 35 K; W, anneal at 35 K. (iv) Cr, 314 nm or anneal at 35 K; Mo, W, 314 nm. (v) Cr, Mo, W (?), 314 nm; W tentative because bands due to WO_2 may be obscured.

C from A were seen most clearly during the matrix photooxidation of $\text{W}(\text{CO})_6$ giving the fullest IR data (Table V); the buildup of the Cr and Mo analogues was restricted, it appeared, by their greater photosensitivity under the conditions used to promote the conversion of A to C (see Scheme II). Photolysis of the W version of A at wavelengths near 367 nm resulted in the appearance of two IR absorptions, at 962.5 and 901.0 cm^{-1} , which showed the same growth characteristics at the $\nu(\text{C}-\text{O})$ absorption associated with C (Table I) and which shared the same decay behavior when the matrix was annealed at 35 K. Absorbance measurements indicated that annealing resulted in the conversion of C to B, with the consumption of CO (Figure 1):



Thermal CO recombination reactions of this sort are often encountered in matrices containing unsaturated metal carbonyl fragments,²⁰ and here the recombination has implications about the number of coordinated CO groups in C (see below). In this section we are concerned with the mode of ligation of the oxygen in C. We believe that C is the dioxo metal carbonyl $M(\text{O})_2(\text{CO})_3$ for three reasons.

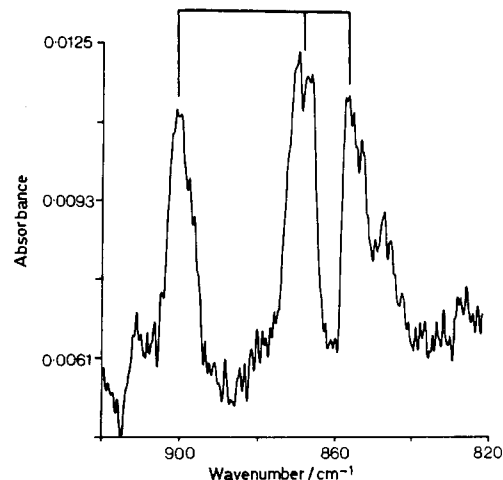


Figure 4. Low-frequency region of the IR spectrum of the intermediate C(W) showing the ^{18}O isotopic pattern. (The spectrum was recorded after successive 30 min at 314 nm, 30 min at 432 nm, and 10 min at 367 nm photolysis of $\text{W}(\text{CO})_6$ in a CH_4 matrix doped with 10% O_2 having the isotopic composition $^{16}\text{O}_2:^{16}\text{O}^{18}\text{O}:^{18}\text{O}_2 = \text{ca. } 3:1:1$.)

Table V. Observed and Calculated ^{18}O Isotopic Shifts (cm^{-1}) of the Low-Frequency Bands of C(Mo,W)

	Mo obsd ^a	W	
		obsd ^a	calcd ^b
$\nu_s (\nu_1)$	$^{16}\text{O}_2$	962.5	962.0
	$^{16}\text{O}^{18}\text{O}$	941.9	944.1
	$^{18}\text{O}_2$	914 (?)	907.6
$\nu_{as} (\nu_3)$	$^{16}\text{O}_2$	881	901.0
	$^{16}\text{O}^{18}\text{O}$	869.6	869.7
	$^{18}\text{O}_2$	841	856.7

^a $\text{CH}_4\text{-O}_2$ matrix. ^b Using an $\text{O}=\text{W}=\text{O}$ bond angle of 152° and $f_r = 761 \text{ N m}^{-1}$ and $f_{rr} = 103 \text{ N m}^{-1}$.

(a) Indirect support for the presence of an $\text{O}=\text{M}=\text{O}$ group in C comes from the observation that the $\nu(\text{C}-\text{O})$ modes of C (Table I) occur at higher energies than those of the peroxy metal carbonyl A, indicating a metal center in C that is more highly oxidized than that in A.

(b) It is hardly likely that the thermal energies available to the matrix through annealing at temperatures up to 35 K are sufficient to break the $\text{O}-\text{O}$ bond of a coordinated dioxygen ligand. Since C takes up CO at low thermal energies to generate B, which contains a linear $\text{O}=\text{M}=\text{O}$ unit, it is likely that rupture of the $\text{O}-\text{O}$ bond has also occurred in C.

(c) Crucial support for the dioxo moiety and elimination of the peroxy possibility comes from the behavior of the low-frequency bands of C on ^{18}O enrichment. If both the low-frequency bands shift when ^{16}O is replaced by ^{18}O , then the bands can arise only from a dioxo-metal group. Although the ^{18}O analogue of the weaker band at 962.5 cm^{-1} was partially obscured by absorption due to other species, the isotopic shift of both bands was clear. Furthermore, by using a mixture of the isotopomers $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$ (in the proportions $^{16}\text{O}_2:^{16}\text{O}^{18}\text{O}:^{18}\text{O}_2 = \text{ca. } 3:1:1$), we were able to show that the feature at 901 cm^{-1} produced the unsymmetrical pattern ($\rho = 0.58$) characteristic of the antisymmetric stretching vibration of a dioxo-metal group (compare Figure 4 with Figure 3b). The isotopic shifts (Table V) lead via eq 1 to upper estimates of bond angles: $152 \pm 5^\circ$ for $\text{O}=\text{W}=\text{O}$ and $160 \pm 10^\circ$ for $\text{O}=\text{Mo}=\text{O}$. We can use the value of $\nu(^{16}\text{O}^{18}\text{O})$ for the W species to calculate approximate $\text{W}=\text{O}$ stretching force constants of $f_r = 761 \text{ N m}^{-1}$ and $f_{rr} = 103 \text{ N m}^{-1}$. On the basis of these parameters, we predict^{12,21} an intensity ratio of 3.3:1 for the absorptions arising from the antisymmetric and symmetric stretching vibrations, in reasonable agreement with the observed value of 3.0:1. However, uncertainties in the mea-

(20) See for example the following: Burdett, J. K.; Turner, J. J. "Cryochemistry"; Moskovits, M., Ozin, G. A., Eds.; Wiley-Interscience: New York, 1976; p 493. Turner, J. J.; Burdett, J. K.; Perutz, R. N.; Poliakov, M. *Pure Appl. Chem.* **1977**, *49*, 271. Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1.

(21) Ogden, J. S. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, *86*, 832.

Table VI. Wavenumbers (cm^{-1}) of IR and Raman Bands Associated with Species D, $\text{M}(\text{O})_2(\text{CO})_2$, in the Low-Frequency Region.

assignt	$\text{Cr}(\text{O})_2(\text{CO})_2^a$		$\text{Mo}(\text{O})_2(\text{CO})_2^b$		$\text{W}(\text{O})_2(\text{CO})_2^b$	
	IR	R	IR	R	IR	R
$\nu_{\text{as}}(^{16}\text{O}=\text{M}=\text{O})$	981		834	837	825.9	834
$\nu_{\text{as}}(^{16}\text{O}=\text{M}=\text{O})$	974		806	c	798.6	c
$\nu_{\text{as}}(^{18}\text{O}=\text{M}=\text{O})$	944		798	c	786.0	c
	$\text{Cr}(\text{O})_2(\text{CO})_2$	$\text{Mo}(\text{O})_2(\text{CO})_2$	$\text{W}(\text{O})_2(\text{CO})_2$			
ρ^d	0.38	1.60	1.37			
O=M=O bond angle, $^\circ$ deg	129	150	~160			

^a Reference 6; Ar matrix (no Raman measurements possible because of the photosensitivity of $\text{Cr}(\text{O})_2(\text{CO})_2$). ^b This work; CH_4 matrix. ^c Not observed. ^d Asymmetry parameter, see text. ^e Upper limit based on eq 1.

sured intensities of the IR bands illustrated in Figure 4 precluded attempts to exploit the method described by Gabelnick et al.²² to analyze the intensities of all the bands observed in this region of the spectrum.

(iii) IR Spectrum of D. Although the species $\text{Cr}(\text{O})_2(\text{CO})_2$ contains a dioxo-metal group, only one of the $\text{Cr}=\text{O}$ stretching modes was sufficiently intense to be observed⁶ in IR absorption during photooxidation of matrix-isolated $\text{Cr}(\text{CO})_6$. Similar results have now been observed on photooxidation of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$. The intermediate D produced by UV photolysis of C was characterized by only one low-frequency band (Table VI), which was observed to shift on $^{18}\text{O}_2$ substitution by only 36 cm^{-1} ($\text{M} = \text{Mo}$) and 39.9 cm^{-1} ($\text{M} = \text{W}$). This shift is substantially smaller than predicted for a peroxy group (48 cm^{-1}), but the results for the tungsten species are consistent with a dioxo-metal group having an $\text{O}=\text{W}=\text{O}$ angle not exceeding $160 \pm 10^\circ$ (eq 1). The presence of a dioxo group was again confirmed by the unsymmetrical band pattern observed after photolysis of $\text{W}(\text{CO})_6$ in a matrix doped with a mixture of the isotopomers $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$ (see Figure 5a). This spectrum can be simulated, as shown in Figure 5b, with use of a bond angle of 160° and the $\text{W}=\text{O}$ stretching force constants $f_t = 651 \text{ N m}^{-1}$ and $f_{\text{tr}} = 101 \text{ N m}^{-1}$.^{12,21} No allowance was made in these calculations for significant intensity "borrowing" between $\nu_s(^{16}\text{O}=\text{W}=\text{O})$ and $\nu_{\text{as}}(^{16}\text{O}=\text{W}=\text{O})$.²² A similar pattern was observed for the Mo version of D (Table VI). The surprisingly low frequencies of the $\nu_{\text{as}}(\text{O}=\text{M}=\text{O})$ vibrations in the Mo and W versions of D, compared to that of $\text{Cr}(\text{O})_2(\text{CO})_2$, are largely a consequence of increased O-M-O bond angles (see Table VI).

In many respects the Mo and W versions of D are analogous to "chromyl carbonyl" (4).⁶ All three occupy identical positions in the photolysis scheme (Scheme II), and all three are dioxo-metal complexes with highly unsymmetrical $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}/^{18}\text{O}_2$ band patterns, with the ρ values listed in Table VI. It may be remarked that ρ is in the opposite sense for "chromyl carbonyl" because for dioxo derivatives of first-row transition metals ν_{as} is higher in frequency than ν_s .

Number of CO Groups in A, C, and D. On the evidence of the number of unambiguously assigned $\nu(\text{C}-\text{O})$ bands (Table I), the intermediates A, C, and D must contain the following *minimum* numbers of CO groups: A, ≥ 3 ; C, ≥ 2 ; D, ≥ 2 . In addition, changes of absorbance associated with free CO show that (a) the concentration of free CO *increases* when A is formed from $\text{M}(\text{CO})_5$ and O_2 and (b) the concentration of free CO *decreases* when the *trans*-dioxo metal tetracarbonyl B⁷ is formed from C. The conditions leading to the buildup of A, involving irradiation of the matrix with visible light (see Figure 1 and Scheme II), must also favor the consumption of free CO by the competing reaction²⁰



This makes the observed *increase* in free CO all the more striking,

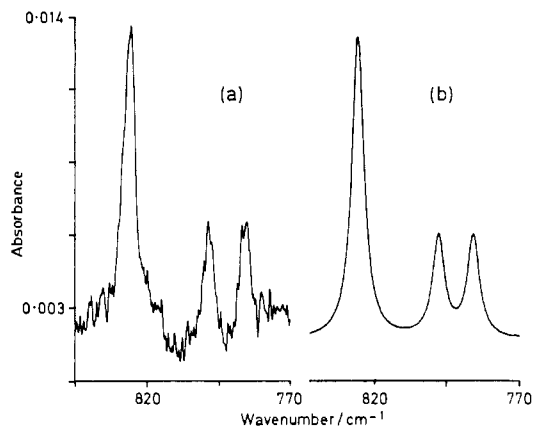
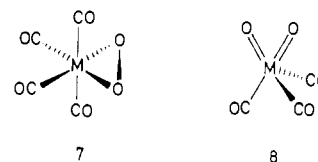


Figure 5. (a) Observed IR spectrum of intermediate D(W) showing the ^{18}O isotopic pattern of the low-frequency band. This was obtained after photolysis of $\text{W}(\text{CO})_6$ in a CH_4 matrix doped with 10% O_2 having the isotopic composition $^{16}\text{O}_2/^{16}\text{O}^{18}\text{O}/^{18}\text{O}_2 = \text{ca. } 3:1:1$. (b) Simulated spectrum using an $\text{O}=\text{W}=\text{O}$ bond angle of $\sim 160^\circ$ and the force constants $f_{\text{W}=\text{O}} = 651 \text{ N m}^{-1}$ and $f_{\text{W}=\text{O},\text{W}=\text{O}} = 101 \text{ N m}^{-1}$ and assuming no coupling between $\nu_s(^{16}\text{O}=\text{W}=\text{O})$ and $\nu_{\text{as}}(^{16}\text{O}=\text{W}=\text{O})$.²²

leading us to conclude that A must contain fewer than five CO groups. The conversion of C to B occurs when the matrix is annealed (q.v.) and seems not to be accompanied by any other reaction. Accordingly, we deduce that free CO is consumed by C to form the tetracarbonyl B and that C therefore contains fewer than four CO groups.

Attempts to confirm the stoichiometry and geometry of the $\text{M}(\text{CO})_x$ fragments in A and C by using ^{13}CO enrichment were inconclusive because many of the bands of the products were obscured by residual absorptions of $\text{M}(\text{CO})_6$ or uncoordinated ^{13}CO . However, the IR spectra of ^{13}CO -enriched A were incompatible with the presence of a tricarbonyl moiety.¹² Thus, we are led finally (Scheme II) to infer that A is a peroxy metal tetracarbonyl, possibly with C_{2v} symmetry as in 7; this view receives



support from the observation of a weak $\nu(\text{C}-\text{O})$ absorption near 2130 cm^{-1} in the IR spectrum of the Cr and Mo versions of A, bringing the total number of $\nu(\text{C}-\text{O})$ bands to four. In the case of C, the mean frequency and relative intensity of the two $\nu(\text{C}-\text{O})$ bands are more characteristic of a tricarbonyl (e.g., 8) than of a di- or tetracarbonyl species.¹²

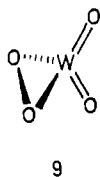
The similarity already noted between the Mo and W versions of D and $\text{Cr}(\text{O})_2(\text{CO})_2$ extends to the $\nu(\text{C}-\text{O})$ region. Thus the Mo and W compounds display the same number of IR-active $\nu(\text{C}-\text{O})$ modes as $\text{Cr}(\text{O})_2(\text{CO})_2$ with similar frequencies and relative intensities. However, attempts to confirm that D is $\text{M}(\text{O})_2(\text{CO})_2$ ($\text{M} = \text{Mo}, \text{W}$) by using ^{13}CO -enriched $\text{M}(\text{CO})_6$ were thwarted by the fact that the yield of the Mo and W compounds was substantially lower than that of $\text{Cr}(\text{O})_2(\text{CO})_2$, making the IR bands too weak.

Binary Oxide Products and Mechanistic Details. Prolonged UV photolysis resulted ultimately in elimination of all the coordinated CO groups and production in one form or another of the binary oxide species MO_2 ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and MO_3 ($\text{M} = \text{Mo}, \text{W}$). There is close agreement between the IR bands we ascribe to CrO_2 and MoO_2 and the most prominent features²³ of the same molecules prepared in the absence of any matrix dopant. By contrast, the tungsten oxide species had an IR band at 899 cm^{-1} , about 38 cm^{-1} lower in energy than the $\nu_{\text{as}}(\text{W}=\text{O})$ mode of WO_2 isolated

(22) Gabelnick, S. D.; Reedy, G. T.; Chasanov, M. G. *J. Chem. Phys.* **1973**, *5*, 4468.

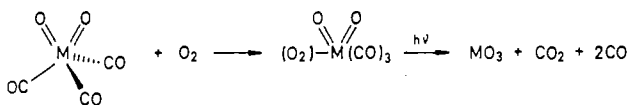
(23) Hewett, W. D., Jr.; Newton, J. H.; Weltner, W., Jr. *J. Phys. Chem.* **1975**, *79*, 2640. Serebrennikov, L. V.; Mal'tsev, A. A. *Vestn. Mosk. Univ., Ser 2: Khim.* **1975**, *16*, 251.

in an Ar matrix.^{5,13} This tungsten oxide species also had a second band centered at 872 cm^{-1} . The results of our experiments using different O_2 isotopomers are consistent¹³ with the assignment of the band at 899 cm^{-1} to $\nu_{\text{as}}(\text{W}-\text{O})$ of a WO_2 unit (with $\theta_u = \text{ca. } 122^\circ$) and of that at 872 cm^{-1} to $\nu(\text{O}-\text{O})$ of a peroxy group in a molecule such as **9**, analogous to SO_4 , which has been generated

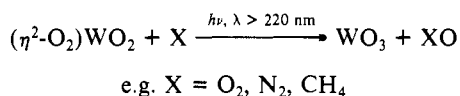


9

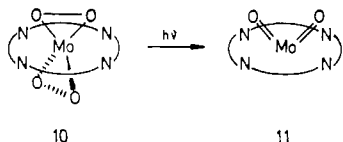
in an argon matrix by the reaction of O atoms with SO_3 .²⁴ The final reaction product MO_3 must arise through the incorporation of a further atom of oxygen. A possible path involves the reaction of a second molecule of O_2 with a coordinatively unsaturated dioxo-metal species such as C, D, or even MO_2 , e.g.



That oxygen atom transfer takes place in the later stages of the UV photooxidation of $\text{W}(\text{CO})_6$ is shown by scavenging experiments employing reactive matrices, e.g., O_2 (giving O_3), N_2 (giving N_2O), and CH_4 (giving CH_3OH and $\text{H}_2\text{C}=\text{O}$).^{13,25} The results suggest that $(\eta^2-\text{O}_2)\text{WO}_2$ (**9**) is the principal precursor to this transfer:



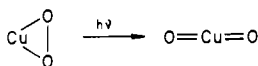
The majority of peroxo complexes appear on photolysis to undergo O_2 loss or oxidation of the auxiliary ligands.¹⁸ However, a reaction analogous to $\text{A} \rightarrow \text{C}$ has been noted for the diperoxo molybdenum porphyrin complex **10**, which is converted to the



10

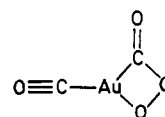
11

cis-dioxo molybdenum complex **11** on irradiation.²⁶ Similarly the formation of the linear CuO_2 molecule²⁷ is now believed²⁸ to proceed via photolysis of the peroxo complex initially present in a matrix formed by cocondensation of Cu atoms with O_2 :



Finally, it must be admitted that our experiments do not provide any new insights into the mechanism for CO_2 production on prolonged UV irradiation or annealing of the matrix.⁷ We note that CO_2 does not appear to be formed directly from **A**, since **A** and $\text{M}(\text{CO})_5$ are unaffected by annealing. Certainly there was no sign of the $\nu(\text{C}-\text{O})$ band of a peroxoformate similar to the

carbonyl gold(II) derivative **12** produced, it is thought,²⁹ on co-



12

condensation of gold atoms with mixtures of CO and O_2 . That CO_2 has the capacity to play an active role in the matrix photooxidation of $\text{M}(\text{CO})_6$ molecules ($\text{M} = \text{Cr}, \text{W}$) is indicated by the identification of the complex $\text{CO}_2 \cdots \text{M}(\text{CO})_5$ in an Ar or CH_4 matrix;³⁰ UV photolysis of this complex causes dissociation of the coordinated CO_2 ligand with the formation of CO and oxo metal carbonyl intermediates like **B**. However, there is as yet little information about the mode of coordination of the CO_2 to the metal center of the complex.

Conclusions

Scheme II presents a mechanism that accounts for the formation of all the oxygen-containing metal carbonyl species reported in this and previous papers.^{6,7} The nature of the MO_2 bonding in each intermediate has now been confirmed by ^{18}O substitution.

The first step is photolysis of $\text{M}(\text{CO})_6$ to form the coordinatively unsaturated C_{4v} molecule $\text{M}(\text{CO})_5$, which, on visible irradiation, react with O_2 with the displacement of a further molecule of CO to form **A**, the peroxo complex $\text{M}(\eta^2-\text{O}_2)(\text{CO})_4$. We have observed weak UV absorption of **A** centered at 380 nm ($\text{M} = \text{Mo}$) or 355 nm ($\text{M} = \text{W}$), corresponding possibly to an LMCT ($\text{O}_2, \pi^* \rightarrow d\sigma$ charge transfer) transition.³¹ Irradiation into this band of the peroxo complex cleaves the O—O bond to give the dioxo-metal complex **C**, thus completing the oxidation of M^{II} to M^{IV} . On UV irradiation, **C** can undergo further decarbonylation to give the dioxo metal dicarbonyl $\text{M}(\text{O})_2(\text{CO})_2$, **D**, and finally the binary dioxide MO_2 . Alternatively, **C** can take up CO on annealing to give the *trans*-dioxo metal tetracarbonyl species **B**.⁷ This process involves only M—CO bond formation and is typical of the thermal reactions of unsaturated metal carbonyl fragments.²⁰

Formation of the dioxo metal tetracarbonyl **B** is favored by Mo and W but not by Cr, which gives as the primary intermediate the dioxo metal dicarbonyl $\text{Cr}(\text{O})_2(\text{CO})_2$. This greater tendency of oxidized Cr to form lower carbonyls is reminiscent of the observation that photochemically generated $\text{Cr}(\text{CO})_5$ reacts in solution with the electron acceptor phenanthroquinone (PQ) to yield $\text{M}^{\text{I}}(\text{CO})_2(\text{PQ})_2$, whereas $\text{Mo}(\text{CO})_5$ and $\text{W}(\text{CO})_5$ react in similar circumstances to yield $\text{M}^{\text{I}}(\text{CO})_4(\text{PQ})$ as the major product.³²

Acknowledgment. We thank the SERC for supporting this research and for funding studentships for M.J.A. and J.A.C. We are grateful to Dr. E. H. Appelman for his help in preparing isotopic O_2 and to Dr. R. N. Perutz for his help and criticism.

Registry No. $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{Mo}(\text{CO})_6$, 13939-06-5; $\text{W}(\text{CO})_6$, 14040-11-0; $\text{Cr}(\text{O})_2(\text{CO})_4$, 94136-92-2; $\text{Mo}(\text{O})_2(\text{CO})_4$, 91444-04-1; $\text{W}(\text{O})_2(\text{CO})_4$, 91444-05-2; $\text{Cr}(\text{O})_2(\text{CO})_2$, 82345-85-5; $\text{Mo}(\text{O})_2(\text{CO})_2$, 99546-45-9; $\text{W}(\text{O})_2(\text{CO})_2$, 99546-46-0; O_2 , 7782-44-7.

(29) Huber, H.; McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 975.

(30) Almond, M. A.; Downs, A. J.; Perutz, R. N. *Inorg. Chem.* **1985**, *24*, 275.

(31) Lever, A. B. P.; Ozin, G. A.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 1823.

(32) Weir, D.; Wan, J. K. S. *J. Organomet. Chem.* **1981**, *220*, 323.

(33) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. **A** and **B** notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

(24) Kugel, R.; Taube, H. *J. Phys. Chem.* **1975**, *79*, 2130.

(25) Almond, M. J.; Downs, A. J., unpublished results.

(26) Ledon, H.; Bonnet, M.; Lallemand, J.-Y. *J. Chem. Soc., Chem. Commun.* **1979**, 702.

(27) (a) Ozin, G. A.; Mitchell, S. A.; Garcia-Prieto, J. *J. Am. Chem. Soc.* **1983**, *105*, 6399. (b) Tevault, D. E. *J. Chem. Phys.* **1982**, *76*, 2859.

(28) Bondybej, V. E.; English, J. H. *J. Phys. Chem.* **1984**, *88*, 2247.