

Photooxidation Reactions of Transition Metal Carbonyls in Low-temperature Matrices

Matthew J. Almond

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, U.K.

1 Introduction

Matrix isolation, an invention of George Pimentel in 1953, is nowadays an established method for prolonging the lifetimes of transient chemical species. A full description of the technique is beyond the scope of this short review and, in any case, such experimental and theoretical details are given elsewhere.^{1–2} The principle behind the method is as follows: when a chemical species is embedded at high dilution in a solid host at low temperature (a typical example being solid argon at 20 K) bimolecular reactions are suppressed and unimolecular decomposition is stopped for any process with an activation barrier larger than a few kJmol^{-1} . The species is thus preserved. There are two main routes to generate matrix-isolated species. First, the reactive entity may be generated in the gas phase by, for example, heating or the action of a microwave discharge, and is then frozen rapidly with an excess of the matrix gas *e.g.* argon. Alternatively a stable precursor is trapped within the matrix and the reactive species is generated *in situ*, typically by photolysis. Thus a wide range of atoms, molecules, ions, and radicals may be isolated in low-temperature matrices, then studied by a number of spectroscopic techniques.^{1–3} One advantage of the matrix isolation method is that, at least to some extent, the method of detection may be tailored to the problem under investigation.

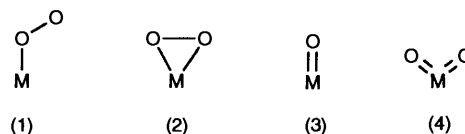
In this review the photo-oxidation reactions of transition metal carbonyls in low-temperature matrices will be discussed. Many simple binary carbonyls and a number of ternary compounds have thus been studied by trapping the carbonyl at high dilution in a matrix containing molecular dioxygen. A typical mixture is $\text{M}(\text{CO})_n:\text{O}_2:\text{Ar} = 1:100:2000$ at 20 K. The matrix is deposited upon a window transparent to IR radiation, *e.g.* CsI held within a high vacuum shroud, and is then subjected to UV-visible photolysis. Depending on the type of experiment being performed the photolysis may be 'broad-band', *i.e.* covering the whole of the UV and visible regions, or at selected wavelengths. Broad-band photolysis is used typically to push the reaction through to its final products which are generally isolated *molecular* binary oxides. Narrow band photolysis is used to form intermediate oxocarbonyl molecules in which both CO and

oxygen, in one form or another, are co-ordinated to the metal centre, and to explore the reaction pathway. In most of the examples mentioned here IR spectroscopy has been used to monitor the progress of the reaction and to characterize intermediate and product compounds, although Raman and UV-visible spectroscopy have been employed in a number of cases.

Oxidation reactions of organometallic compounds is currently an area of considerable research interest. Thus, in transition metal chemistry, the synthesis of organometallic oxides such as $(\text{CH}_3)_2\text{ReO}_3$,⁴ and cp^*ReO_3 ($\text{cp}^* = \eta\text{-C}_5\text{Me}_5$),⁵ and the properties of such molecules as catalysts^{6–8} attract considerable attention. Under appropriate conditions main group organometallics will also yield isolable products with O_2 . The 1992 Meldola lecture by Barron was concerned with reactions of the group 13 alkyls with dioxygen, forming products which are sufficiently stable to be structurally characterized by single crystal X-ray diffraction.⁹ One aim of this review is to show that matrix isolation is an excellent means to study reactions of this type, since intermediates may be stabilized and mechanisms explored. This information is of value to chemists working in diverse areas such as: (i) selective oxidation of organic substrates at transition metal centres; (ii) transport of oxygen by living organisms; (iii) metal oxide chemistry; (iv) corrosion; (v) chemical vapour deposition of oxide thin layers.

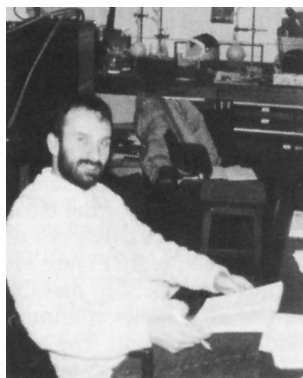
2 Identification of Products and Intermediates

It is instructive to consider briefly how the structure of molecules such as binary oxides and oxocarbonyls may be studied in a matrix when vibrational spectroscopy is the only readily available technique. The first question to answer is: *how does oxygen bind to the metal centre?* Four different modes of bonding are commonly encountered. These are superoxo (end on) (1) or peroxo (side on) (2) binding of O_2 or monoxo (3) or dioxo (4) coordination where the O–O bond has been ruptured. Superoxo derivatives typically show IR absorption arising from $\nu(\text{O}=\text{O})$ vibrations in the region $1000\text{--}1200\text{ cm}^{-1}$; peroxo derivatives show IR absorption from the $\nu(\text{O}=\text{O})$ vibration in the region $700\text{--}1000\text{ cm}^{-1}$, the same region in which absorption from $\nu(\text{M}=\text{O})$ vibrations of (3) or (4) occurs. Thus a definitive characterization of the mode of binding of oxygen relies upon experiments utilising the isotope ^{18}O .



Using a mixture of $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$, causes the absorption associated with the O–O stretching mode of the $\eta^2\text{-O}_2$ peroxo group to take the form of a single symmetrical triplet. A monoxo species gives rise to a simple doublet, whilst under similar conditions (4) forms two asymmetric triplets derived from the antisymmetric and symmetric stretching fundamentals. The two unsymmetrical triplets are produced by the strong coupling of the two $^{16}\text{O}=\text{M}=\text{O}^{18}\text{O}$ stretching modes, caused by the reduction of local symmetry induced by the unsymmetrical isotope substitution. This situation is illustrated schematically in Figure 1. The superoxo species (2) would be expected to give a quartet of bands representing the four possibilities of isotopic

Matthew J. Almond was born at Blackburn, Lancashire in 1960. He obtained his B.Sc. from the University of Reading in 1981 then moved to the Inorganic Chemistry Laboratory of the University of Oxford. There he obtained his D.Phil. for spectroscopic studies of unstable species in low-temperature matrices. Two years of postdoctoral work were shared between the University of Oxford and the University of Münster (Germany), before, in 1986, he returned to Reading to take up a post as lecturer. He has published two books and almost 50 research papers. He is a Fellow and currently also a member of Council of The Royal Society of Chemistry.



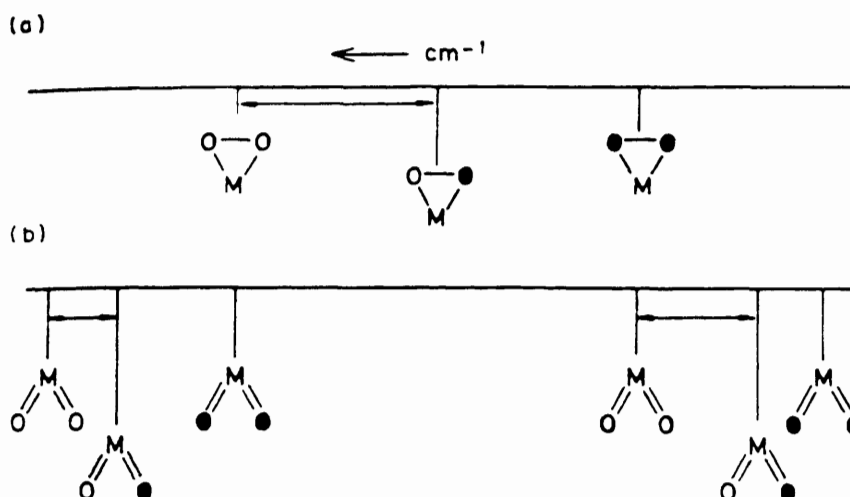


Figure 1 Predicted ^{18}O isotopic splitting patterns in the infrared spectra of (a) the $\nu(\text{O}-\text{O})$ band of a dioxigen complex and (b) the symmetric and antisymmetric $\nu(\text{M}=\text{O})$ bands of a bent dioxometal complex, assuming a scrambled 1:2:1 $^{16}\text{O}_2$: $^{16}\text{O}^{18}\text{O}$: $^{18}\text{O}_2$ mixture ($\circ = ^{16}\text{O}$, $\bullet = ^{18}\text{O}$). The horizontal arrows in (a) and (b) indicate that the $\Delta\nu(^{16}\text{O}_2-^{16}\text{O}^{18}\text{O})$ wavenumber spacing is equal to the $\Delta\nu(^{16}\text{O}^{18}\text{O}-^{18}\text{O}_2)$ spacing in (a) but not in (b). (Reproduced with permission from reference 15)

combinations of the $\eta\text{-O}-\text{O}$ unit, *i.e.* $\text{M}-^{16}\text{O}^{16}\text{O}$, $\text{M}-^{16}\text{O}^{18}\text{O}$, $\text{M}-^{18}\text{O}^{16}\text{O}$, and $\text{M}-^{18}\text{O}^{18}\text{O}$, although it must be said that the splitting of the two central features resulting from the mixed oxygen isotopomers may be quite small.

It is possible also to distinguish $\nu(\text{M}=\text{O})$ from $\nu(\text{O}-\text{O})$ vibrations by the magnitude of the shift in frequency when ^{16}O is replaced by ^{18}O . In the case of MO_2 (or indeed MO_3) units the wavenumber shift will depend upon the $\angle\text{OMO}$ bond angle.^{10, 12} The shift in position of $\nu_{\text{asym}}(\text{O}=\text{M}=\text{O})$ upon ^{18}O substitution gives an upper limit θ_u for this angle by the equation

$$\sin \frac{\theta_u}{2} = \frac{\{m(\text{X})[m(^{16}\text{O}) - m(^{18}\text{O})]R_1\}^{\frac{1}{2}}}{\{2(m(^{16}\text{O}))(m(^{18}\text{O}))(R_1 - 1)\}^{\frac{1}{2}}}$$

where $m(\text{X})$ is the mass of the appropriate metal atom and $R_1 = \{\nu(^{18}\text{O})/\nu(^{16}\text{O})\}^2$. This calculation gives an upper limit rather than a true value for the bond angle since the vibration is necessarily *anharmonic*. Similarly isotopic substitution of the metal atom (or observation of bands arising from isotopes of the metal atom in their natural abundance) gives a lower limit, θ_l , by

$$\sin \frac{\theta_l}{2} = \frac{\{m(^{\text{M}})(m(^{\text{M}}))(1 - R_2)\}^{\frac{1}{2}}}{\{2(m(\text{O}))[R_2(m(^{\text{M}})) - m(^{\text{M}})]\}^{\frac{1}{2}}}$$

where $R_2 = \{\nu(^{\text{M}})/\nu(^{\text{M}})\}^2$. Unfortunately the calculated values of θ become more sensitive to the precise value of the isotopic shift as the molecule approaches linearity.

It is also possible to approximate θ by measurement of the intensity ratio of infrared bands arising from ν_{asym} and $\nu_{\text{sym}}(\text{O}=\text{M}=\text{O})$

$$\frac{I_{\text{asym}}}{I_{\text{sym}}} = \tan^2(\theta/2) \frac{(m(\text{O}) + 2m(\text{M})\sin^2(\theta/2))}{(m(\text{O}) + 2m(\text{M})\cos^2(\theta/2))}$$

Likewise $(\text{C}-\text{M}-\text{C})$ angles of metal dicarbonyl moieties may be estimated by the simplified equation $I_{\text{asym}}/I_{\text{sym}} = \tan^2(\theta/2)$.

To characterize fully more complex metal carbonyl fragments requires experiments utilising isotopic substitution with ^{13}C or C^{18}O and careful fitting of the *positions* and *intensities* of the pattern of bands observed by means of force constant calculations generally involving the use of computer programs.

3 Matrix Reactions of the Group 6 Carbonyls with O_2

Photooxidation of the Group 6 binary carbonyls $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$) proceeds *via* oxocarbonyl intermediates, ultimately to yield binary oxide products. In each of these systems it has proved possible to generate selectively particular intermediates by specific wavelength photolysis. Thus more-or-less complete mechanisms for the photooxidation processes have been proposed. It is found that these pathways vary somewhat from metal to metal. When $\text{M} = \text{Cr}$ the principal oxocarbonyl intermediate observed is the molecule 'chromyl carbonyl' $\text{O}_2\text{Cr}(\text{CO})_2$ (5).¹⁰ Intensity measurements of the bands arising from ν_{sym} and ν_{asym} ($\text{Cr}(\text{CO})_2$) and isotopic shift calculations on $\nu_{\text{asym}}(\text{OCrO})$ have allowed the $\text{C}-\text{Cr}-\text{C}$ bond angle to be estimated as 118° and an upper limit for the $\text{O}=\text{Cr}=\text{O}$ angle has been set at 129° . This molecule is of interest as it was the first example of a chromium(IV) carbonyl compound yet it *appears* to be one of the most stable intermediates in the photooxidation of $\text{Cr}(\text{CO})_6$. Structure (5) shows ν_{asym} and $\nu_{\text{sym}}(\text{Cr}(\text{CO})_2)$ vibrations at 2125 and 2065 cm^{-1} , the high frequency of these features reflecting the limited ability of the metal centre to engage in back-donation to the π^* orbitals of CO when in a high oxidation state. The vibration $\nu_{\text{asym}}(\text{OCrO})$ gives rise to an infrared band at 981 cm^{-1} , which, as expected, yields an asymmetrical triplet when the molecule is generated from a scrambled mixture of the oxygen isotopomers. Continued photolysis causes loss of all coordinated CO groups (*nb* by-products of all of the photooxidation reactions discussed in this article are invariably 'free' CO and CO_2) and the formation of molecular CrO_2 .¹¹ CrO_2 has previously been made in low-temperature matrices by the reaction of Cr atoms (formed by sputtering) and O_2 .¹² Thus definitive characterization of our compound may be made by comparison with these spectra. Our photooxidation experiments allow facile ^{18}O isotopic substitution, hence the upper limit for the $\text{O}-\text{Cr}-\text{O}$ bond angle may be estimated as 117° .

When $\text{M} = \text{Mo}$ or W , analogues of 'chromyl carbonyl' are not seen as *major* intermediates. Rather the principal oxocarbonyl species seen here are the previously unknown complexes *trans*-dioxotetracarbonylmolybdenum(IV) and *trans*-dioxotetracarbonyltungsten(IV) (6).¹³ The square planar array of four CO groups is confirmed by isotopic substitution with ^{13}C . The linear $\text{O}=\text{M}=\text{O}$ moiety is demonstrated both by isotopic substitution with ^{18}O and by observation of splitting of the band arising from $\nu_{\text{asym}}(\text{O}=\text{M}=\text{O})$ due to the various isotopes of molybdenum in their natural isotopic abundance. In Figure 2 is illustrated the observed spectrum. Thus it can be seen that the observed molybdenum isotope splitting also allows confirmation of the dioxo rather than a monoxo formulation. The high symmetry of these molecules is reflected in the simplicity of their infrared spectra and in the non-coincidence of infrared and

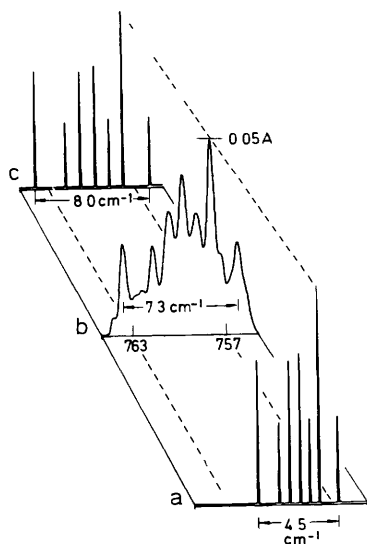
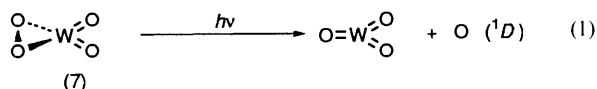


Figure 2 Observed and calculated Mo isotope structure in the IR absorption spectra of monooxo and dioxo species isolated in an O₂-doped CH₄ matrix at 20 K (a) calculated isotope frequency pattern for a monooxo species assuming the Mo=O group to be a simple harmonic oscillator, (b) observed molybdenum isotope structure for the 757 cm⁻¹ band of (6), (c) isotope pattern for a linear dioxo species calculated by using equation 2 with $\theta_{1/2} = 90^\circ$. The calculated spectra are depicted as stick plots with heights given by the relative natural abundances of the molybdenum isotopes (Reproduced with permission from reference 13)

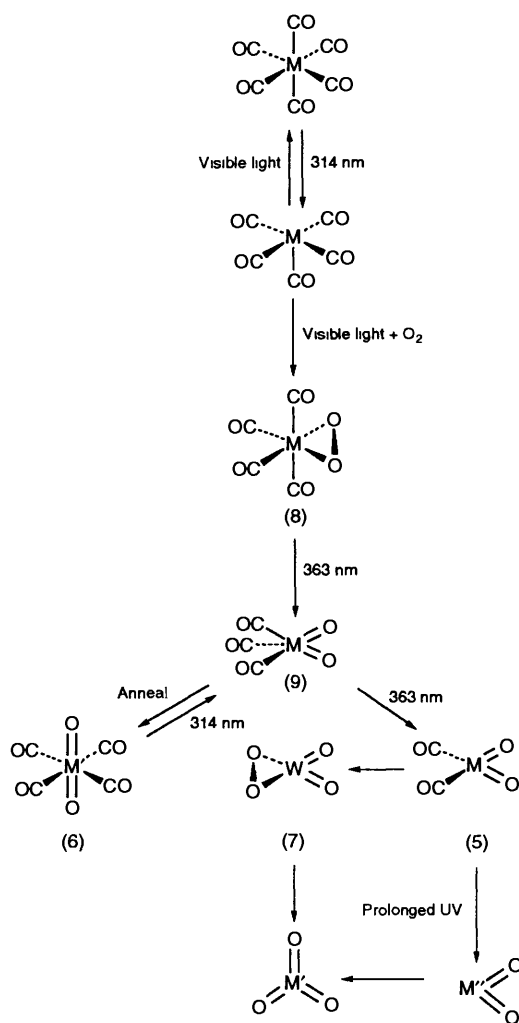
Raman bands Thus, when M = Mo, (6) shows an infrared-active $\nu(\text{CO})$ vibration at 2110 cm⁻¹ and a Raman-active $\nu(\text{CO})$ vibration at 2175 cm⁻¹ the symmetric and antisymmetric stretches of the linear O=Mo=O unit give rise to a Raman band at 820 and an infrared band at 758 cm⁻¹ respectively Spectra of the tungsten analogue are similar

Prolonged broad band photolysis of Mo(CO)₆ in O₂-doped Ar matrices leads to the formation of a mixture of MoO₂ and MoO₃¹³ By contrast, when W(CO)₆ is treated similarly, the final product is WO₃, but this is not produced from WO₂ Rather the precursor to WO₃ appears to be WO₂ unit coordinated to O₂ (7) which forms WO₃ by loss of an oxygen atom (equation 1) Evidence for the formation of oxygen atoms comes from experiments performed in (i) pure O₂, (ii) O₂-doped N₂, and (iii) O₂-doped CH₄ matrices Under these conditions, concomitant with the production of WO₃, are seen (i) O₃, (ii) N₂O, and (iii) methanol and formaldehyde¹³



All of these reactions of O atoms are known from gas-phase studies, the last three are typical of O atoms in the excited ¹D state

In order to establish the route by which these oxocarbonyl intermediates and oxide products are formed, and to gain an understanding of the overall reaction mechanism, experiments utilising narrow band photolysis and isotopic substitution were employed Thus the reaction mechanism given in Scheme 1 may be proposed¹⁵ The reaction is initiated by loss of CO from M(CO)₆ to yield the 16-electron species M(CO)₅¹⁵ A common intermediate in these reactions is (O₂)M(CO)₄ (8) which contains a peroxo unit with an intact O—O bond Each of these molecules shows an infrared-active $\nu(\text{O—O})$ vibration and the frequency of this mode decreases as the mass of the metal increases thus when M = Cr, $\nu(\text{O—O}) = 995.2 \text{ cm}^{-1}$, M = Mo, $\nu(\text{O—O}) = 954.0 \text{ cm}^{-1}$, M = W, $\nu(\text{O—O}) = 914.0 \text{ cm}^{-1}$ This



M = Cr, Mo, or W, M' = Mo or W only, M'' = Cr or Mo only

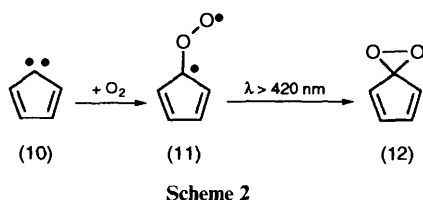
Scheme 1

sequence reflects presumably not only the effect of the mass of the metal upon the $\nu(\text{O—O})$ vibration but also the increased capacity of the heavier metals to donate electronic charge to the π^* orbitals on the O₂ group These peroxo species each yield, upon near-UV photolysis, (O₂)M(CO)₃ (9) where the O—O bond has been cleaved Compound (9) may in turn act as a precursor to (O₂)₂M(CO)₂ (5) or *trans*-(O₂)M(CO)₄ (6) by loss or uptake of CO

4 Photooxidation of Fe(CO)₅ and Ni(CO)₄ in Low-temperature Matrices

Photooxidation of Fe(CO)₅ in low-temperature matrices is initiated in the same way as photooxidation of the Group 6 hexacarbonyls *ie* by loss of CO from the parent carbonyl, to yield the corresponding unsaturated 16-electron species, in this case Fe(CO)₄¹⁶ Fe(CO)₄ differs from M(CO)₅ (M = Cr, Mo, or W) in having a triplet as opposed to a singlet ground-state It has been noted that unsaturated metal carbonyl fragments are related to the divalent carbon compound carbenes by the so-called 'isolobal relationship'¹⁷ (*nb* two molecular fragments are said to be *isolobal* if the number, symmetry properties, shapes, and approximate energies of their frontier orbitals are the same) Like Fe(CO)₄, carbenes have triplet ground-states Thus it was hoped that some similarities might be found between the chemistry of Fe(CO)₄ and of carbenes in low-temperature matrices containing O₂ The carbene cyclopentadienylidene (10), under these conditions, is known to yield an end-bonded

adduct with O₂ (11) which upon visible photolysis is isomerized to a side-bonded form (12) (Scheme 2).^{18,19}



Fe(CO)₄ forms a side-bonded, peroxo, adduct (13).²⁰ This complex shows an intriguing example of Fermi resonance between the $\nu(\text{O}-\text{O})$ fundamental and the first overtone of the $\nu_{\text{sym}}(\text{FeO}_2)$ fundamental. Thus two bands, rather than the expected single feature, are seen in the region of the IR spectrum associated with the $\nu(\text{O}-\text{O})$ vibration *vide infra*. These features are seen at 914 and 885 cm⁻¹. It can be shown by experiments involving ¹⁸O that these bands do indeed arise from a $\nu(\text{O}-\text{O})$ vibration rather than from ν_{sym} and ν_{asym} vibrations of an O=Fe=O unit. Thus the magnitude of the ¹⁶O-¹⁸O shift is too large for a dioxo unit and the intensity ratio of the two bands reverses upon ¹⁸O-substitution. This latter phenomenon (see Figure 3) is only explicable in terms of Fermi resonance. A similar effect has been observed for the O₂ adduct oxyhaemoglobin (almost certainly end-bonded O₂) where Fermi resonance is

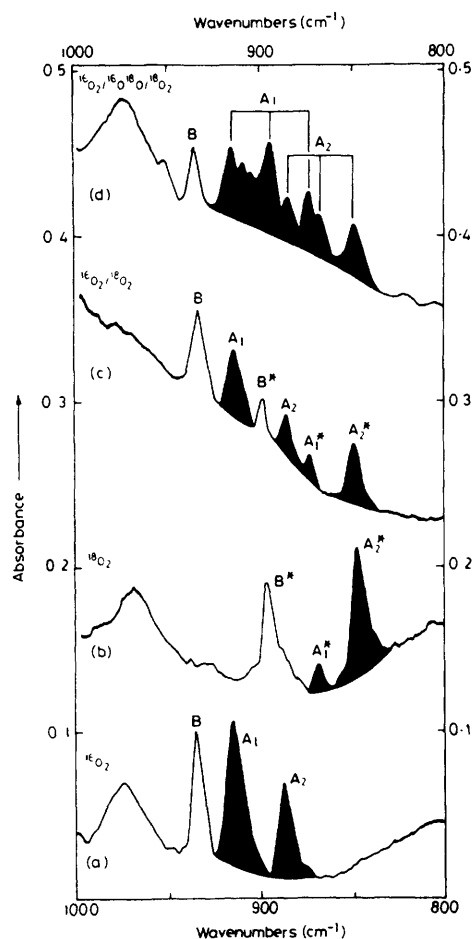
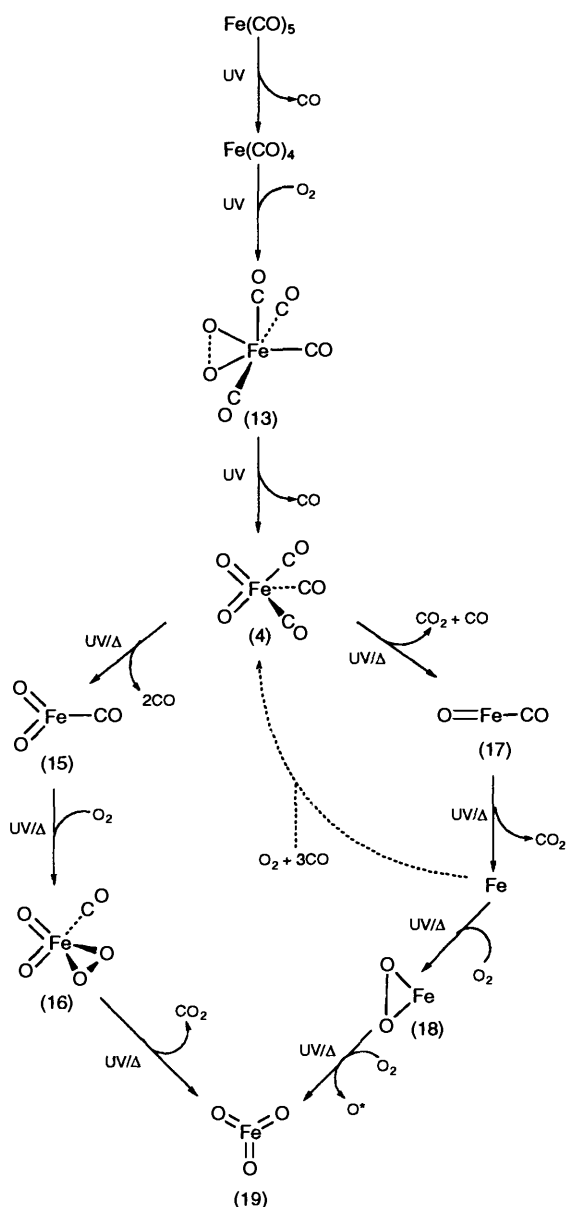


Figure 3 IR spectrum of (13) in the region 800–1000 cm⁻¹ (bands marked by black infilling are due wholly or mainly to (13): (a) for a sample generated from ¹⁶O₂; (b) for a sample generated from ¹⁸O₂; (c) for a sample generated from a mixture of ¹⁶O₂ and ¹⁸O₂ (¹⁶O₂:¹⁸O₂ = 3:2); (d) for a sample generated from a mixture of ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂ (¹⁶O₂:¹⁶O¹⁸O:¹⁸O₂ = 1:2:1). The subscripts 1 and 2 are used to denote the two distinct bands due to (13) and the asterisks to denote bands due to Fe¹⁸O species.

(Reproduced with permission from reference 20.)



Scheme 3

seen between the $\nu(\text{O}-\text{O})$ fundamental and the first overtone of the $\nu(\text{Fe}-\text{O}_2)$ fundamental.

Continued near-UV irradiation causes the decay of (13) and the growth and decay of a number of oxocarbonyl intermediates [(14)–(17)]. Photolysis proceeds by rupture of the O–O bond and loss of CO. Unfortunately this system displays little photo-selectivity: thus it is difficult to build up large concentrations of specific intermediates. However, these molecules have been characterized more-or-less certainly and the pathway given in Scheme 3 has been proposed for the photo-oxidation of matrix-isolated Fe(CO)₅.

The final products of this reaction are the binary oxides ($\eta^2\text{-O}_2$)Fe (18) and FeO₃ (19).²¹ Compound (18) had previously been made by reaction of Fe atoms and O₂. FeO₃ had not previously been observed although its infrared band at 945 cm⁻¹, which is assigned to $\nu_{\text{asym}}(\text{FeO}_3)$, is in an almost identical position to a band previously ascribed to matrix-isolated FeO₂.^{22–23} There has been some uncertainty regarding the probable structure of this ‘FeO₂’ molecule with either the peroxo ($\eta^2\text{-O}_2$)Fe or dioxo (FeO₂) forms being proposed. More recent reports favour the dioxo formulation.²³ The spectra shown in Figure 4, in which the isotopes ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂ have

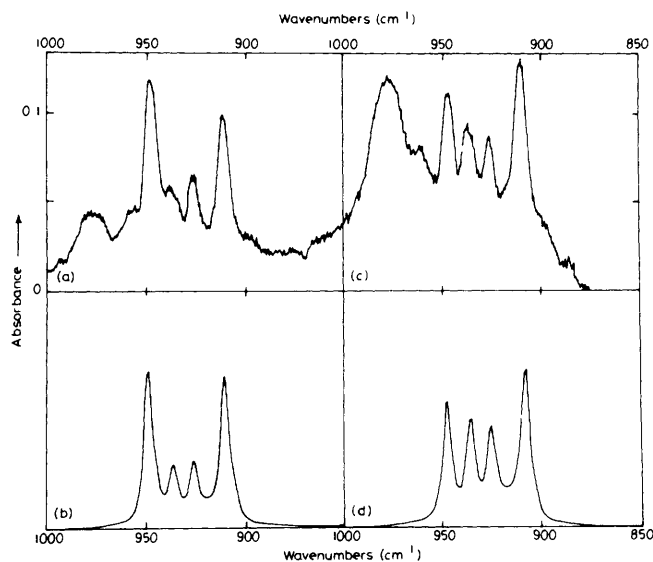


Figure 4 IR spectrum of matrix-isolated (19) in the region 850–1000 cm^{-1} (a) spectrum observed for the product generated from $\text{Fe}(\text{CO})_5$ and an equimolar mixture of $^{16}\text{O}_2$ and $^{18}\text{O}_2$, (b) spectrum predicted for ν_3 of a planar FeO_3 molecule with D_{3h} symmetry (c) spectrum observed for the product generated from $\text{Fe}(\text{CO})_5$ and $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ in the statistical proportions 1 2 5 1 2, (d) spectrum predicted for ν_3 of a planar FeO_3 molecule with D_{3h} symmetry. In each case the matrix had the composition $\text{Ar O}_2 \text{Fe}(\text{CO})_5 = ca 1000 50 1$ and was maintained at $ca 20 \text{ K}$. Photolysis was at $\lambda = ca 213 \text{ nm}$ for 300 min and then at $\lambda = 290\text{--}370 \text{ nm}$ for 360 min. Calculations were based on an energy-factored force field for the $\nu(\text{Fe}=\text{O})$ modes (Reproduced with permission from reference 21)

been utilised to generate the various ^{16}O and ^{18}O isotopomers of (19), leave little doubt, however, that (19) is not any form of FeO_2 but rather FeO_3 with planar D_{3h} symmetry

5 $\text{V}(\text{CO})_6$

$\text{V}(\text{CO})_6$ is unique amongst simple binary metal carbonyls in being a paramagnetic 17-electron compound. Oxo-vanadium species exhibit an extremely complex chemistry, including a wide range of peroxides such as the orthovanadate ion $[\text{O}_2\text{V}(\eta^2\text{-O}_2)]^{3-}$ and the peroxovanadium cation $[\text{V}(\eta^2\text{-O}_2)]^{3+}$. As such there is an interest in studying the photooxidation of matrix-isolated $\text{V}(\text{CO})_6$ in order to search for novel oxo or peroxy compounds of vanadium and to compare the results with those obtained for the diamagnetic metal carbonyls.

The first step in the photooxidation of $\text{V}(\text{CO})_6$ in a low-temperature matrix is entirely analogous to that in the photooxidation of $\text{Fe}(\text{CO})_5$ or $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$), *i.e.* loss of CO to generate $\text{V}(\text{CO})_5$. The reaction, however, is extremely rapid when broad-band UV-visible photolysis is employed: all of the $\text{V}(\text{CO})_6$ is consumed after $ca 20\text{--}60$ minutes' photolysis (the exact time depending upon the concentration of O_2 in the matrix). It is perhaps for this reason that it is remarkably difficult to identify intermediate oxocarbonyl species in this system. Moreover, the reaction scheme shows little photosensitivity, thus, even by utilising narrow-band filters, it proved impossible to characterize unambiguously any of the reaction intermediates. The speed of reaction does, however, facilitate the build up of a large yield of the final oxide product in a relatively short time. The product shows four infrared-active vibrations at 1129.0, 969.5, 960.0, and 563.5 cm^{-1} .²⁴ Experiments utilising mixtures of the dioxygen isotopes including $^{16}\text{O}^{18}\text{O}$ and $^{18}\text{O}_2$ (Figure 5) show that this product is either the anionic species (20) or the neutral compound (21). Although the symmetrical *triplet* of bands seen in place of the single band at 1129.0 cm^{-1} when the three $^{16}\text{O}/^{18}\text{O}$ isotopes are utilised might point towards (20) as the most likely structure, on a balance of

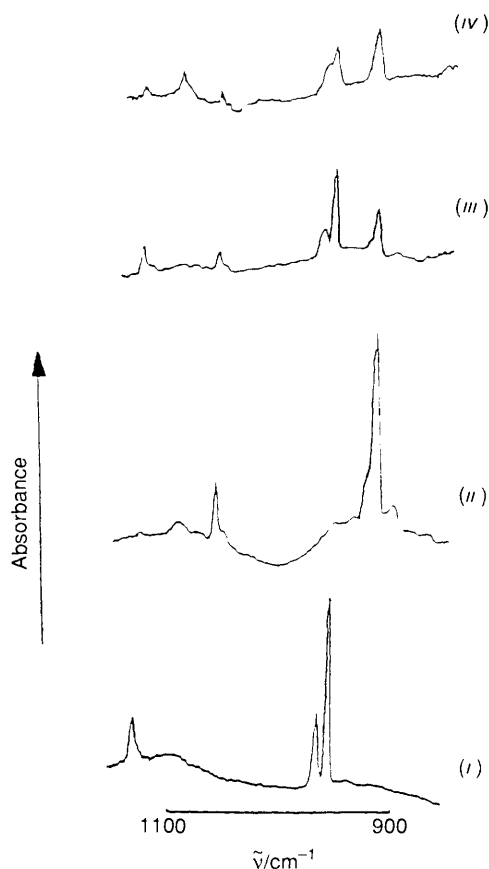
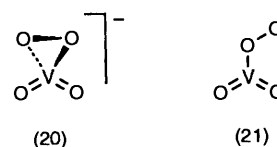


Figure 5 The region 850–1150 cm^{-1} of the infrared absorption spectra of matrices (20 K) after broad-band UV/VIS photolysis for 20 min (i) initial matrix composition $[\text{V}(\text{CO})_6]^{16}\text{O}_2 \text{Ar} = ca 1 100 1000$ (ii) initial matrix composition $[\text{V}(\text{CO})_6]^{18}\text{O}_2 \text{Ar} = ca 1 100 1000$ (iii) initial matrix composition $[\text{V}(\text{CO})_6]^{16}\text{O}_2 \text{Ar} = ca 1 50 50 1000$, (iv) initial matrix composition $[\text{V}(\text{CO})_6]^{16}\text{O}_2 \text{Ar} = ca 1 25 50 25 1000$ (Reproduced with permission from reference 24)

all the experimental evidence (21) is favoured. The $\text{O}=\text{V}=\text{O}$ bond angle is calculated, by isotopic shift and intensity measurements, to be in the range 108–115°.



6 $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, and $\text{Co}_2(\text{CO})_8$

The photochemistry of binuclear metal carbonyls is always likely to be more complex than that of the analogous mononuclear derivatives since more potential primary photochemical steps, and hence more photochemical pathways, exist. The binuclear carbonyls $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ both have $\text{M}-\text{M}$ bonded structures with no bridging CO groups. As such, the two most likely primary photochemical steps are (i) loss of a CO group to yield $\text{M}_2(\text{CO})_9$ ($\text{M} = \text{Mn}$ or Re), or (ii) cleavage of the $\text{M}-\text{M}$ bond to form two $\text{M}(\text{CO})_5$ radicals.

Photolysis of $\text{Mn}_2(\text{CO})_{10}$ in matrices containing O_2 results in the rapid formation of the binary oxide Mn_2O_7 .²⁵ This is a complex photochemical reaction involving at least four molecules of O_2 , the loss of all ten carbonyl groups, the breaking of the $\text{Mn}-\text{Mn}$ bond of the starting material, and the formation of an $\text{Mn}-\text{O}-\text{Mn}$ bridge. Unfortunately, little can be concluded regarding the *mechanism* of the reaction since no intermediate

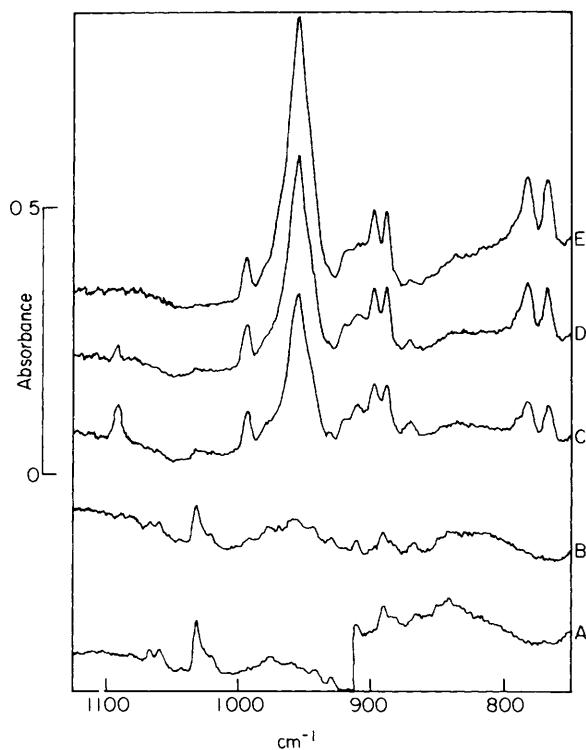
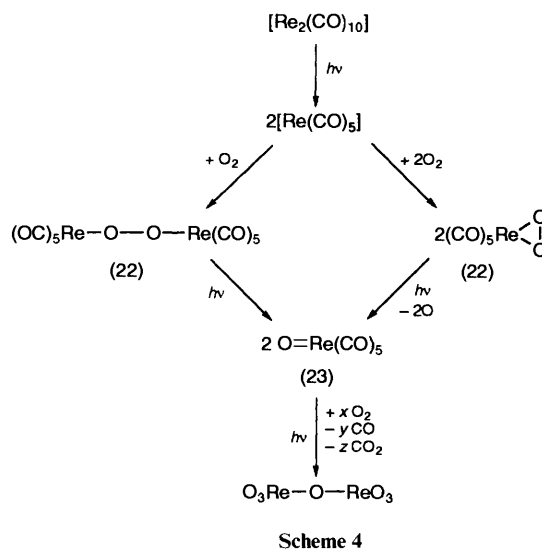


Figure 6 IR absorption spectra in the region 750–1100 cm^{-1} of a matrix initially containing $\text{Mn}_2(\text{CO})_{10}$, $^{16}\text{O}_2$, and Ar in the approximate proportions 1/100/2000. A, after deposition at 12 K. B, after 20 min broad-band UV/VIS photolysis. C, after 150 min broad-band UV/VIS photolysis. D, after 220 min broad-band UV/VIS photolysis. E, after 400 min broad-band UV/VIS photolysis. (The spectra show the build-up of absorptions due to Mn_2O_7 .) (Reproduced with permission from reference 25.)

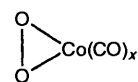
can clearly be identified. As with $\text{V}(\text{CO})_6$ the photolysis is rapid and non-specific. Although a low yield of $\text{Mn}_2(\text{CO})_9$ is formed (then consumed) at an early stage of the reaction it is not clear whether or not this represents the primary photoproduct in the oxidation pathway. There is no sign of the species $(\eta^1\text{-O}_2)\text{Mn}(\text{CO})_5$ which has been detected by ESR spectroscopy upon condensation of $\text{Mn}_2(\text{CO})_{10}$ vapour at 77 K.²⁶ This result is perhaps not too surprising when it is borne in mind that the ESR technique is much more sensitive than is infrared spectroscopy, thus a radical formed at low yield may well escape detection by infrared measurements whilst giving rise to intense signals in the ESR spectrum. The infrared spectra illustrated in Figure 6 show the formation of Mn_2O_7 from $\text{Mn}_2(\text{CO})_{10}$ in an O_2 -doped (5%) Ar matrix.

Although the photooxidation of $\text{Re}_2(\text{CO})_{10}$ is also non-specific²⁷ the reaction does proceed much more slowly than that of the congener $\text{Mn}_2(\text{CO})_{10}$. Thus more definite conclusions regarding reaction mechanism may be drawn. The reaction product is Re_2O_7 . It is formed *via* two detectable oxocarbonyl intermediates. Both appear to contain $\text{Re}(\text{CO})_5$ units and they are believed to adopt the structures (22) (*n b* two structures have been proposed for this species – see Scheme 4 – either of which, on the basis of the experimental evidence, would appear to be equally plausible) and (23). Experiments using filtered photolysis suggest that the reaction is initiated by Re–Re rather than Re–C bond rupture. Although this is a well-known primary photoreaction in solution it is less common in solid matrices since the ‘matrix cage effect’ suppresses the formation of the $\text{M}(\text{CO})_5$ radical. In an O_2 -containing matrix, however, the cage effect may be overcome if the radicals once formed react rapidly with O_2 . A plausible mechanism (albeit only showing some of the reaction steps) for the formation of Re_2O_7 from $\text{Re}_2(\text{CO})_{10}$ is given in Scheme 4.

The photochemical oxidation of $\text{Co}_2(\text{CO})_8$ is likely to follow



an extremely complex mechanism. As well as competition between Co–Co and Co–C bond cleavage there have been identified three separate isomers of $\text{Co}_2(\text{CO})_8$ in matrices and these are known to interconvert photochemically. In the event the photooxidation of $\text{Co}_2(\text{CO})_8$ provides a rather curious result which is not in keeping with the findings obtained for the other binary carbonyls reported here. Two oxocarbonyls are formed, these are $(\eta^2\text{-O}_2)\text{Co}(\text{CO})_x$ ($x = 1$ or 2) (24).²⁸ Identification of these products is possible because the same compounds are formed when Co atoms are reacted with CO/O_2 mixtures at 10–12 K.²⁹ The only other molecule to be seen is the non-CO-bridged species $\text{Co}_2(\text{CO})_7$. There is no sign of any mononuclear *binary* cobalt carbonyl nor of the species $(\eta^1\text{-O}_2)\text{Co}(\text{CO})_4$ which, like $(\eta^1\text{-O}_2)\text{Mn}(\text{CO})_5$ has been detected by ESR spectroscopy.²⁶ Nor, intriguingly, was there any sign of a binary cobalt oxide product.



(24) ($x = 1$ or 2)

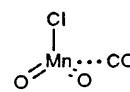
7 $\text{Mn}(\text{CO})_5\text{Cl}$ and $\text{Re}(\text{CO})_5\text{Cl}$

It is clear from the above discussion that photooxidation of matrix-isolated binary metal carbonyls is an excellent method to generate isolated *molecular* metal oxides. The logical progression of the work was to investigate whether or not it is possible to form *ternary* species such as oxohalides in the same way.

When the carbonyl halide $\text{Re}(\text{CO})_5\text{Cl}$ is subjected to photolysis in O_2 -doped argon matrices a product (25) is formed which shows an infrared absorption of medium intensity at 971 cm^{-1} together with weak bands at 1004 and 435 cm^{-1} .³⁰ After *ca* 4 hours' broad-band irradiation all of the starting material has been consumed and, alongside (25) the only other matrix ingredients are free CO and CO_2 . The infrared spectrum of (25) shows a marked similarity to that of the molecule ReO_3Cl which has previously been studied in low-temperature matrices. The behaviour of the band 971 cm^{-1} (which is assigned to the degenerate asymmetric stretch of the ReO_3 unit) upon isotopic substitution with ^{18}O supports this assertion. The weak band at 1004 cm^{-1} is assigned to $\nu_{\text{sym}}(\text{ReO}_3)$ and that at 435 cm^{-1} to $\nu(\text{Re–Cl})$. Unfortunately no isotopic shift data (^{16}O – ^{18}O or ^{35}Cl – ^{37}Cl) could be obtained for these very weak features.



(25)



(26)

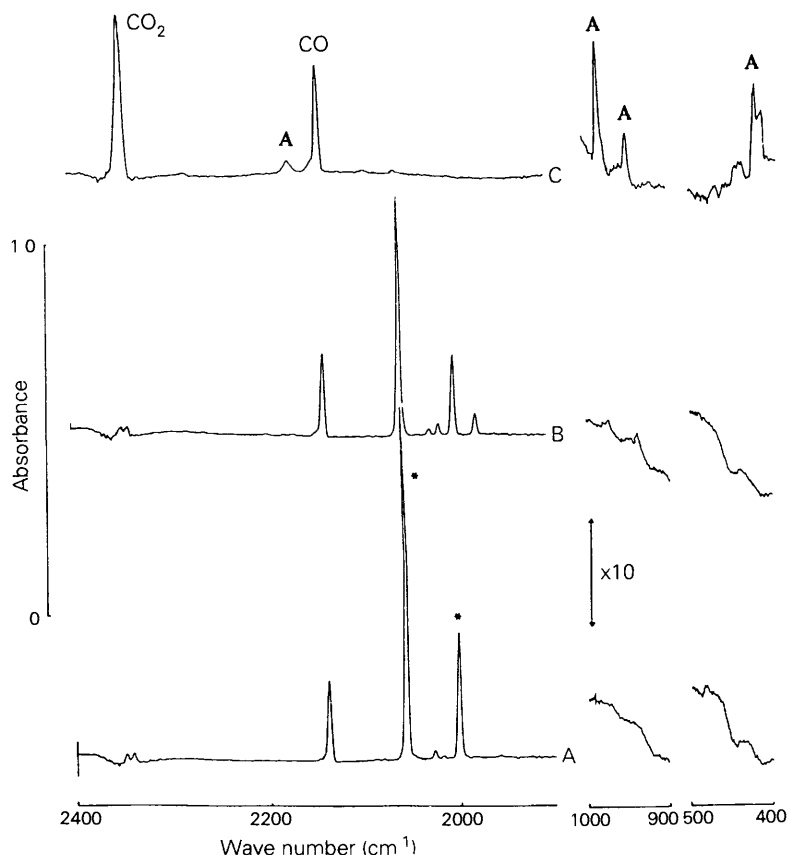


Figure 7 IR absorption spectra of a matrix (20 K) initially composed of $\text{Mn}(\text{CO})_5\text{Cl}$, O_2 , and Ar in the approximate proportions 1 250 1000 (A) after spray-on, (B) after 10 min broad-band UV/VIS photolysis, (C) after 110 min broad-band UV/VIS photolysis. Bands marked A are assigned to $\text{MnO}_n\text{Cl}\cdots\text{CO}$ and those marked * are due to $\text{Mn}(\text{CO})_5\text{Cl}$ (Reproduced with permission from reference 30)

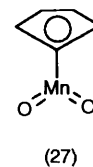
The molecule $\text{Mn}(\text{CO})_5\text{Cl}$ is also readily photooxidized under these conditions, generating free CO and CO_2 and a product (26) which shows infrared absorptions at 2171 (weak intensity), 976 (medium), 938 (weak), and 416/408 cm^{-1} (weak). From these infrared data it is clear that (26) is not MnO_3Cl , since this molecule, when isolated in an argon matrix, shows ν_{asym} and ν_{sym} (MnO_3) at 951.9 and 889.9 cm^{-1} and $\nu(\text{Mn}-\text{Cl})$ at 459 (^{35}Cl) and 453 (^{37}Cl) cm^{-1} .³¹ Isotopic substitution experiments involving ^{18}O show that the features at 976 and 938 cm^{-1} arise from ν_{asym} and ν_{sym} (MnO_2) vibrations while the separation of the low-frequency band into two components at 416 and 408 cm^{-1} suggest that it arises from a $\nu(\text{Mn}-\text{Cl})$ vibration where the splitting is caused by the presence of the isotopes ^{35}Cl and ^{37}Cl in their natural abundance. The absorption at 2171 cm^{-1} shifts to low frequency upon substitution with ^{13}CO , it is thus presumed to belong to a co-ordinated CO group. The high frequency is typical for a group where the CO moiety is behaving essentially as a σ -donor. Compound (26) is thus likely to be the species $\text{MnO}_2\text{Cl}\cdots\text{CO}$, infrared spectra of (26) are illustrated in Figure 7.

8 $\text{CpMn}(\text{CO})_3$, $\text{CpRe}(\text{CO})_3$, and $\text{CpV}(\text{CO})_4$

There has been some interest of late in the so-called organometallic oxides of rhenium, especially MeReO_3 , CpReO_3 , and Cp^*ReO_3 (where $\text{Cp} = \eta\text{-C}_5\text{H}_5$ and $\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$) as such species have been implicated as useful catalysts for a range of important chemical processes including olefin oxidation, metathesis, and polymerization.⁶⁻⁸ One aim of our current research is to extend our matrix photooxidation experiments to

generate organometallic oxides which are not stable under normal conditions. Our starting point was the oxidation reaction of cyclopentadienylmanganese tricarbonyl $\text{CpMn}(\text{CO})_3$.

It is found that broad-band irradiation of this compound when isolated in an O_2 -doped Ar matrix causes the formation of a product (27) which shows infrared bands which may be assigned to motion of the cyclopentadienyl ring at 1421, 1020, 1006, 820.5, and 793.5 cm^{-1} . In addition two bands are seen at 938 and 893 cm^{-1} which isotopic substitution experiments with ^{18}O show to arise from ν_{asym} and ν_{sym} (MnO_2) vibrations. (27) is thus believed to be CpMnO_2 .³² The spectra illustrated in Figure 8 show the appearance and growth of features associated with (27). There is no sign of any further oxidation of the cyclopentadienyl group under the conditions of this experiment.



$\text{CpRe}(\text{CO})_3$ behaves, under similar conditions, in a rather different way. It is oxidized very slowly, the bands associated with the starting compound are seen to disappear only after 25 hours' broad-band photolysis of the material in a pure- O_2 matrix. Here there is no sign of any oxidized product which contains a coordinated Cp group. Rather, the two most prominent features in the infrared spectrum of the photolysed matrix are at 966 and 891 cm^{-1} , together with a much weaker band at 815 cm^{-1} . When $\text{CpRe}(\text{CO})_3$ is replaced by $\text{Cp}^*\text{Re}(\text{CO})_3$ as the starting material photolysis proceeds even more slowly, bands due to the starting material are still visible (though weak) after 66 hours' broad-band photolysis in a pure- O_2 matrix. In this case the photolysed matrix shows, in the $\text{Re}=\text{O}$ stretching region, bands of medium intensity at 965, 925, and 898 cm^{-1} and a weak band at 815 cm^{-1} . There is also some evidence for bands

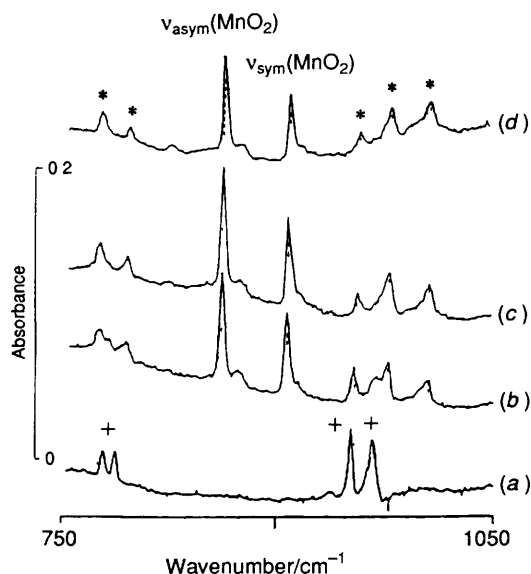
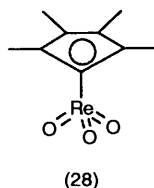


Figure 8 The region 750–1050 cm^{-1} of the IR absorption spectrum of a matrix initially composed of $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$, O_2 and Ar in the approximate proportions 1 250 1000, (a) after deposition at 20 K, (b) after 30 min of broad-band UV/VIS irradiation, (c) after 120 min of such irradiation, and (d) after 260 min of such irradiation. Bands marked + arise from vibrations of the cyclopentadienyl ring of the starting material, while those marked * arise from vibrations of the cyclopentadienyl ring of (28). (Reproduced with permission from reference 32)

due to a coordinated Cp^* group in one of the products. Interestingly the bands at 965 and 815 cm^{-1} appear only at high O_2 concentrations, they are not seen in a 20% O_2 -doped argon matrix. One possible explanation is that these last two absorptions arise from the molecule Re_2O_7 . The feature at 898 cm^{-1} is close to the reported position of $\nu_{\text{asym}}(\text{ReO}_3)$ of the molecule Cp^*ReO_3 (28) in solution. Compound (29) is a likely product of this photooxidation reaction, it is known that (28) is formed from $\text{Cp}^*\text{Re}(\text{CO})_3$ upon photolysis in the presence of O_2 in solutions containing tetrahydrofuran. The origin of the feature at 925 cm^{-1} remains unclear. Thus a possible photooxidation route for the organometallic compounds $\text{CpRe}(\text{CO})_3$ and $\text{Cp}^*\text{Re}(\text{CO})_3$ emerges, in which the initial process yields the organometallic oxide (28) then further reaction results in oxidation of the organic group to produce Re_2O_7 .



$\text{CpV}(\text{CO})_4$ is oxidized rapidly under similar conditions and although it is clear that a number of oxo-metal species are generated it has not, so far, proved possible to characterize any of these unequivocally. There is, however, evidence for the formation of the peroxo-compound $\text{Cp}^*\text{V}(\text{CO})_3(\text{O}_2)$ when $\text{Cp}^*\text{V}(\text{CO})_4$ is photolysed in O_2 -doped argon matrices.³³

9 Use of Alternative Oxidants

So far few experiments have been carried out in which oxidants other than O_2 itself are utilised. The only report concerns the use of N_2O and CO_2 as oxidants for the Group 6 carbonyls $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}$ or W).³⁴ Here photolysis proceeds more slowly than when O_2 is the oxidant. Ultimately, binary metal oxides are

formed and it appears that photolysis proceeds, first *via* loosely-bound complexes $\text{X}\cdots\text{M}(\text{CO})_5$ ($\text{X} = \text{OCO}$ or N_2O) and then through monoxo-metal species of the type $\text{O}=\text{M}(\text{CO})_5$. It is clear that this area is ripe for further experimentation. In particular, points to be addressed are the possible roles of O atoms alongside O_2 molecules in the oxidation process, and whether-or-not the oxidation reaction is affected by the *electronic state* of the O atoms.

10 Conclusions

Matrix isolation is an excellent method for monitoring photo-oxidation reactions. This approach has allowed a number of binary metal oxide species to be synthesized and characterized, and has recently been extended to some ternary compounds. It is clear that there are many more systems which could be investigated in this way, *e.g.* the range of organometallic oxides (of the type CpMnO_2) could be enlarged and the work could be extended to the main group organometallics such as Me_3Ga and Me_2Zn .

It is instructive to consider briefly the results described above. One equation to answer is *to what extent does the thermodynamic stability of the oxides dictate what products are formed?* When the Group 6 hexacarbonyls are considered a clear and entirely expected trend emerges. Thus $\text{Cr}(\text{CO})_6$ is oxidized to CrO_2 (Cr in the +IV oxidation state), $\text{Mo}(\text{CO})_6$ gives a mixture of MoO_2 (Mo^{IV}) and MoO_3 (Mo^{IV}), while $\text{W}(\text{CO})_6$ gives WO_3 (W^{VI}) *via* $(\text{O}_2)\text{WO}_2$ (also W^{VI}). This sequence would appear to reflect the greater ease of oxidation to high oxidation states of the heavier transition metals. Likewise the highest oxidation state product observed upon photooxidation of $\text{Fe}(\text{CO})_5$ contains Fe^{VI} . Thus it is perhaps surprising to find that $\text{Mn}_2(\text{CO})_{10}$ is readily oxidized to give the manganese(VII) compound Mn_2O_7 . When oxidation of the ternary compounds $\text{CpM}(\text{CO})_5$ and $\text{Cp}^*\text{M}(\text{CO})_3$ ($\text{M} = \text{Mn}$ or Re) is considered it is found that manganese is oxidized only to the (unusual) +V state whereas rhenium gives the +VII state. Naturally a consideration of thermodynamic stability tells us little or nothing about the *rate* of oxidation. Thus, as a general observation, we find that matrix-isolated rhenium compounds are invariably oxidized more slowly than their manganese analogues. However, it is important to bear in mind that one of the overriding factors in many of these reactions may simply be the match between output of the photolysis source and absorption bands of reactants and intermediates.

It is presumably a similar point which dictates whether or not a range of intermediates are seen in these reactions. The Group 6 hexacarbonyls show a high degree of photoselectivity, thus several different intermediates may be built up selectively by photolysis at different wavelengths. The $\text{Fe}(\text{CO})_5$ system shows little wavelength selectivity, but it is possible to build up intermediates by carefully controlling the time of photolysis. By contrast $\text{V}(\text{CO})_6$ and $\text{Mn}_2(\text{CO})_{10}$ which are oxidized very rapidly, give only fleeting glimpses of any possible intermediate species. Presumably those systems where absorption bands of reactants and intermediates overlap will give only low concentrations of intermediates. Certainly this would appear to be the case for the $\text{Fe}(\text{CO})_5$ reaction where quite extensive UV-visible spectroscopic measurements have been made, and have shown that absorption bands of reactant and intermediates do indeed overlap.

Lastly we may comment that the matrix isolation technique allows us to trap unusual molecules which would not be stable under normal conditions and we may thus compare the structure and bonding of these species with known molecules. To take selected examples first, the molecule $\text{O}_2\text{M}(\text{CO})_4$ ($\text{M} = \text{Mo}$ or W) adopts the *trans* configuration. For a d^2 system of this type, simple molecular orbital considerations suggest that the *trans* isomer should be more stable than the *cis* and it is found that other similar, but stable, d^2 species also adopt a *trans* configuration, *e.g.* $[\text{O}_2\text{Re}(\text{CN})_4]^{3-}$. Secondly, it is shown that the same oxide products are often obtained by oxidation of the

metal carbonyl as by reaction of metal atoms with O_2 , thus it might be appropriate to consider the metal carbonyls, under photolysis conditions, simply as sources of isolated reactive metal atoms. Upon photooxidation of $Co_2(CO)_8$ the same intermediate oxocarbonyl species are observed as when Co atoms are reacted with CO/O_2 mixtures. Thirdly, it is of interest to consider some of the metal peroxides which have been generated in the work discussed above. The peroxo-iron complex $(O_2)Fe(CO)_4$ shows spectral similarities to known peroxo-iron porphyrin complexes and even to oxyhaemoglobin itself.³⁵ Moreover, the similarity between this peroxo-iron product and the organic peroxides species obtained upon oxidation of the cyclopentadienylidene radical may be explained in terms of the isobal theory which suggests that there should be similarities in the chemistry of $Fe(CO)_4$ and C_5H_5 : When the Group 6 compounds $(O_2)M(CO)_4$ ($M = Cr, Mo, \text{ or } W$) are considered it is seen that the position of the infrared absorption arising from $\nu(O-O)$ follows a sequence which suggests increased back-donation to the $O_2 \pi^*$ orbital from the metal as the group is descended. This is entirely in line with infrared spectroscopic and single-crystal diffraction measurements for various sequences of transition metal peroxides where the O—O bond is seen to weaken and lengthen as the group is descended.³⁶ One last point is that this approach of matrix photooxidation allows some materials, which are hazardous under normal conditions, to be generated in small quantities and studied spectroscopically entirely in safety. Thus Mn_2O_7 , which is a highly explosive oil, and quite difficult to handle ordinarily,³⁷ may conveniently be produced by photooxidation of $Mn_2(CO)_{10}$ in a low-temperature matrix.

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