Production of Binary Oxides by Photolysis of $M(CO)_6$ Molecules (M = Cr, Mo, or W) isolated in O_2-doped Argon Matrices

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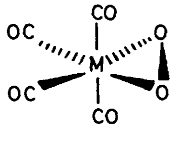
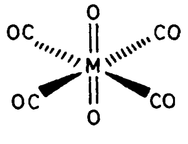
Oxides of the metals chromium, molybdenum, and tungsten have been generated by u.v. photolysis of O_2-doped argon matrices containing $[M(CO)_6]$ molecules (M = Cr, Mo, or W) at *ca.* 20 K. In addition to CO and CO_2, produced irrespective of the nature of M, the final products of photolysis are MO_2 (M = Cr) and MO_3 (M = Mo and W). The MO_3 molecules are produced from another metal oxide species, (**X**), and studies involving ^{18}O substitution for the tungsten version suggest that (**X**) is a peroxide $(\eta^2\text{-}O_2)WO_2$. U.v. photolysis of (**X**) yields MO_3 and O atoms in the excited ^1D state. The presence of the $O(^1D)$ atoms is demonstrated by experiments in which O_3 is produced in pure dioxygen matrices, N_2O in O_2-doped dinitrogen matrices, and CH_3OH and $H_2C{=}O$ in O_2-doped methane matrices.

Recent studies carried out partly at Nottingham[1–3] and partly in this Laboratory[2,3] have shown that photolysis of $[M(CO)_6]$ molecules (M = Cr, Mo, or W) isolated in an O_2-doped inert matrix at 10—20 K results in the release of CO and CO_2 and oxidation of the metal to the binary oxide. The vibrational spectrum of such a matrix signals that a photo-oxidation entails the intermediacy of four oxo-carbonyl species (**A**)—(**D**).


(**A**)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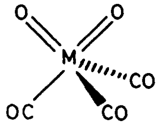
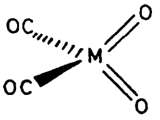
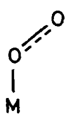
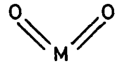

(**C**)


(**D**)

The mechanism of the reaction and the characterization of the intermediates provided the primary focus of these earlier experiments. The oxo-carbonyl intermediates evoke interest because they may be akin to the active agents generated by heterogeneous catalysts like Mo–SiO_2 and MoO_{3-x}–TiO_2–$SnMe_4$ used in olefin epoxidation[4a] and metathesis[4b,c] reactions. Oxo derivatives of metals like Ru co-ordinated by porphyrin or polypyridyl ligands have also been invoked as active catalysts in the epoxidation of olefins and other reactions involving selective oxidation of organic substrates.[4d] Similarly, monoxo and dioxo complexes of molybdenum have been shown to cause oxidation–reduction reactions of various substrates,[4e] thereby acting as models for the 'oxo-transferase' enzymes. Furthermore, alkanes larger than methane are oxidized by the ion CrO^+ in the gas phase;[4f] for example, ethane is oxidized to ethanol. For a catalyst selectively to promote the reaction of dioxygen with a substrate, it is desirable that both O_2 and the substrate should bind reversibly to the metal centre. The attraction of matrix isolation is that it offers a means of exploring the response of O_2 to a co-ordinatively unsaturated metal centre. According to the conditions, the O–O bond may be retained[5] with the formation of a metal–dioxygen complex involving either *O*-co-ordination (**1**) or *O,O'*-co-ordination (**2**) of the O_2 ligand, or it may be ruptured[6,7] with the formation of a dioxometal moiety (**3**). A full understanding of the characters and interrelationship of the different units (**1**)—(**3**) is likely to hold the mechanistic key to oxidation reactions of O_2.


(**1**)


(**2**)


(**3**)

The earlier experiments[1–3] on the matrix photo-oxidation of $[M(CO)_6]$ molecules paid little attention to the ultimate stages whereat none of the CO remains co-ordinated to the metal. In this paper we describe the characterization and photochemistry of the final products, mainly with reference to the case where M = W. We have drawn on the results of experiments with $^{18}O_2$ and $^{16}O^{18}O$ to assist the identification of the binary metal oxides. Hence we have established that the final photoproducts, in addition to CO and CO_2, are MO_2 (M = Cr) and MO_3 (M = Mo or W). The tungsten system affords an intermediate believed to be a peroxo derivative $(\eta^2\text{-}O_2)WO_2$ which, under the action of u.v. radiation, functions as a source of WO_3 and oxygen atoms. When the matrix is composed of molecules X capable of reacting with oxygen atoms, the photoproducts include molecules of the type XO, where X = O_2, N_2, or CH_4. There is evidence too, with CH_4 as the matrix, that W=O bonds are photolabile with respect to oxidation of CH_3OH to $H_2C{=}O$. The results of our experiments naturally invite comparisons with those in which metal atoms have been co-condensed with O_2 in an inert matrix. Not only do our experiments shed new light on the photochemistry of some of the binary metal oxide molecules, they are less susceptible to the complications of partial aggregation of metal atoms or other unsaturated metal centres.

Experimental

The experiments were carried out in accordance with procedures described elsewhere.[2,3] An Air Products Displex CS 202B closed-cycle refrigerator gave window temperatures of *ca.* 20 K inside a shroud maintained at a pressure below 10^{-7} Torr

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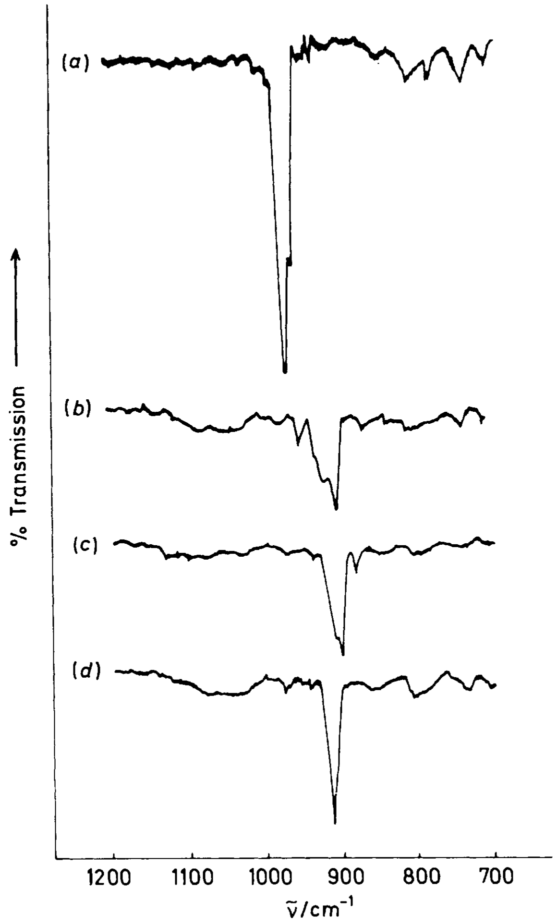


Figure 1. Infrared transmission spectra showing the products generated on prolonged photolysis of argon matrices initially containing $^{16}O_2$ and $[M(CO)_6]$ molecules (M = Cr, Mo, or W) in the approximate proportions $Ar:O_2:[M(CO)_6]$ = 2 000:100:1. (*a*) M = Cr, after unfiltered photolysis for 5 h; (*b*) M = Mo, after unfiltered photolysis for 2.5 h; (*c*) M = W, after unfiltered photolysis for 0.5 h; and (*d*) M = W, the same matrix as in spectrum (*c*) after unfiltered photolysis for 2.5 h

(*ca.* 1.33×10^{-5} Pa). Matrices were invariably formed by pulsed deposition.[8] I.r. spectra were recorded with a Perkin-Elmer model 580A or 225 spectrophotometer, affording a resolution and accuracy not exceeding 0.5 cm^{-1}.

The matrix gases Ar, N_2, $^{16}O_2$, and CH_4 were used as supplied by B.O.C. (grade 'X'), as were $Cr(CO)_6$ (B.D.H. or Ventron Alfa Products), $Mo(CO)_6$ (B.D.H. or Ralph N. Emmanuel), and $W(CO)_6$ (Koch-Light). Samples of $^{18}O_2$ were also used as received from B.O.C. Prochem. Isotopically scrambled O_2 was prepared either by the reaction of KSO_4F with ^{18}O-enriched water,[9] or by the addition of a high-frequency electric discharge on a mixture of $^{16}O_2$ and $^{18}O_2$ followed by u.v. photolysis *via* a quartz window to bring about decomposition of the ozone thus formed.

Either a Philips HPK-125 W medium-pressure mercury arc or a Hanova Uvitron high-pressure mercury arc was used for u.v. photolysis in conjunction, when appropriate, with the following filters: (*i*) a quartz cell (25 mm) containing either Cl_2 ($200 < \lambda < 280$ nm) or Br_2 ($220 < \lambda < 360$ nm), or (*ii*) two cells in tandem, one containing a saturated solution of $CoSO_4$ and the other a saturated solution of $NiSO_4$ ($220 < \lambda < 370$ nm).

Table 1. Wavenumbers (cm^{-1}) of i.r. bands due to the binary metal oxides MO_2 (M = Cr or Mo) and MO_3 (M = Mo or W) isolated in argon matrices

M = Cr		M = Mo		M = W		
This work[a]	Previous work[b]	This work[a]	Previous work[c]	This work[a]	Previous work[d]	Assignment
971 964 [e]	978	894	890	*f*	937	ν_3 MO_2
f	*f*	945	945	*f*	975	ν_1 MO_2
f	*f*	920[g]	921	914	918	ν_3 MO_3

[a] Wavenumbers ±1 cm^{-1}. [b] Ref. 18. [c] Ref. 6. [d] Ref. 7. [e] Matrix-split band. [f] Shoulder. [g] Not observed.

Table 2. Observed and calculated wavenumbers of the bands associated with the isotopomers $W^{16}O_x{}^{18}O_{3-x}$ (x = 0—3)

Origin	Observed[a]	Calculated[b]
$W^{16}O_3 + W^{16}O_2{}^{18}O$	914	918
$W^{16}O^{18}O_2$	893	892
$W^{16}O_2{}^{18}O$	883	881
$W^{18}O_3 + W^{16}O^{18}O_2$	873	873

[a] Wavenumbers observed ±1 cm^{-1}. [b] Wavenumbers calculated, see ref. 7.

Results

Production of WO_3.—Prolonged u.v. irradiation of an argon matrix containing $[W(CO)_6]$ and O_2 with the composition $Ar:O_2:[W(CO)_6]$ = *ca.* 2 000:100:1 caused the gradual disappearance of i.r. bands attributable to the stretching vibrations of co-ordinated CO groups. When all trace of co-ordinated CO groups had been lost, the i.r. spectrum retained, in addition to the bands due to free CO[10] and CO_2,[11] a number of bands in the region 800—1 000 cm^{-1} the most likely source of which are the stretching fundamentals of one or more binary tungsten oxides. After exposure of the matrix to the unfiltered emission of a medium-pressure mercury arc for 0.5 h, the principal feature in this part of the spectrum was an absorption close to 900 cm^{-1} [Figure 1(*c*)]. This does not coincide with any feature of the known oxide molecules WO, WO_2, or WO_3, the i.r. characteristics of which have been established in earlier matrix experiments with Ar as the matrix gas.[7] Accordingly we assign the new absorption to a hitherto unknown tungsten oxide derivative (**X**). Continued broad-band u.v. irradiation of the matrix for a further 2 h caused the band to decay and give way to a broad absorption centred at 914 cm^{-1} [Figure 1(*d*), Table 1], corresponding closely in energy to the most intense i.r. absorption of WO_3 isolated in an argon matrix.[7]

When this experiment was repeated using an argon matrix doped with a mixture of 57% $^{16}O_2$ and 43% $^{18}O_2$, broad-band u.v. photolysis gave rise ultimately to the i.r. spectrum illustrated in Figure 2. Hence it appears that the singlet at 914 cm^{-1} has now given way to a *quartet* with components at 914, 893, 883, and 873 cm^{-1}. The multiplicity and energies reproduce closely the results reported previously[7] for the fundamental $\nu_3(e')$ of WO_3 with partial enrichment in ^{18}O to give all four of the isotopomers $W^{16}O_x{}^{18}O_{3-x}$ (x = 0—3) in appreciable abundance (see Table 2). There is, however, one noteworthy difference in our experiments in that the two central features of the quartet, which arise exclusively from the mixed isotopomers $W^{16}O^{18}O_2$ and $W^{16}O_2{}^{18}O$, were significantly *weaker* than expected in relation to the two outer features which arise only partially from these species. This can be explained on the assumption that the WO_3 molecules are derived from a WO_2 unit in which *both* oxygen atoms originate in the same O_2

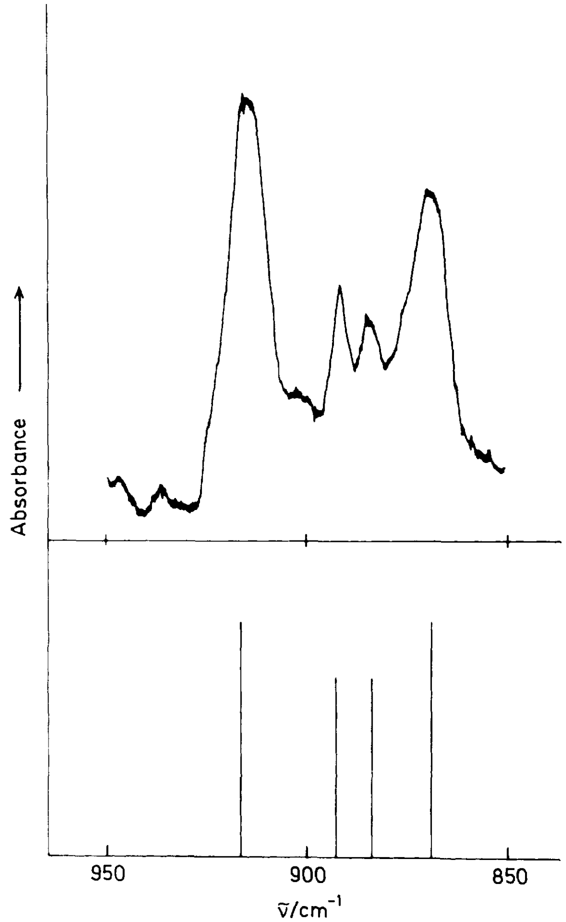
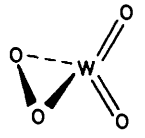


Figure 2. Observed and calculated i.r. absorption spectra for the isotopomers $W^{16}O_x{}^{18}O_{3-x}$ (x = 0—3). Observed spectrum: WO_3 generated by prolonged unfiltered u.v. irradiation of a matrix initially composed of $[W(CO)_6]$, $^{16}O_2$, $^{18}O_2$, and Ar in the approximate proportions 1:57:43:2 000. Calculated spectrum: see ref. 7

molecule. Such a premise is in keeping with our previous findings that the two oxygen atoms of the oxometal carbonyl intermediates (**A**)—(**D**) invariably originate in a common O_2 molecule.[2,3]

The precursor to WO_3 in our experiments is (**X**), but the i.r. spectrum of (**X**) does not tally with that of matrix-isolated WO_2 as characterized previously.[7] The most obvious inference we can draw is that (**X**) is a derivative of WO_2 in which the vibrations of the WO_2 unit are perturbed by co-ordination to some other species present in the matrix. The most obvious candidate for the co-ordinating species is O_2.

Identity of the Unknown Species (**X**).—The i.r. spectrum of (**X**), as generated in a $^{16}O_2$-doped argon matrix, was marked by a broad region of absorption consisting of a band centred at 902 cm⁻¹ accompanied by a weaker feature at 876 cm⁻¹. When the experiment was repeated using $^{18}O_2$ in place of $^{16}O_2$, these features shifted to 857 and 825 cm⁻¹ respectively. When the matrix was doped with a mixture of the isotopomers $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ in the proportions 1:1:1, the band at 902 cm⁻¹ gave way to a triplet with components at 902, 874, and 857 cm⁻¹ (Figure 3 and Table 3). Unfortunately it was not possible to discern clearly the corresponding features derived from the absorption at 876 cm⁻¹ for the $[W(CO)_6]$–$^{16}O_2$ system, problems of diffuseness and low intensity being compounded by overlapping with the more intense absorptions making up the triplet at 902, 874, and 857 cm⁻¹.



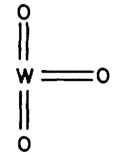
(**4**)

If (**X**) is indeed a molecule in which O_2 is co-ordinated to a WO_2 unit, it might be expected to have a structure such as (**4**). The ^{16}O–^{18}O shift of 45 cm⁻¹ exhibited by the more intense band at 902 cm⁻¹ is consistent with that expected for the antisymmetric W=O stretching mode of a WO_2 unit with an upper limit for the O=W=O bond angle of approximately 150°.[1–3] On this basis the corresponding symmetric W=O stretching mode is likely to occur at *higher* energy with an intensity in i.r. absorption less than one tenth that of the antisymmetric mode. That we failed to detect any clear sign of an absorption attributable to this symmetric stretching mode comes therefore as no surprise. Nevertheless, the unsymmetrical pattern of the triplet derived from the band at 902 cm⁻¹ when $^{16}O_2$ is replaced by a mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ lends weight to the identification of the absorber as an O=W=O moiety. The asymmetry parameter ρ, defined as in equation (1),[3,*] is 1.23 implying substantial interaction between the two W=O stretching modes in the unsymmetrically substituted

$$\rho = \frac{2\nu(^{16}O_2) - \nu(^{16}O^{18}O)}{\nu(^{16}O_2) - \nu(^{18}O_2)} \qquad (1)$$

$^{16}OW^{18}O$ oscillator. Similar aguments have been used to support the identification of the dioxometal carbonyls $[MO_2(CO)_x]$ [(**B**)—(**D**); M = Cr, Mo, or W; x = 2—4[1–3]].

A triangular peroxometal group is usually characterized by an i.r. absorption in the range 950—800 cm⁻¹ approximating to the ν(O–O) fundamental;[3] in this case ^{18}O enrichment gives a value of ρ close to unity with $\nu(^{16}O^{18}O)$ almost exactly halfway between $\nu(^{16}O^{16}O)$ and $\nu(^{18}O^{18}O)$. For the reasons already noted, we were unable to determine ρ for the weaker absorption at 876 cm⁻¹, but the ^{16}O—^{18}O shift of 51 cm⁻¹ deduced from the separate experiments with $^{16}O_2$ and $^{18}O_2$ respectively is close to that predicted (50 cm⁻¹) for ν(O–O) of a peroxometal group.[3] Such an isotopic shift is too large for the band to be attributed realistically to ν_{asym}(W=O) of a second O=W=O group. It is also too large for the band to be due to the stretching vibration of a unique W=O bond, as in a WO_3 molecule not with D_{3h} symmetry but with a T-shaped skeleton [*e.g.* (**5**)] and a symmetry no higher than C_{2v}. Such a structure has been proposed, for example, for the UO_3 molecule isolated in an argon or krypton matrix.[12]



(**5**)

Hence our results are consistent with the proposed structure (**4**) for the photoproduct (**X**). There is an obvious analogy with the molecule SO_4 generated in an argon matrix by the reaction

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* See ref. 3, p. 22 but note that the expression given there is incorrect and should take the form given in equation (1).

Table 3. Wavenumbers[a] of i.r. absorptions of (**X**), $(\eta^2\text{-}O_2)WO_2$, produced by photolysis at wavelengths between 220 and 370 nm, of $[W(CO)_6]$ isolated in argon matrices doped with (*i*) $^{16}O_2$, (*ii*) $^{16}O_2 + {}^{18}O_2$, (*iii*) $^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$, and (*iv*) $^{18}O_2$

Isotopes	$\nu_{asym.}(W^{16}O_2)$	$\nu_{asym.}(W^{18}O_2)$	$\Delta\nu$	$\nu(^{16}O\text{-}^{16}O)$	$\nu(^{18}O\text{-}^{18}O)$	$\Delta\nu$
$^{16}O_2$	902[b]			876		
$^{16}O_2 + {}^{18}O_2$	902	857	45	876	824	52
$^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$	902	857[b]	45	874[c]	825	51
$^{18}O_2$		857			825	

[a] All figures are wavenumbers or isotopic shifts ±1 cm^{-1}. [b] The average wavenumber for a matrix split band has been taken. [c] Shoulder.

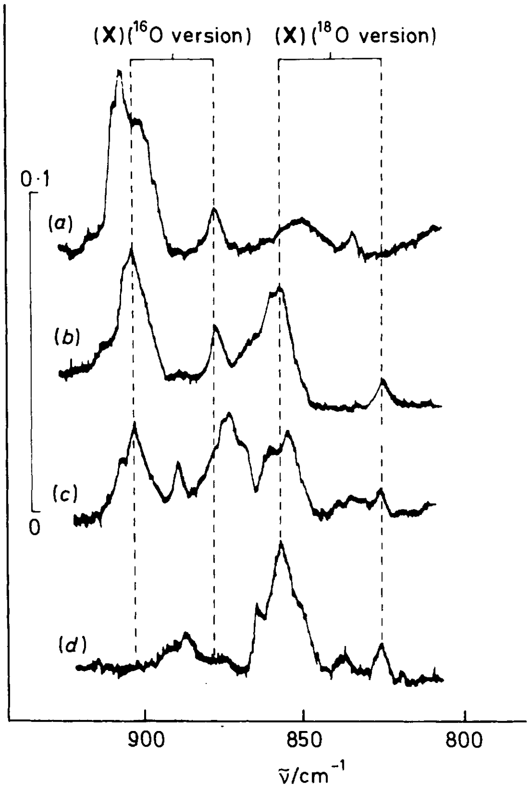


Figure 3. Infrared absorption spectra showing the various isotopomers of (**X**), $(O_2)WO_2$, produced by irradiation (λ = 220—370 nm) for 1 h of argon matrices containing $[W(CO)_6]$ and O_2 in the approximate proportions $Ar:O_2:[W(CO)_6]$ = 2 000:100:1. The following isotopomers of O_2 were employed: (*a*) $^{16}O_2$ only, (*b*) 57% $^{16}O_2$ and 43% $^{18}O_2$, (*c*) a scrambled mixture of the isotopomers $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ containing *ca.* 50 atom% ^{18}O, and (*d*) $^{18}O_2$ only

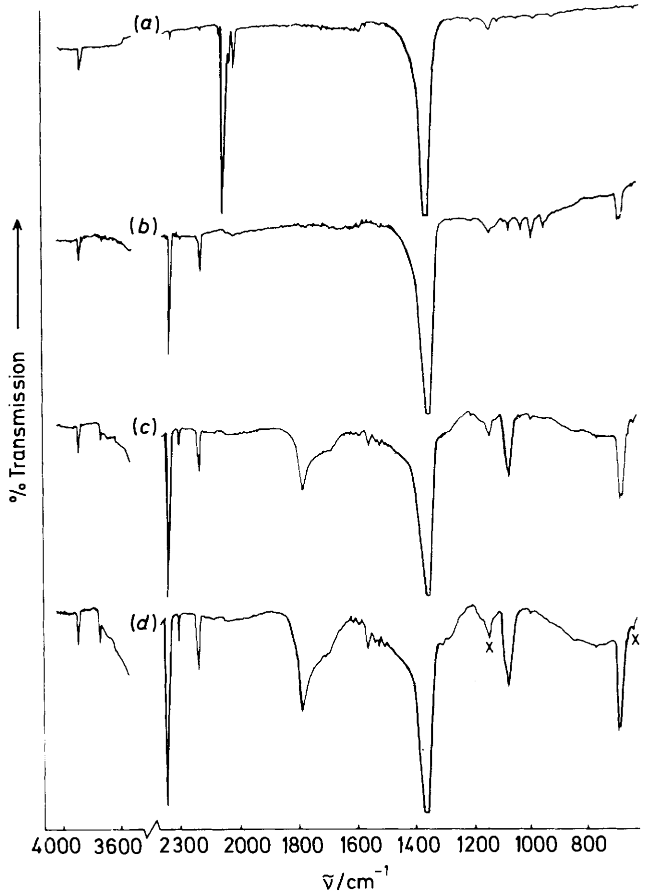


Figure 4. Infrared transmission spectra of a matrix initially composed of $[W(CO)_6]$, O_2, and CH_4 in the approximate proportions 1:100:2 000: (*a*) after deposition, (*b*) after irradiation at λ = 220—370 nm for 0.5 h, (*c*) after irradiation for 1 h, and (*d*) after irradiation for 4 h. Bands marked X are due to impurities deposited on the *outside* windows of the vacuum shroud from the atmosphere

of oxygen atoms with SO_3:[13] SO_4 is characterized by i.r. bands at 1 434, 1 267, and 925 cm^{-1}, which have been ascribed to the fundamentals $\nu_{asym}(S{=}O)$, $\nu_{sym}(S{=}O)$, and $\nu(O\text{-}O)$ respectively for a molecule structurally akin to (**4**). With due allowance for the different masses of the central atom, the magnitudes of the ^{16}O–^{18}O isotopic shifts are consistent with those of the corresponding modes of (**X**).

Production and Role of Oxygen Atoms.—The most obvious photolytic reaction for the formation of WO_3 from (**X**) implies the production of oxygen atoms [equation (2)]. In order to

$$(\eta^2\text{-}O_2)WO_2 \xrightarrow[\text{Argon matrix}]{h\nu} WO_3 + O \qquad (2)$$

determine whether free oxygen atoms are indeed released in this way, we have carried out experiments involving the photolysis of $[W(CO)_6]$–O_2 mixtures in potentially reactive matrices. Thus we have charted the course of photolysis by i.r. measurements involving the following matrices: pure O_2, N_2, and CH_4.

(*a*) *Dioxygen.* When a solid dioxygen matrix containing $[W(CO)_6]$ with the composition $O_2:[W(CO)_6]$ = *ca.* 2 000:1 was photolysed for 15 min with radiation having λ = 220—370 nm, there was no sign in the i.r. spectrum of the deposit that any species containing co-ordinated CO groups had survived. By contrast, the change of matrix resulted in a higher yield of the species (**X**) absorbing near 900 cm^{-1}. Continued photolysis at these wavelengths for a further 45 min caused (**X**) to decay and give place to WO_3. At the same time the appearance and growth

Table 4. Wavenumbers of new bands which develop on u.v. photolysis of $[W(CO)_6]$ isolated in an O_2-doped methane matrix, and changes in their intensity with time of photolysis at wavelengths between 220 and 370 nm

Wave-number[a]/ cm^{-1}	Time of u.v. photolysis[b]/min 30	60	240	Assignment
3 641	app.	inc.	inc.	CH_3OH, ν(O–H)
1 720		app.	inc.	H_2CO, ν(C=O)
1 497		app.	inc.	H_2CO, $\delta(CH_2)$
1 474		app.	inc.	CH_3OH, $\delta(CH_3)$
1 463		app.	inc.	CH_3OH, $\delta(CH_3)$
1 446		app.	inc.	CH_3OH, $\delta(CH_3)$
1 034	app.	inc.	inc.	CH_3OH, ν(C–O)
980	app.	dec.	disapp.	WO_2, $\nu_1(WO_2)$
950	app.	dec.	disapp.	WO_2, $\nu_3(WO_2)$
913	app.	disapp.		WO_3, $\nu_3(WO_3)$
900	app.	disapp.		$(O_2)WO_2$, $\nu_{asym.}(WO_2)$

[a] Error limits ±2 cm^{-1}. [b] app. = Appears, inc. = increases, dec. = decreases, and disapp. = disappears.

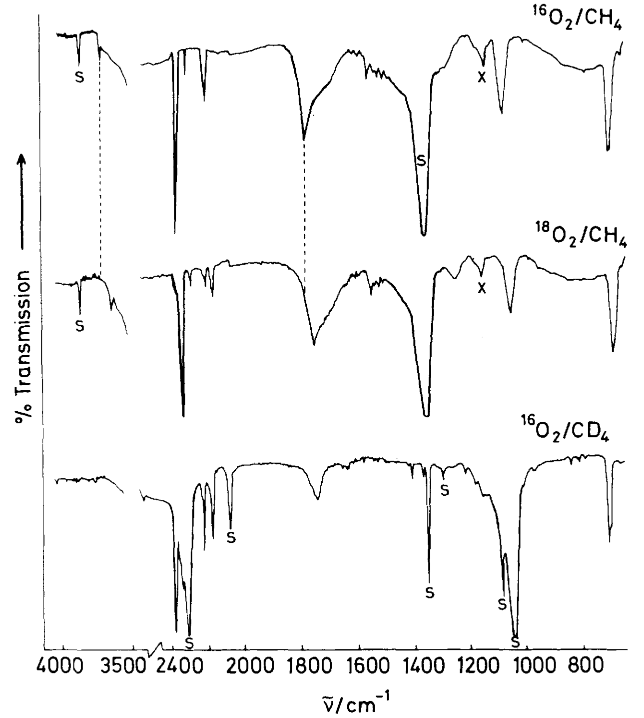


Figure 5. Infrared transmission spectra of matrices initially containing $[W(CO)_6]$, $^{16}O_2$ or $^{18}O_2$, and CH_4 or CD_4 in the approximate proportions 1:100:2 000. Each matrix has been subjected to irradiation at λ = 220—370 nm for 4 h. Bands marked S were observed after deposition of the matrix and are associated with the i.r. spectrum of either CH_4 or CD_4, those marked X are due to impurities deposited on the *outside* windows of the vacuum shroud from the laboratory atmosphere

of bands at 1 040/1 032 and 702 cm^{-1} signalled the formation of ozone molecules.[14]

(*b*) *Dinitrogen matrix.* In a similar experiment $[W(CO)_6]$ was isolated in an O_2-doped dinitrogen matrix with the composition $N_2:O_2:[W(CO)_6]$ = *ca.* 1 600:400:1. Photolysis of the matrix at wavelengths between 220 and 370 nm resulted after 60 min in the appearance of absorptions attributable to the molecules CO,[10] CO_2,[11] WO_3,[7] (**X**) (in low concentration), and N_2O.[15]

(*c*) *Methane matrix.* In order to demonstrate further the intermediacy of oxygen atoms in the matrix photochemistry of $(\eta^2\text{-}O_2)WO_2$, we isolated $[W(CO)_6]$ in an O_2-doped methane matrix with the composition $CH_4:O_2:[W(CO)_6]$ = *ca.* 2 000:100:1. Photolysis of the matrix at wavelengths between 220 and 370 nm resulted after 60 min in the appearance of bands testifying to the presence of the molecules CO,[10] CO_2,[11] CH_3OH,[8,16] H_2CO,[17], WO_3,[7] and (**X**), together with a low concentration of what appeared to be unco-ordinated WO_2.[7] Of particular interest was the growth of bands at 3 641, 1 474, 1 446, and 1 034 cm^{-1} clearly identifiable with the formation of CH_3OH; the appearance of weaker bands at 1 720 and 1 497 cm^{-1} we attribute to the formation of H_2CO.

After photolysis of the matrix for a further 180 min, we found that the i.r. bands associated with CH_3OH and H_2CO had grown, while the weaker features due to binary tungsten oxides had decayed. The wavenumbers of the bands exhibited by the matrix after photolysis are listed in Table 4, and the changes in the i.r. spectrum are illustrated in Figure 4.

We confirmed the identities of the photoproducts CH_3OH and H_2CO by repeating the experiment, first using an $^{18}O_2$-doped methane matrix, and then using a $^{16}O_2$-doped tetradeuteriomethane matrix. We confirmed too that binary tungsten oxides are responsible, at least in part, for the photo-oxidation of CH_3OH to H_2CO by examining the effects of u.v. photolysis on a methane matrix containing $[W(CO)_6]$, O_2, and CH_3OH. By contrast, control experiments with methane matrices containing O_2 or a mixture of O_2 and CH_3OH, *but no* $[W(CO)_6]$, gave no hint of response to irradiation with light having λ = 220—370 nm.

The relevant results derived from these experiments are given in Figure 5 and Table 5. It is noteworthy that the energies of some of the bands we ascribe to CH_3OH and H_2CO are shifted by as much as 36 cm^{-1} from the values reported previously[8,16,17] for the individual molecules isolated in an argon matrix.

Products of Photolysis of $[Cr(CO)_6]$ *or* $[Mo(CO)_6]$ *in* O_2*-doped Matrices.*—We have extended the studies described in the preceding sections by carrying out experiments involving prolonged u.v. photolysis of O_2-doped argon matrices containing either $[Cr(CO)_6]$ or $[Mo(CO)_6]$ [Figure 1(*a*) and (*b*)]. Irrespective of the nature of the metal atom, the products were found to be CO and CO_2, together with one or more binary metal oxides. The wavenumbers of the i.r. bands observed to develop on prolonged photolysis are listed in Table 1, which also includes details of the vibrational properties reported previously for the molecules CrO_2,[18] MoO_2,[6] and MoO_3[6] isolated in matrices at low temperatures. Hence it appears that CrO_2 is the only chromium-containing product derived ultimately from $[Cr(CO)_6]$, whereas both MoO_2 and MoO_3 are derived from $[Mo(CO)_6]$ in similar circumstances.

The behaviour of the $[Mo(CO)_6]$–O_2 system is of particular interest because the wavenumbers of the i.r. bands attributable to MoO_2 differ only slightly from those reported previously for this molecule in a matrix environment.[6] Evidently the presence of O_2 in the matrix does not perturb the vibrational properties of the MoO_2 unit to the same extent as it perturbs those of WO_2. There is accordingly no *direct* evidence to suggest the formation of a molybdenum analogue of (**X**). On the other hand, exposure to radiation with λ = 220—370 nm for 2 h caused a solid dinitrogen matrix having the composition $N_2:O_2:[Mo(CO)_6]$ = *ca.* 1 600:400:1 to develop the i.r. absorptions characteristic of N_2O.[15] This photosensitization of O_2 leads us to infer that a molybdenum analogue of (**X**) is formed in the matrix. It may be that the concentration of the

Table 5. Wavenumbers and assignments of the bands which develop on prolonged u.v. irradiation of $[W(CO)_6]$ isolated in (*i*) a $^{16}O_2$-doped, (*ii*) an $^{18}O_2$-doped methane matrix, and (*iii*) a $^{16}O_2$-doped tetradeuteriomethane matrix[a]

$^{16}O_2/CH_4$		$^{18}O_2/CH_4$		$^{16}O_2/CD_4$		
This work	Previous work	This work	Previous work	This work	Previous work	Assignment
3 641	3 667[b]	3 620	3 656[b]	2 672	2 706[b]	CH_3OH, ν(O–H)
1 720	1 742[c]	1 686		1 680	1 698[c]	H_2CO, ν(C=O)
1 497	1 499[c]	1 488		1 098	1 099[c]	H_2CO, $\delta(CH_2)$
1 474	1 474[b]	1 473		*d*	1 133[b]	CH_3OH, $\delta(CH_3)$
1 463	1 466[b]	1 464		1 083	1 068[b]	CH_3OH, $\delta(CH_3)$
1 446	1 451[b]	1 448		*d*		CH_3OH, $\delta(CH_3)$
1 034	1 034[b]	1 000	1 008[b]	990	991[b]	CH_3OH, ν(C–O)
980	975[e]	936	924[e]	980		WO_2, $\nu_1(WO_2)$
950	937[e]	896	890[e]	950		WO_2, $\nu_3(WO_2)$
913	918[f]	870	872[f]	915		WO_3, $\nu_3(WO_3)$
900		854		901		$(O_2)WO_2$, $\nu(WO_2)$

[a] All figures are wavenumbers ±1—5 cm^{-1}. [b] Argon matrix, ref. 16. [c] Argon matrix, ref. 17. [d] Not observed. [e] Krypton matrix, ref. 7. [f] Argon matrix, ref. 7.

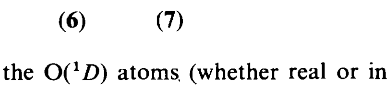
species is too low for it to be detected by its i.r. spectrum, but an alternative explanation of our results is that co-ordination by O_2 entails relatively little perturbation of the MoO_2 substrate in the molybdenum version of (**X**).

Discussion

(*i*) *Products formed by Oxidation of the Matrix.*—The production of O_3 on u.v. photolysis of a dioxygen matrix containing $[W(CO)_6]$ and of N_2O on u.v. photolysis of a dinitrogen matrix containing $[W(CO)_6]$ and O_2 points to the intermediacy of oxygen atoms formed in accordance with equation (2). The addition of oxygen atoms to O_2 to give O_3 under matrix conditions has not been studied systematically,[19] although the process is a familiar and important one in relation to atmospheric photochemistry.[20] Whether the oxygen atoms are in the ground (^3P) or the excited (^1D) state is believed to make little difference to this reaction, although there is still some controversy on this score. By contrast, the spontaneous oxidation of N_2 to N_2O is characteristic of oxygen atoms not in the ^3P but in the ^1D state [equation (3)].[19,21] Another reaction

$$N_2 + O(^1D) \longrightarrow N_2O \qquad (3)$$

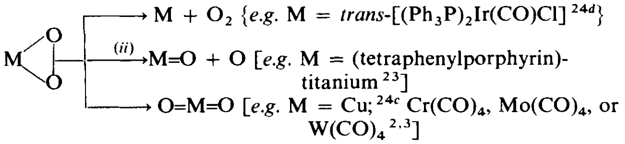
characteristic of $O(^1D)$, but not of $O(^3P)$, in the fluid phases involves insertion into the C–H bonds of CH_4 and oxidation to give CH_3OH and H_2CO,[22] although it does not seem to have been investigated previously under matrix conditions. Our finding that u.v. photolysis of $[W(CO)_6]$ in an O_2-doped methane matrix results in oxidation of the host to CH_3OH and H_2CO is consistent therefore with the intermediacy of $O(^1D)$ atoms in the final stages of photolysis. It is by no means certain, however, that the $O(^1D)$ atoms have an independent existence in the matrix. The results of our experiments could be interpreted on the basis of oxygen-atom transfer *via* a peroxo bridge linking the reaction centres in a mechanism similar to that envisaged in the second stage of reaction (4) in which the peroxotitanium(IV) tetraphenylporphyrin complex (**6**) is converted into the oxotitanium derivative (**7**).[23]



(4)

(**6**) (**7**)

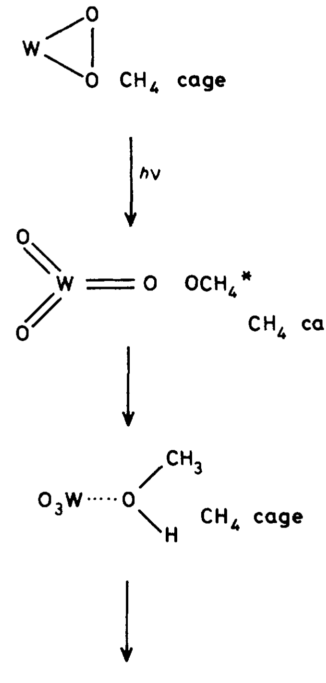
The source of the $O(^1D)$ atoms (whether real or incipient) must be an O_2 molecule activated with respect to photodissociation since the wavelengths of the photolysing radiation employed (220—370 nm) exceeded the threshold (220 nm) for dissociation of an isolated O_2 molecule.[19,22] Such activation is provided, we believe, in the intermediate (**X**) where an O_2 molecule is co-ordinated in the form of a peroxo unit to a WO_2 fragment. Evidence from various sources[3,19,24] shows that peroxometal species are susceptible to photolysis, typically in the mid-u.v. region. The photolysis gives access to three possible reaction channels: (*i*) dissociation of the M–O_2 bond with liberation of O_2, (*ii*) dissociation of the O–O bond with the formation of an oxometal species and the release or transfer of an oxygen atom, and (*iii*) intramolecular dissociation of the O–O bond with the formation of a dioxometal species (Scheme 1). Clearly the proposed photodissociation of $(\eta^2\text{-}O_2)WO_2$ in accordance with equation (2) corresponds to the second of these channels. A potential analogy is thus provided by the peroxotitanium porphyrin complex (**6**);[23] enrichment with $^{18}O_2$ implies that the conversion into the oxotitanium derivative (**7**) [equation (4)] involves reductive elimination of O_2, *i.e.* channel (*i*) followed by oxygen-atom transfer from (**6**) to the titanium(II) intermediate thus formed. That the yield of O_2 is less than 80% of that required by equation (4), with the rest of the oxygen apparently reacting with the solvent, has been taken to suggest that the evolved oxygen is in the electronically excited singlet state.[23] Photolysis of $[PtO_2(PPh_3)]$ has been reported[24e] also to yield singlet O_2.



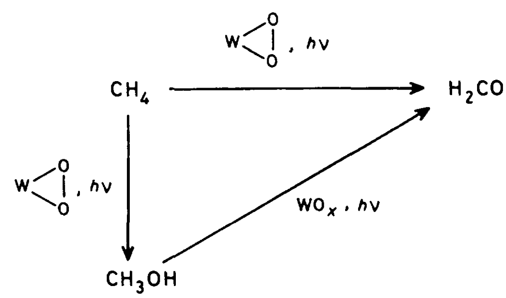
Scheme 1.

The situation in solid methane matrices is complicated by at least one other photochemical process. This is the photo-oxidation of CH_3OH to H_2CO by high-valent tungsten oxide molecules present in the matrix. Only in this way can we account for the decrease in intensity of the i.r. bands associated with binary tungsten oxides accompanying the growth of the bands due to H_2CO on prolonged u.v. photolysis. It is unlikely that a similar process is responsible for the initial photo-oxidation of CH_4, since depletion of the matrix of binary tungsten oxides was observed to occur only *after* an appreciable concentration of CH_3OH had accumulated. Little is known about the matrix photochemistry of metal oxide molecules and, to the best of our knowledge, this is the first example of a photo-induced oxidation involving such a molecule. It is noteworthy too that an Fe_2O_3–MoO_3 catalyst is used in the production of formaldehyde by the air oxidation of methanol vapour at 350—400 °C.[25]

We have remarked previously that the energies of some of the vibrational transitions originating in the CH_3OH and H_2CO produced in our experiments are shifted appreciably from the values reported previously.[8,16,17] The discrepancies could be due to aggregation of the CH_3OH and H_2CO molecules. However, we tend to discount this possibility (*i*) because neither of the molecules was formed in high concentration (CH_4:CH_3OH and CH_4:H_2CO > 1 000:1), and (*ii*) because the energies of the transitions we observed did not tally with those ascribed previously to the matrix-isolated aggregates $(CH_3OH)_n$[16] and $(H_2CO)_n$.[17] A more plausible explanation is that the CH_3OH and H_2CO molecules formed in our experiments are perturbed by co-ordination to a tungsten metal centre. Such co-ordination could well provide the conditions essential to photo-oxidation of CH_3OH by the higher-valent tungsten oxides. Independent studies[26] have shown that any O(^1D) atom generated in a matrix cage is most likely to react with a molecule within or forming part of that cage. Hence we envisage the following sequence in Scheme 2 in which photolysis results in the photo-oxidation of a CH_4 molecule of the matrix to form CH_3OH or H_2CO co-ordinated to WO_3. Continued photolysis opens up a second route to H_2CO by photo-oxidation of the co-ordinated CH_3OH with elimination of hydrogen, possibly resulting in the conversion of W=O into W–OH or W–OH_2 groups. Although the i.r. spectrum of the methane matrix established that W=O bonds are implicated in the reaction, we were unfortunately unable to detect the growth of any new bands attributable to products other than CH_3OH and H_2CO. The ν(C=O) mode of the H_2CO formed in our experiments exhibits a red shift of 22 cm^{-1} compared with the same molecule isolated in an argon matrix.[17] This suggests that the H_2CO remains co-ordinated to a tungsten centre; the relatively slight vibrational perturbation experienced by the molecule is consistent with a weak interaction of the type $H_2CO \cdots W$ quite different from the η^2 ligation of the same molecule in the complex $[Os(CO)_2(\eta^2\text{-}H_2CO)(PPh_3)_2]$.[27] Such formaldehyde complexes are of interest in relation to their potential role in reactions encompassing the reduction of CO.[28]



Scheme 2. OCH_4* = vibrationally activated adduct



Scheme 3.

The photochemical changes observed to take place in solid methane matrices are summarized in Scheme 3.

(*ii*) *Production of* CO *and* CO_2.—In keeping with the results of earlier experiments,[1–3] we have found that CO_2, as well as CO, is invariably produced on u.v. photolysis of $M(CO)_6$ (M = Cr, Mo, or W) isolated in a matrix containing O_2 molecules. However, our experiments have shed no further light on the mechanism by which CO_2 is produced. Evidently, the CO_2 is produced by photolysis of one or more of the intermediates (**B**)—(**D**), but our findings lend no positive support to any one of the reaction channels (5)—(9) where $x < 4$.

$$O_2W(CO)_x \longrightarrow OW(CO)_{x-1} + CO_2 \qquad (5)$$

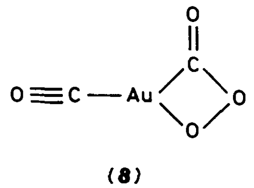
$$O_2W(CO)_x \longrightarrow W(CO)_x + O_2{}^* \qquad (6)$$

$$O_2W(CO)_x \longrightarrow W(CO)_{x-2} + 2CO_2 \qquad (7)$$

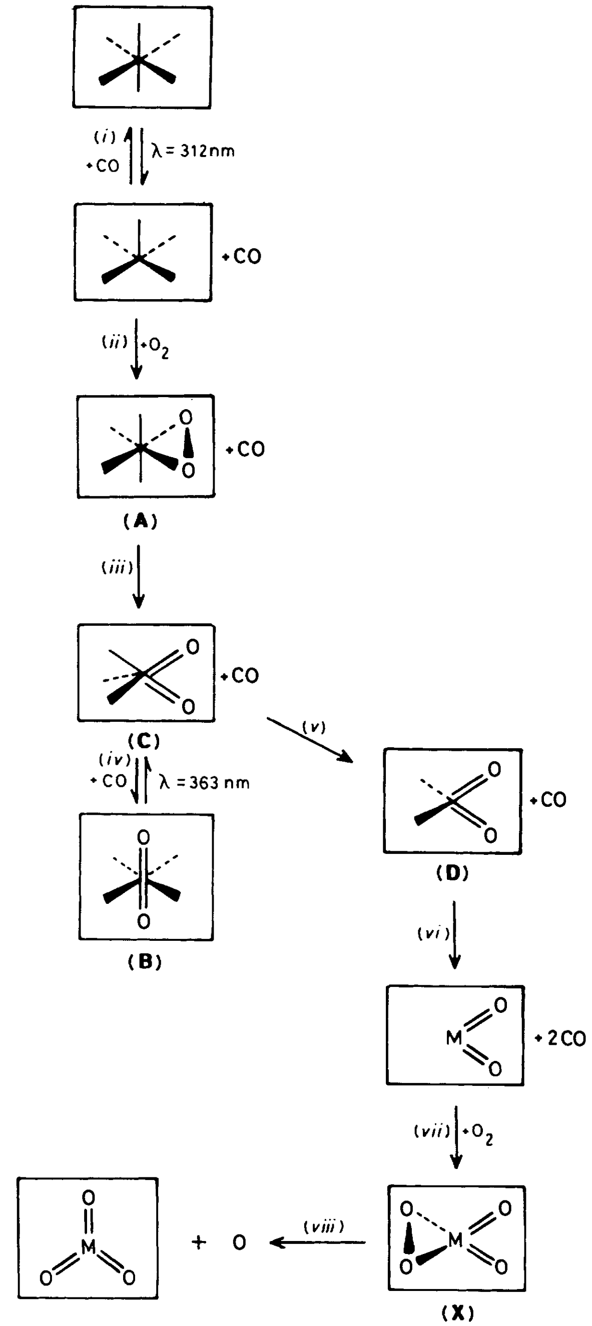
$$O_2W(CO)_x \longrightarrow W + 2CO_2 + (x-2)CO \qquad (8)$$

$$O_2W(CO)_x \longrightarrow W(CO)_{x-1} + CO_3 \qquad (9)$$

However, the following points should be noted. Experiments involving $^{18}O_2$ in place of $^{16}O_2$ yield $C^{16}O$ and $C^{16}O^{18}O$ but *no* $C^{18}O$ or $C^{18}O_2$. This shows that one oxygen atom in photoejected CO_2 comes from an O_2 molecule and the other from the original carbonyl.[1–3] We have also established that all intermediates (**A**)—(**D**) contain two oxygen atoms *both* derived from the same dioxygen molecule.[1,2] Studies to determine the effect of different O_2 concentrations prompt us to conclude that only *one* molecule of O_2 is involved in the early stages of photolysis. Furthermore, we found no signs in the i.r. spectra either of monoxotungsten species, or of binary carbonyls other than $[W(CO)_6]$ or $[W(CO)_5]$.[29] Nor did we obtain any evidence for a co-ordinated peroxoformate group similar to that in the carbonyl gold(II) derivative (**8**), produced, it is thought,[30] on co-condensation of gold atoms with mixtures of CO and O_2.



(**8**)



Scheme 4. (*i*) M = Cr, Mo, or W, λ = 312 nm; (*ii*) M = Cr, λ = 543 nm; M = Mo, λ = 405 nm; M = W, λ = 435 nm; (*iii*) M = Cr or W, λ = 366 nm; M = Mo, λ = 312 nm; (*iv*) M = Mo or W only; M = Mo, λ = 403 nm or annealing at 35 K; M = W, annealing at 35 K; (*v*) M = Cr, λ = 312 nm or annealing at 35 K; M = Mo or W, λ = 312 nm; (*vi*) M = Cr, Mo, or W(?), λ = 312 nm; the results for W are tentative because bands due to free WO_2 may be obscured or too weak to be detected, but there is evidence that this molecule is formed in methane matrices (see Table 4 and Figure 4); (*vii*) M = Mo(?) and W only; the results for Mo are tentative because no *direct* evidence for the step was found; (*viii*) M = Mo(?) and W only; λ = 220—370 nm. The labelling of intermediates (**A**)—(**D**) and (**X**) is in line with the conventions of earlier papers[1,2]

In one of our experiments we observed very weak bands which could possibly belong to free CO_3.[31a] However, these bands were not seen to increase in intensity during this experiment and neither could they be reproduced in other experiments. Thus we conclude that CO_3 can play only a minor role in the production of CO_2.

In this context it is interesting that although O_2 does not undergo photodissociation at wavelengths longer than 220 nm,[19,22] Raper and DeMore[32] have found that photolysis of solutions of O_2 in liquid CO at 77 K with 253.7 nm radiation produces O_3 and CO_2. They have interpreted their results on the basis of an initial reaction (10) in which O_2 in an

$$O_2{}^* + CO \longrightarrow CO_3{}^* \qquad (10)$$

electronically excited state (believed to be $^3\Sigma u^+$) adds to CO; the $CO_3{}^*$ intermediate thus formed gives access, it is argued, to the reactions (11)—(14).

$$CO_3{}^* \longrightarrow CO + O_2 \qquad (11)$$

$$CO_3{}^* \longrightarrow CO_2 + O \qquad (12)$$

$$CO_3{}^* \longrightarrow CO_2{}^* + CO_2 \qquad (13)$$

$$CO_3{}^* \longrightarrow CO_2 + O_3 \qquad (14)$$

With these results in mind we carried out experiments in which we subjected CO matrices, containing 5—20% O_2, to photolysis at λ = 254 nm. We saw only a very slight production of CO_2, and when photolysis of the same matrices was carried out at 312 or 363 nm no CO_2 was produced. However, a similar mechanism involving electronically excited O_2 molecules could be responsible for the photoejected CO_2 molecules which feature in the matrix systems Ar–$[M(CO)_6]$–O_2 (M = Cr, Mo, or W), despite the fact that CO_2 is produced in these systems on photolysis at 312 or 363 nm. It should be noted that our experiments differ from those of Raper and DeMore in that they include, in addition to O_2, a second photolabile species, namely $M(CO)_6$.

Conclusions

Prolonged u.v. photolysis of $[M(CO)_6]$ molecules (M = Cr, Mo, or W) trapped in O_2-doped argon matrices generates free CO and CO_2, together with one or more binary metal oxides. With M = Cr the metal oxide produced ultimately is CrO_2, whereas with M = Mo or W the ultimate product is MO_3. It appears that MoO_3 or WO_3 is produced *via* another binary metal oxide (**X**) in which an O_2 molecule is co-ordinated to an MO_2 fragment, probably in the form $(\eta^2\text{-}O_2)MO_2$. This species acts as a photochemical source of oxygen atoms, yielding on u.v. photolysis, and in the presence of a suitable receptor E, the product EO, where E = O_2, N_2, or CH_4. Addition to N_2 and insertion into the C–H bonds of CH_4 are reactions diagnostic of oxygen atoms in the ^1D excited state.[22]

Thus, photolysis of a metal carbonyl in the presence of O_2 affords a means of generating binary metal oxide molecules in a matrix environment. This approach has the advantage over matrix co-condensation of metal atoms with O_2[5] that it avoids the complications associated with partial aggregation of the unsaturated metal centres. On the other hand, it still suffers from the need to dope the matrix with relatively high concentrations of O_2, and the metal oxide molecules are liable to be perturbed by their proximity not only to O_2 but also to the photoejected CO and CO_2 molecules. The identification of the species (**X**) and the recognition of its individual photochemistry demonstrate well the complications which may ensue from the proximity of potentially reactive molecules.

Taken in conjunction with the results of earlier studies,[1–3] the findings reported here lead us to propose in Scheme 4 a complete mechanism for the photo-oxidation of $[M(CO)_6]$ (M = Cr, Mo, or W) in an O_2-doped matrix.

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References

1 M. Poliakoff, K. P. Smith, J. J. Turner, and A. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1982, 651.

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

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

4 (*a*) Y. Iwasawa, T. Nakamura, K. Takamatsu, and S. Ogasawara, *J. Chem. Soc., Faraday Trans. 1*, 1980, 939; (*b*) R. A. Sheldon and J. K. Kochi, 'Metal-Catalyzed Oxidations of Organic Compounds,' Academic Press, New York, 1981; (*c*) M. Sasaki, K. Tanaka, K. Tanaka, and I. Toyoshima, *J. Chem. Soc., Chem. Commun.*, 1986, 764; (*d*) J. C. Dobson, W. K. Seok, and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 1513 and refs. therein; D. P. Riley and J. D. Oliver, *ibid.*, 1986, **25**, 1814, 1821, 1825; (*e*) E. W. Harlan, J. M. Berg, and R. H. Holm, *J. Am. Chem. Soc.*, 1986, **108**, 6992; (*f*) H. Kang and J. L. Beauchamp, *ibid.*, p. 7502.

5 H. Huber, W. Klotzbücher, G. A. Ozin, and A. Vander Voet, *Can. J. Chem.*, 1973, **51**, 2722; J. H. Darling, M. B. Garton-Sprenger, and J. S. Ogden, *Symp. Faraday Soc.*, 1974, **8**, 75; D. E. Tevault, R. R. Smardzewski, M. W. Urban, and K. Nakamoto, *J. Chem. Phys.*, 1982, **77**, 577; T. Watanabe, T. Ama, and K. Nakamoto, *J. Phys. Chem.*, 1984, **88**, 440.

6 W. D. Hewett, jun., J. H. Newton, and W. Weltner, jun., *J. Phys. Chem.*, 1975, **79**, 2640.

7 D. W. Green and K. M. Ervin, *J. Mol. Spectrosc.*, 1981, **89**, 145.

8 R. N. Perutz and J. J. Turner, *J. Chem. Soc., Faraday Trans. 2*, 1973, 452.

9 E. H. Appelman, unpublished work; E. H. Appelman, L. J. Basile, and R. C. Thompson, *J. Am. Chem. Soc.*, 1979, **101**, 3384.

10 H. Dubost, *Chem. Phys.*, 1976, **12**, 139.

11 L. Fredin, B. Nelander, and G. Ribbegard, *J. Mol. Spectrosc.*, 1974, **53**, 410; R. Guasti, V. Schettino, and N. Brigot, *Chem. Phys.*, 1978, **34**, 391.

12 S. D. Gabelnick, G. T. Reedy, and M. G. Chasanov, *J. Chem. Phys.*, 1973, **59**, 6397.

13 R. Kugel and H. Taube, *J. Phys. Chem.*, 1975, **79**, 2130.

14 L. Brewer and J. L-F. Wang, *J. Chem. Phys.*, 1972, **56**, 759; L. Andrews and R. C. Spiker, jun., *ibid.*, 1972, **56**, 3208; M. Spoliti, S. N. Cesaro, and B. Mariti, *J. Chem. Phys.*, 1973, **59**, 985; D. W. Green and K. M. Ervin, *J. Mol. Spectrosc.*, 1981, **88**, 51.

15 J. Laane and J. R. Ohlsen, *Prog. Inorg. Chem.*, 1980, **27**, 465.

16 A. J. Barnes and H. E. Hallam, *Trans. Faraday Soc.*, 1970, **66**, 1920.

17 H. Khoshkhoo and E. R. Nixon, *Spectrochim. Acta, Part A*, 1973, **29**, 603.

18 L. V. Serebrennikov and A. A. Mal'tsev, *Vestn. Mosk. Univ. Khim.*, 1975, **16**, 251; M. J. Almond, A. J. Downs, and R. N. Perutz, *Inorg. Chem.*, 1985, **24**, 275.

19 R. N. Perutz, *Chem. Rev.*, 1985, **85**, 77.

20 B. A. Thrush, *Acc. Chem. Res.*, 1981, **14**, 116; M. Horvath, L. Bilitzky, and J. Hüttner, 'Ozone,' Elsevier, Amsterdam, 1985.

21 J. R. McNesby and H. Okabe, *Adv. Photochem.*, 1964, **3**, 157; R. V. Taylor and W. C. Walker, *J. Chem. Phys.*, 1979, **70**, 284; R. V. Taylor, W. Scott, P. R. Findley, Z. Wu, and W. C. Walker, *ibid.*, 1981, **74**, 3718.

22 C. L. Lin and W. B. DeMore, *J. Phys. Chem.*, 1973, **77**, 863.

23 C. J. Boreham, J-M. Latour, J. C. Marchon, B. Boisselier-Cocolios, and R. Guilard, *Inorg. Chim. Acta*, 1980, **45**, L69.

24 (*a*) M. H. Gubelmann and A. F. Williams, *Struct. Bonding (Berlin)*, 1983, **55**, 1; (*b*) H. Ledon, M. Bonnet, and J-Y. Lallemand, *J. Chem. Soc., Chem. Commun.*, 1979, 702; (*c*) G. A. Ozin, S. A. Mitchell, and J. Garcia-Prieto, *J. Am. Chem. Soc.*, 1983, **105**, 6399; D. E. Tevault, *J. Chem. Phys.*, 1982, **76**, 2859; V. E. Bondybey and J. H. English, *J. Phys. Chem.*, 1984, **88**, 2247; (*d*) G. L. Geoffroy, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, 1975, **97**, 3933; (*e*) A. Vogler and H. Kunkely, *ibid.*, 1981, **103**, 6222.

25 R. P. A. Sneeden, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 8, p. 39.

26 E. H. Appelman, A. J. Downs, and C. J. Gardner, *J. Phys. Chem.*, in the press.

27 K. L. Brown, G. R. Clark, C. E. L. Headford, K. Marsden, and W. R. Roper, *J. Am. Chem. Soc.*, 1979, **101**, 503.

28 G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 136; E. L. Muetterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479; C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61; R. Eisenberg and D. E. Hendrickson, *Adv. Catal.*, 1979, **28**, 79.

29 R. N. Perutz, Ph.D. Thesis, University of Cambridge, 1974; R. N. Perutz and J. J. Turner, *Inorg. Chem.*, 1975, **14**, 262.

30 H. Huber, D. McIntosh, and G. A. Ozin, *Inorg. Chem.*, 1977, **16**, 975.

31 (*a*) N. G. Moll, D. R. Clutter, and W. E. Thompson, *J. Chem. Phys.*, 1966, **45**, 4469; E. Weissberger, W. H. Breckenridge, and H. Taube, *ibid.*, 1967, **47**, 1764; (*b*) R. P. A. Sneeden, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 8, p. 225.

32 O. F. Raper and W. B. DeMore, *J. Chem. Phys.*, 1964, **40**, 1047.

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