Photo-oxidation of $[Re_2(CO)_{10}]$ in Low-temperature Matrices containing O_2*

Matthew J. Almond and Rachel H. Orrin
Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, UK

Photo-oxidation of $[Re_2(CO)_{10}]$ isolated in low-temperature matrices containing O_2 generates, alongside free CO and CO_2, the binary oxide Re_2O_7. The reaction appears to be initiated by Re–Re bond cleavage and proceeds *via* at least two detectable oxorhenium carbonyl species. Infrared spectroscopic studies, including isotopic substitution with ^{18}O and ^{13}C, suggest that these intermediates are most likely to be $(OC)_5Re-O-O-Re(CO)_5$ and $O{=}Re(CO)_5$.

Photolysis of metal carbonyl molecules trapped in low-temperature matrices containing O_2 has proved to be a convenient route for preparing matrix-isolated molecular metal oxides. Thus, photo-oxidation of $[Cr(CO)_6]$ yields CrO_2,[1] while $[Mo(CO)_6]$ gives rise to a mixture of MoO_2 and MoO_3,[2] and the final product of photo-oxidation of $[W(CO)_6]$ is WO_3.[2] In all of these cases various oxocarbonyl intermediates have been identified and spectroscopically characterized. These species have both oxygen, in one form or another, and CO co-ordinated to the metal centre.[3,4] Thus it has been possible to propose a more-or-less complete scheme for the photo-oxidation of $[M(CO)_6]$ (M = Cr, Mo or W) in O_2-doped matrices. Similar experiments have also been performed for matrix-isolated $[Fe(CO)_5]$[5] and $[Ni(CO)_4]$.[6]

Recently we turned our attention to the analogous reactions of the binuclear metal carbonyls $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$. Here the reactions are likely to be somewhat more complex. Thus, for example, the first stage of the process could be either M–M (M = Mn or Re) or M–C bond rupture.[7] In our preliminary studies[8] we found that the final product of photo-oxidation of $[Mn_2(CO)_{10}]$ was Mn_2O_7 but we could not identify any oxocarbonyl intermediate molecules and thus could derive no mechanistic information about this reaction.

In this paper we report our experiments on the Group VII analogue $[Re_2(CO)_{10}]$. We hoped to be able to answer two major questions. First, is Re_2O_7 formed as the final photoproduct of the reaction? Secondly, if we could observe intermediates, is the reaction initiated by Re–Re or Re–C bond breaking? We also hoped to obtain some information about the reaction mechanism. At the outset of this research we anticipated that $[Re_2(CO)_{10}]$ might behave somewhat differently from $[Mn_2(CO)_{10}]$. On simple thermodynamic grounds one would expect the oxidation of $[Re_2(CO)_{10}]$ to Re_2O_7 to be more facile than the oxidation of $[Mn_2(CO)_{10}]$ to Mn_2O_7.[9] Although the photochemistry of $[Re_2(CO)_{10}]$ has been rather less well explored than has that of $[Mn_2(CO)_{10}]$[10] certain differences are known to pertain. Flash photolysis studies suggest that the ratio of M–M to M–C bond cleavage is greater for $[Re_2(CO)_{10}]$ than for $[Mn_2(CO)_{10}]$.[11] Furthermore, $[Re_2(CO)_{10}]$ is much less photolabile than is $[Mn_2(CO)_{10}]$; indeed the photochemistry of the mixed binuclear carbonyl $[MnRe(CO)_{10}]$ is known to be dominated by selective loss of CO from the manganese atom.[11] We felt that the different photochemical properties of $[Re_2(CO)_{10}]$ might allow us to induce some photoselectivity into the rhenium system where we had failed in the manganese system. An impetus was given to our studies by the considerable current interest in the organometallic derivatives of rhenium. Compounds containing rhenium metal centres are known to be potent activators of the C–H bonds of alkanes,[12] while other recent experiments have focused upon the mode of co-ordination of hydrogen to Mn or Re.[13] Other work[14] has shown that the compound $[ReCl(CO)_3(bipy)]$ (bipy = 2,2′-bipyridine) will readily reduce CO_2 to CO upon photolysis. The organometallic oxides of Re, *e.g.* $[Re(CH_3)O_3]$ and $[Re(cp)O_3]$ (cp = η-C_5H_5)[15–18] have also attracted much attention. These surprisingly stable species, as well as being of theoretical interest, are thought to have a number of practical applications for example in the deposition of thin layers of rhenium oxides.

Experimental

The experiments were carried out in accordance with procedures described elsewhere.[18] Matrices were formed by slow spray-on, the vapour over a sample of $[Re_2(CO)_{10}]$ held at 20 °C being co-condensed with pre-mixed gaseous samples of Ar and O_2. The matrix support was a CsI plate cooled to 12 K using an Air Products Displex 202 OSP closed-cycle refrigerator. Infrared spectra were recorded with a Perkin-Elmer model 983 spectrometer which gave a typical resolution and accuracy not exceeding 0.5 cm^{-1}, UV/VIS spectra using a Kontron model 860 spectrophotometer (resolution 0.5 nm) calibrated by means of a holmium oxide glass filter.

The matrix gases Ar and $^{16}O_2$, and $[Re_2(CO)_{10}]$, were used as supplied by Aldrich. Samples of $^{18}O_2$ and $^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$ scrambled mixtures were used as supplied by Merck, Sharp and Dohme. An Applied Photophysics 150 W high-pressure xenon lamp was used for photolysis. Filters employed were either a sheet of Pyrex or a cell fitted with quartz windows and filled with *ca.* 1 atm pressure of Cl_2 gas.

Results and Discussion

When the vapour above a sample of $[Re_2(CO)_{10}]$ held at 10 °C is co-condensed at 12 K with a large excess (*ca.* 1000–2000-fold) of a mixture of O_2 and Ar (*ca.* 1:10) and the resulting matrix is subjected to broad-band UV/VIS photolysis a very low yield of $[Re_2(CO)_9]$ is generated initially, as evidenced by the growth of weak or very weak infrared absorptions at 2066, 2000, 1956 and 1943 cm^{-1}.[10,19] As photolysis proceeds two intermediates **A** and **B** are generated in much higher yield: **A** absorbs at 2049s, 1988m and 882w cm^{-1}, **B** at 2060s, 1998m and a doublet at 953m and 946m cm^{-1}. It appears that both **A** and **B** are oxocarbonyl intermediates which contain both co-ordinated oxygen and CO groups.

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* *Non-SI unit employed:* atm = 101 325 Pa.

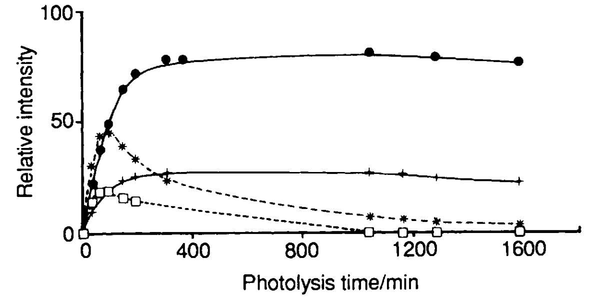


Fig. 1 Change in relative intensity of IR absorption bands at 2060 (■), 2049(*), 1998 (+) and 1988 cm^{-1} (□) with time of broad-band UV/VIS photolysis of a matrix at 20 K initially composed of $[Re_2(CO)_{10}]$, O_2 and Ar in the approximate proportions 1:200:2000

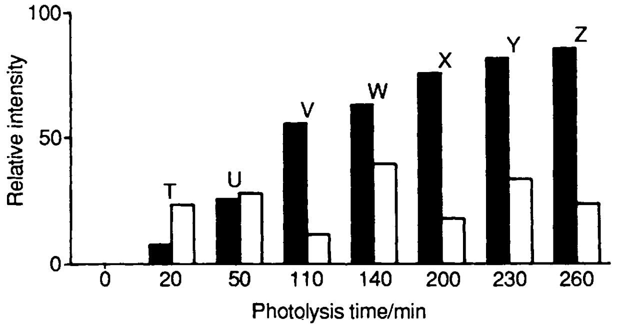


Fig. 2 Relative concentrations of species A (□) and B (■) (as witnessed by the relative intensities of IR absorptions at 2049 and 2060 cm^{-1}) upon (*i*) deposition of a mixture of $[Re_2(CO)_{10}]$, O_2 and Ar in the approximate proportions 1:200:2000 with concurrent broad-band UV/VIS photolysis, (*ii*) continued photolysis when spray-on has been stopped. Histograms: T, W and Y, spray-on with photolysis; U, V, X and Z, photolysis only

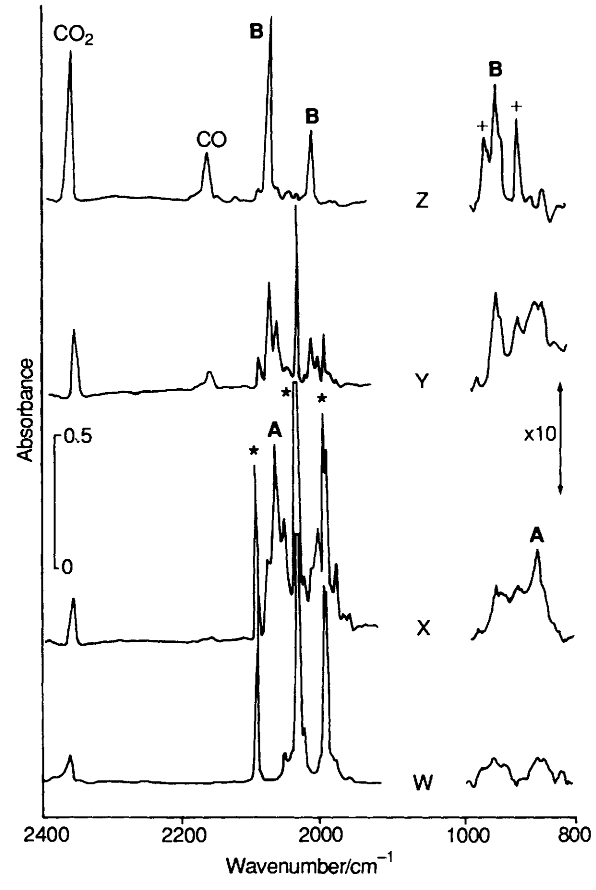


Fig. 3 Infrared absorption spectra of a matrix (20 K) initially composed of $[Re_2(CO)_{10}]$, O_2 and Ar in the approximate proportions 1:200:2000: W, after deposition; X, after 2 h of broad-band UV/VIS photolysis; Y, after 6 h of photolysis; Z, after 24 h of photolysis. Bands marked * are due to $[Re_2(CO)_{10}]$, those marked + to Re_2O_7

In Fig. 1 is illustrated the change in intensity of the peaks at 2060, 2049, 1998 and 1988 cm^{-1} with time of photolysis. It can clearly be seen that the intensity change of the peak at 2049 cm^{-1} parallels that at 1988 cm^{-1}, while the change in intensity of the peak at 2060 cm^{-1} parallels that at 1998 cm^{-1}. The absorptions at 953, 946 and 882 cm^{-1} are considerably weaker than the bands arising from ν(CO) modes plotted in Fig. 1 and thus accurate intensity measurements are difficult. However, the band at 882 cm^{-1} shows approximately the same behaviour as those at 2049 and 1988 cm^{-1} while the bands at 953 and 946 cm^{-1} clearly belong to the same species as those at 2060 and 1998 cm^{-1}.

In order to verify the order of production of species **A** and **B**, and to show that **B** is generated by the photolysis of **A**, we carried out an experiment in which the matrix was alternately photolysed (*a*) during spray-on of $[Re_2(CO)_{10}]$, O_2 and Ar and (*b*) after spray-on had been stopped. In Fig. 2 are plotted in histogram form the relative intensities of the bands at 2060 (**B**) and 2049 cm^{-1} (**A**) during this experiment. It is clear that both **A** and **B** are produced during spray-on with photolysis. However, once spray-on is stopped the concentration of **B** in the matrix *increases* while that of **A** *decreases*. This experiment demonstrates quite clearly that **A** is converted into **B** by photolysis. By allowing the beam of the spectrometer to impinge upon the matrix we have demonstrated that the IR spectrometer source itself facilitates neither the conversion of **A** into **B** nor the reverse reaction.

One of the features to emerge from the data presented in Fig. 1 is the remarkable photostability of species **B**. Whilst **A** decays to a low concentration after *ca.* 10 h of photolysis, **B** remains a principal ingredient of the matrix even after 26.5 h of photolysis. However, after *ca.* 10 h of photolysis a gradual diminution in the intensity of the bands of **B** is noted and there is a concomitant appearance and growth of the features at 975, 915 and 804 cm^{-1} which may be assigned to Re_2O_7.[20–22] During the experiment a build-up of matrix-isolated CO[23] and CO_2[24] is noted which is slow in the early stages of photolysis but more rapid later on. In control experiments we have shown that over a long period CO_2 does build up from atmospheric leaks in the apparatus. However the rate of accretion of CO_2 in this way is slower by at least a factor of 20 than its photochemical production from $[Re_2(CO)_{10}]$. The spectra illustrated in Fig. 3 show changes witnessed in the ν(CO) (2400–1900 cm^{-1}) and ν(ReO) or ν(OO) (1000–800 cm^{-1}) regions of the infrared spectrum during this experiment. The infrared bands seen during the experiment are listed in Table 1 where approximate assignments are also given.

In order to probe more fully the mechanism of photolysis we have employed selected wavelengths of light to irradiate the matrix. Two filters were used for these experiments, namely (*i*) Pyrex glass (which transmits at $\lambda \geqslant 288$ nm) and (*ii*) a sealed gas cell fitted with quartz windows and filled with *ca.* 1 atm pressure of Cl_2 gas (this filter blocks at $\lambda = 290–378$ nm). In Fig. 4 are overlayed the UV/VIS absorption spectra of the two filters and of $[Re_2(CO)_{10}]$ in hexane solution. It can clearly be seen that the Pyrex filter allows selective photolysis into the band of $[Re_2(CO)_{10}]$ at 308 nm (marked * in Fig. 4), which is reported to promote Re–Re bond cleavage, while the chlorine filters allows selective photolysis into the band at 273 nm (marked + in Fig. 4), which is reported to promote Re–C bond breaking.[7,25] We find that when the Pyrex filter is employed the overall rate of photolysis is slowed but that the intermediates **A** and **B** and the oxide product Re_2O_7 are formed in the same sequence as when unfiltered light is used for photolysis. However, the chlorine filter effectively stops the reaction. After 3 h

Table 1 Behaviour of infrared bands seen upon photo-oxidation of matrix-isolated [$Re_2(CO)_{10}$]

	Photolysis time^b/min						
$\tilde{\nu}^a$/cm^{-1}	0^c	100	200	500	1000	1500	Origin
2340m	—	app	inc	inc	inc	inc	CO_2[d]
2142w	—	app	inc	inc	inc	inc	CO[e]
2075s	app	dec	dec	dec	dec	—	[$Re_2(CO)_{10}$][f]
2066vw	—	app	dis	—	—	—	[$Re_2(CO)_9$][f]
2060s	—	app	inc	inc	inc	dec	**B**
2049s	—	app	dec	dec	dec	dec	**A**
2018vs	app	dec	dec	dec	dis	—	[$Re_2(CO)_{10}$][f]
2000w	—	app	dis	—	—	—	[$Re_2(CO)_9$]
1998m	—	app	inc	inc	unc	dec	**B**
1988m	—	app	dec	dec	dis	—	**A**
1980s	app	dec	dec	dec	dis	—	[$Re_2(CO)_{10}$][f]
1956vw	—	app	dis	—	—	—	[$Re_2(CO)_9$][f]
1943vw	—	app	dis	—	—	—	[$Re_2(CO)_9$][f]
975m	—	—	app	inc	inc	inc	Re_2O_7[g]
953m[h]	—	app	inc	inc	unc	dec	**B**[h]
946m[h]	—	app	inc	inc	unc	dec	**B**[h]
915m	—	—	app	inc	inc	inc	ReO_3(?)[g,i]
882wm	—	app	dec	dec	dis	—	**A**
804vw	—	—	—	app	inc	inc	Re_2O_7[g]
665m	—	app	inc	inc	inc	inc	CO_2[e]
593m	app	dec	dec	dis	—	—	[$Re_2(CO)_{10}$][f]
400m	app	dec	dec	dis	—	—	[$Re_2(CO)_{10}$][f]

[a] ± 1 cm^{-1}. Letters indicate approximate *maximum* intensity: s = strong, m = medium, w = weak, v = very. [b] app = Appears, dis = disappears, inc = increases in intensity, dec = decreases in intensity, unc = unchanged in intensity. [c] Spray on. [d] Ref. 23. [e] Ref. 24. [f] Ref. 10. [g] Ref. 20. [h] Doublet, see text. [i] See text for a discussion of the origin of this band.

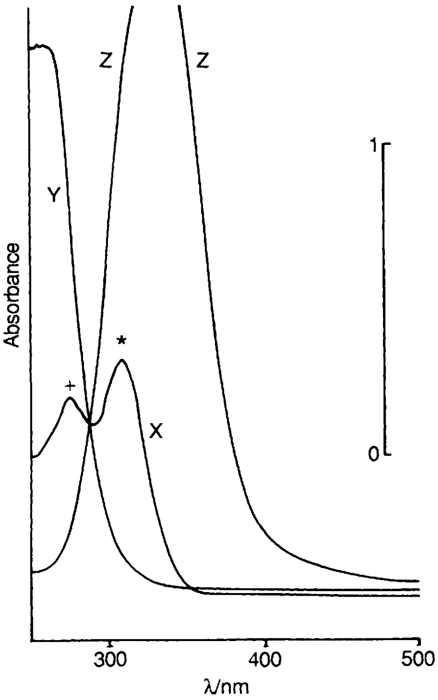


Fig. 4 The UV/VIS absorption spectra of: X, $Re_2(CO)_{10}$ in hexane solution; Y, Pyrex filter; Z, chlorine filter. For explanation of symbols + and * see text

of photolysis, using this filter, there is no sign of **A**, **B** or Re_2O_7; after 23 h a very low yield of **A** and **B**, but no Re_2O_7, is seen. Thus we conclude that the primary photochemical step of the reaction is cleavage of the Re–Re bond. This finding possibly also explains why only a low yield of [$Re_2(CO)_9$] is seen in these experiments. It appears that the Re–Re bond-breaking route to yield the [$Re(CO)_5$] radical is more efficient than Re–C bond breaking to yield [$Re_2(CO)_9$]. In a pure argon matrix [$Re_2(CO)_9$] is seen rather than [$Re(CO)_5$][19] as the principal photolysis product because matrix cage effects allow the rapid recombination of [$Re(CO)_5$] radicals. In an O_2-doped matrix, however, [$Re(CO)_5$] is quickly consumed by reaction with O_2. In this context it is noteworthy that Re–Re bond breaking is known to initiate other oxidation reactions of [$Re_2(CO)_{10}$], *e.g.* conversion into [$ReCl(CO)_5$] in CCl_4 solution.[25]

Intermediate **A**.—Three infrared bands at 2049, 1988 and 882 cm^{-1} are assigned to species **A**. The presence of at least two ν(CO) bands implies a carbonyl-containing moiety $Re(CO)_n$ where $n \geq 2$. The results of ^{13}CO-enrichment experiments are inconclusive for this species which is never produced in very high yield and which is always accompanied by relatively high concentrations of **B** and of unreacted [$Re_2(CO)_{10}$]. The presence of these molecules enormously complicates the ν(CO) region of the spectrum on partial ^{13}CO enrichment. However, certain conclusions may be drawn about the value of n in the $Re(CO)_n$ fragment of **A**. First, very little photoejected CO or CO_2 is seen in the matrix at this stage in photolysis. Secondly the pattern of bands, *i.e.* 2049s and 1988m cm^{-1}, seems incompatible with a non-linear dicarbonyl[4,26] or pyramidal tricarbonyl[4,5] moiety where the higher-frequency (B_2 or E mode) is expected to have the stronger intensity. The spectrum is more redolent of a C_{4v} $M(CO)_5$ fragment, *e.g.* in matrix-isolated [$MnCl(CO)_5$] where absorptions of strong and medium intensity are seen at 2064.0 and 2002.1 cm^{-1} respectively.[27] An alternative proposition is that the spectrum belongs to an $Re(CO)_4$ moiety. Many such species with $M(CO)_4$ units have been reported. These include the polymeric species [{$Re(CO)_4$}$_n$],[28] the matrix-isolated manganese tetracarbonyls [$MnX(CO)_4$] (X = H, CH_3, Cl, Br or I),[27,29,30] where the $M(CO)_4$ fragment is known to take C_{2v} symmetry, and the initial product of photo-oxidation of [$Fe(CO)_5$], *i.e.* [$Fe(CO)_4(\eta^2-O_2)$][5] or of [$M(CO)_6$] (M = Cr, Mo or W).[4] If an $Re(CO)_5$ unit is the correct interpretation the expected high-frequency A_1 mode is presumably too weak to be observed or is obscured by photoejected CO {N.B. the high-frequency A_1 mode of matrix-isolated [$MnCl(CO)_5$] has weak intensity and occurs at 2142.1 cm^{-1}}.[27] For a C_{2v} $Re(CO)_4$ fragment, four IR bands are expected of which the highest-frequency feature

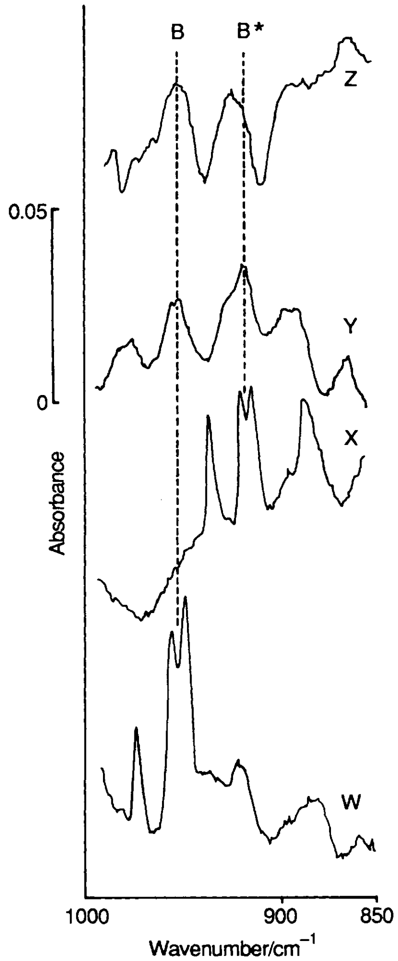


Fig. 5 Infrared absorption spectra of O_2-doped argon matrices initially containing $[Re_2(CO)_{10}]$ after *ca.* 24 h of photolysis so as to generate a high yield of species **B**: W, matrix dopant is $^{16}O_2$; X, matrix dopant is $^{18}O_2$; Y, matrix dopant is a *ca.* 50:50 mixture of $^{16}O_2$ and $^{18}O_2$; Z, matrix dopant is a *ca.* 25:50:25 mixture of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$. Bands marked B are due to the ^{16}O isotopomer of **B** and those marked B* are due to the ^{18}O isotopomer of **B**

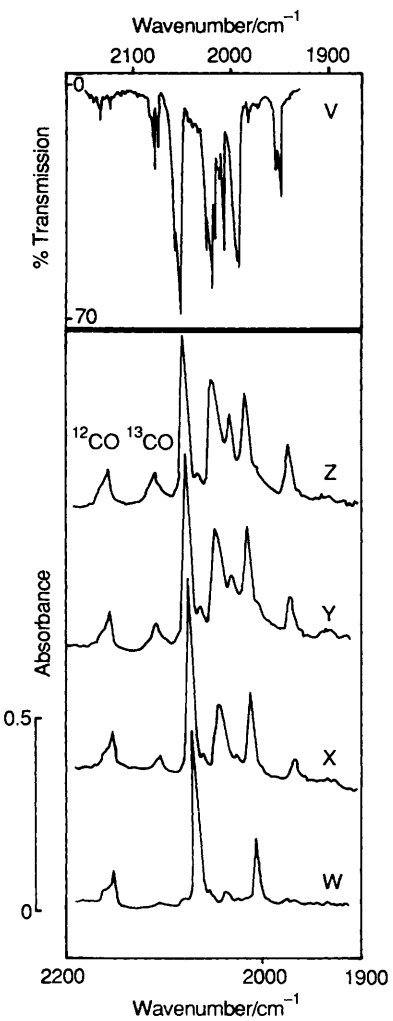
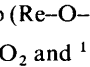


Fig. 6 Infrared absorption spectra of $^{16}O_2$-doped argon matrices initially containing $[Re_2(CO)_{10}]$ enriched in ^{13}CO after *ca.* 24 h of photolysis so as to generate a high yield of species **B**: W, natural abundance of ^{13}C only; X, *ca.* 25% enrichment in ^{13}C; Y, *ca.* 33% enrichment in ^{13}C; Z, *ca.* 50% enrichment in ^{13}C. Spectrum V: *ca.* 50% ^{13}CO-enriched $[MnCl(CO)_5]$ reproduced from ref. 27 by kind permission of the authors

should be weak in intensity while the other three should have strong-to-medium intensities. Thus, under these circumstances, one would expect to see at least three ν(CO) modes for **A**. Although not conclusive, these data suggest a stoichiometry of $Re(CO)_4$ or $Re(CO)_5$, on balance the pentacarbonyl formulation being the more likely. When, in this experiment, $^{16}O_2$ is replaced by $^{18}O_2$ the band at 882 cm^{-1} shifts by 50 cm^{-1} to 832 cm^{-1}. The calculated $^{16}O/^{18}O$ shifts from 882 cm^{-1} (Δ) for ν(O–O) and ν(Re–O) vibrations are 50 and 46 cm^{-1} respectively. For ν_{asym} of an ReO_2 or ReO_3 unit Δ depends upon the O–Re–O angle (θ) but is expected to be less than 50 cm^{-1}, *e.g.* for ReO_2 if $\Delta = 44$ cm^{-1} then $\theta = 112°$, whereas if $\Delta = 50$ cm^{-1}, θ = (quite implausibly) 5°.[31] Thus, on balance, a ν(O–O) vibration is the favoured assignment for this band. The wave number of this vibration (882 cm^{-1}) is not compatible with a σ-superoxo moiety (Re–O–O)[32] but is compatible with a η^2-peroxo  or μ-peroxo (Re–O–O–Re) unit.[33] Experiments utilizing a 1:1 mixture of $^{16}O_2$ and $^{18}O_2$ or a scrambled (1:2:1) mixture of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ give only limited information. In neither case can be discerned any bands belonging to **A** which are intermediate in frequency between 882 and 832 cm^{-1}. For the unscrambled mixture this observation is entirely consistent with the above assignment provided the O–O peroxo unit is derived from one oxygen molecule. Not too much emphasis should be placed on the experiment using scrambled oxygen isotopomers. The spectra are of poor quality, principally because the extreme weakness of intensity precludes the accurate observation of the bands in this region.

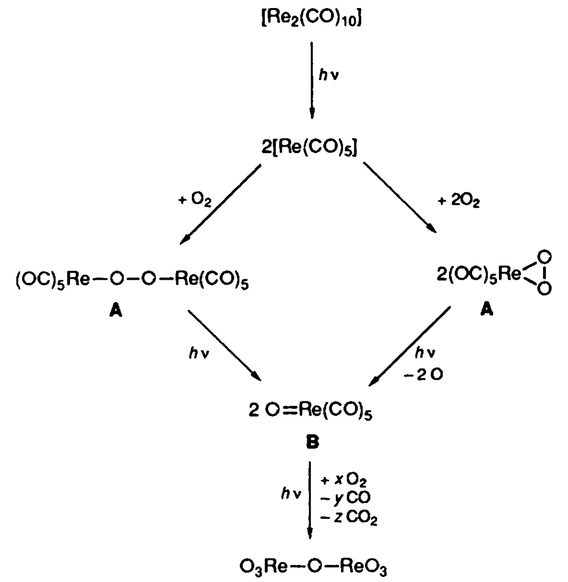
Intermediate **B**.—Bands at 2060, 1998 and a sharp doublet at 953 and 946 cm^{-1} are assigned to species **B**. The striking similarity in the pattern of bands in this region of the spectrum for **A** and **B** leads us to conclude that **B** contains the same $Re(CO)_n$ fragment as does **A**. Thus **B** would appear also to contain an $Re(CO)_4$ or $Re(CO)_5$ moiety. The increase in average ν(CO) frequency of **B** (2029 cm^{-1}) compared to **A** (2018 cm^{-1}) suggests that the rhenium centre in **B** might be more oxidized than that in **A**. Experiments utilizing ^{13}CO are much more conclusive for **B** than they are for **A**. In Fig. 6 are illustrated the IR spectra seen for **B** at various levels of ^{13}CO enrichment and these spectra are compared with that of ^{13}CO-enriched $[MnCl(CO)_5]$[27] which is known to have a C_{4v} pentacarbonyl moiety. The similarity between the spectra of these two compounds is quite striking and reinforces our belief that **B** (and **A**) contain C_{4v} $Re(CO)_5$ units.

The doublet at 953 and 946 cm^{-1} shifts to 905 and 898 cm^{-1} on ^{18}O substitution (see Fig. 5). These shifts of 48 cm^{-1} are more-or-less consistent with those expected (50 cm^{-1}) for an Re=O monoxo moiety. [They are too small to be compatible

Table 2 Effect of ^{16}O–^{18}O isotopic substitution on infrared bands seen upon photo-oxidation of matrix-isolated $[Re_2(CO)_{10}]$

$\tilde{\nu}(^{16}O)^a$/ cm^{-1}	$\tilde{\nu}(^{18}O)^a$/ cm^{-1}	$\Delta\tilde{\nu}^b$/cm^{-1}	R^c	Assignment
975	924	51	0.948	$\nu_{asym}(ReO_3)$, Re_2O_7
953^d	905^d	48	0.950	ν(ReO), **B**
946^d	898^d	48	0.949	ν(ReO), **B**
915	865	50	0.945	$\nu_{asym}(ReO_3)$, ReO_3(?)^e
882	832	50	0.943	ν(O–O), **A**
804	—	—	—	ν_{asym}(ReORe), Re_2O_7

^{a} ±1 cm^{-1}. ^{b} $\Delta\tilde{\nu} = \tilde{\nu}(^{16}O) - \tilde{\nu}(^{18}O)$; ±2 cm^{-1}. ^{c} $R = \tilde{\nu}(^{18}O)/\tilde{\nu}(^{18}O)$; ±0.002. ^{d} Doublet, see text. ^{e} See text for a discussion of the origin of this band.



Scheme 1 Intermediates **A** and **B** could contain $Re(CO)_4$ rather than $Re(CO)_5$ fragments, see text

with a ν(O–O) vibration where a shift of 55 cm^{-1} is calculated.] They are also consistent with an O-bridged Re–O–Re moiety with a bond angle in the region of 120°.[8] It is possible to obtain much clearer spectra of **B** than **A** since this species may be built up in higher yield. Thus experiments using unscrambled mixtures of $^{16}O/^{18}O$ dioxygen isotopomers assume a greater importance. In both cases it is clear (see Fig. 5) that there is no absorption intermediate in wavenumber between 946 and 905 cm^{-1}. These observations are entirely consistent with the presence of an Re=O monoxo or Re–O–Re bridging group in **B**. However, the known ranges for ν(Re=O) and for ν_{asym}(Re–O–Re) are 912–995 and 720–860 cm^{-1} respectively;[34] thus we conclude that the most likely formulation for **B** is $O{=}Re(CO)_5$.

Dirhenium Heptaoxide, Re_2O_7.—The final product of the photo-oxidation of $[Re_2(CO)_{10}]$ in O_2-containing matrices is Re_2O_7. This assertion is supported by the growth of bands at 975m, 915m and 804w cm^{-1} which match those seen by Spoliti *et al.*[20] in the spectrum obtained by matrix isolation of the vapour over a sample of Re_2O_7. The band at 975 cm^{-1} is assigned to $\nu_{asym}(ReO_3)$ (terminal) and that at 804 cm^{-1} to ν_{asym}(ReORe) (bridging). There is no sign of a band near to 1016 cm^{-1} due to $\nu_{sym}(ReO_3)$ (terminal) but this is not surprising considering the reported weak intensity of this vibration.[20] Nor is there any hint of a band which may be assigned to ν_{sym}(ReORe) (bridging) but again this is entirely expected given the known wide Re–O–Re angle of Re_2O_7[35] and the failure of Spoliti *et al.*[20] to observe any such band in their spectra. There remains the difficulty in assigning the feature at 915 cm^{-1}. Spoliti *et al.*[20] reported this feature for Re_2O_7 isolated in N_2 but not in Ar and assign it to an $Re_2O_7 \cdots Re_2O_7$ aggregate which is formed in nitrogen but not in argon matrices. We have carried out experiments in which the vapour over heated Re_2O_7 was trapped in various matrices.[36] The results of these experiments will be published in detail elsewhere. However, we find that the band at 915 cm^{-1} is invariably present even in pure argon matrices. An alternative suggestion is that this absorption belongs not to Re_2O_7 but rather to ReO_3. Solid ReO_3 is reported to absorb in the infrared region at 905 cm^{-1}.[37] Although there is no reason to suppose that matrix-isolated molecular ReO_3 would necessarily show an IR absorption at a frequency close to that shown by the solid compound, the matrix-isolated molecules $ReClO_3$ and $ReFO_3$ (which are expected to have rather higher Re–O force constants due to the increased oxidation state of the rhenium centre) show $\nu_{asym}(ReO_3)$ at 963 and 978 cm^{-1} respectively.[38,39]

The redox chemistry of heated rhenium oxides is highly complex involving various disproportionation reactions[40–42] and mass spectrometric and infrared spectroscopic evidence shows that both ReO_3 and Re_2O_7 are present in the vapours above either heated ReO_3 *or* Re_2O_7.[40–42] Thus it is quite plausible that the band seen by Spoliti *et al.* at 915 cm^{-1} arises from the presence of ReO_3, and that ReO_3 is an end-product of our photo-oxidation reactions also.

On ^{18}O substitution the bands at 975 and 915 cm^{-1} shift to 924 and 865 cm^{-1}. We have been unable to detect any ^{18}O counterpart of the weak band at 804 cm^{-1} nor have we been able to derive useful information from experiments using unscrambled or scrambled mixtures of $^{16}O/^{18}O$ dioxygen isotopomers. In part this failure arises from the weakness and complexity of the spectra and in part from the ubiquitous presence of species **B** alongside Re_2O_7 which further complicates the spectrum. The effect of ^{16}O–^{18}O isotopic substitution upon the infrared bands of **A**, **B** and Re_2O_7 is summarised in Table 2.

The Mechanism of Photolysis.—While not being 100% conclusive, our experimental results provide a great deal of information about the photo-oxidation of $[Re_2(CO)_{10}]$ to Re_2O_7. The most likely sequence of events is that species **A** is formed by reaction of $[Re(CO)_5]$ with O_2; it appears to be a peroxo species with four or five CO groups attached to the metal centre. The peroxo-bridged formulation $(OC)_5Re{-}O{-}O{-}Re(CO)_5$ as well as satisfying the spectroscopic evidence appears to be the most likely on electronic grounds: this 18-electron species seems to be a more plausible intermediate than the 17- or 19-electron species $[Re(CO)_n(\eta^2\text{-}O_2)]$ (n = 4 or 5).

Our experiments show that species **B** is almost certainly a monooxorhenium carbonyl, with five CO groups. Although this 19-electron formulation may, at first sight, appear unlikely, there appears to be no other way adequately to explain our spectral data for **B**. Moreover, a quite likely photochemical reaction of **A** (if indeed **A** is a μ-peroxo species) would be cleavage of the O–O bond to yield a monooxo species. A plausible mechanism is thus as shown in Scheme 1. The formation of Re_2O_7 as a final product suggests that the two rhenium atoms of one $[Re_2(CO)_{10}]$ precursor molecule are never far removed from one another within the matrix. The observation that the ν(Re=O) mode of **B** always occurs as a sharp doublet (953 and 946 cm^{-1}) suggests the possibility that two such molecules lie close to one another in the matrix and thus cause a slight perturbation to this vibration. This phenomenon seems not to be a simple matrix splitting since it is seen in O_2–Ar matrices where the proportion of O_2 is varied from 5 to 100%. The doublet pattern is unaffected by changing the temperature of a 10% O_2–Ar matrix in the approximate range 12–25 K, but at *ca.* 30–35 K it disappears to be replaced by a rather broad feature centred at 953 cm^{-1}. This latter effect is probably caused by the molecules being able to reorder themselves in the matrix.

For two $O{=}Re(CO)_n$ (n = 4 or 5) molecules held close within the matrix Re_2O_7 may be produced by reaction with O_2 and expulsion of CO and CO_2. It is at this stage of photolysis that the largest yields of CO and CO_2 are seen. We also observe $CO \cdots CO_2$ aggregates[43,44] suggesting the concurrent production of CO and CO_2 at the metal centre. Unfortunately we see no sign of any oxocarbonyl intermediate produced after **B** in the photolytic system. If we are correct in our hypothesis that molecular ReO_3 is also a photoproduct it is possible that this molecule is generated from an isolated $O{=}Re(CO)_4$ molecule which is held in the wrong orientation or is too far removed to combine with another such molecule.

Comparison of $[Re_2(CO)_{10}]$ *with* $[Mn(CO)_{10}]$.—In one broad respect the photo-oxidation of $[Re_2(CO)_{10}]$ resembles that of $[Mn_2(CO)_{10}]$,[8] *i.e.* the final oxidation products are Re_2O_7 and Mn_2O_7 respectively. However there are also a considerable number of differences. First is the stability of the oxocarbonyl intermediates, especially **B**, in the rhenium system. We have attempted to discover analogous oxocarbonyl intermediates in the manganese system by using filtered UV radiation for the photolysis but without any success. Secondly, photo-oxidation of $[Re_2(CO)_{10}]$ proceeds much more slowly than that of $[Mn_2(CO)_{10}]$: a considerable amount of **B** is present after 26.5 h of photolysis whereas no species containing co-ordinated CO groups remains in the manganese system after 3.5 h of photolysis under identical conditions. The slowness of photo-oxidation of $[Re_2(CO)_{10}]$ is unexpected on thermodynamic grounds whence it is expected that rhenium is much more readily oxidized to the +7 state than is manganese.[9] This behaviour may also be contrasted with the reaction of $[M_2(CO)_{10}]$ (M = Mn or Re) with N_2 in liquid xenon solution where the relative rate of production of $[M_2(CO)_9(N_2)]$ is in the order Re > Mn.[45] This latter process is believed to proceed *via* $[M_2(CO)_9]$ by CO dissociation from $[M_2(CO)_{10}]$, whereas the evidence presented here suggests that the photo-oxidation of $[M_2(CO)_{10}]$ is initiated by M–M cleavage. As Firth *et al.*[45] point out, it is the relative quantum yields of these photoprocesses which determine the relative reaction rates. Thus both sets of data {*i.e.* that $[Re_2(CO)_{10}]$ reacts more quickly with N_2, while $[Mn_2(CO)_{10}]$ is more quickly photo-oxidized} are consistent with the results of flash photolysis experiments which suggest that for $[Re_2(CO)_{10}]$ the ratio of M–M cleavage to dissociation of CO is lower than for $[Mn_2(CO)_{10}]$.[11] Of course the absorption properties of the intermediates involved in the photo-oxidation processes will also, to some extent, dictate the overall rate of reaction. At present we have no complete explanation for these subtle differences in photochemical behaviour between the two Group VII congeners.

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