Photo-oxidation of $[V(CO)_6]$ in Low-temperature Matrices containing O_2: Formation of a Novel Superoxovanadium Species

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Irradiation of $[V(CO)_6]$ in low-temperature matrices containing O_2 led to the formation of a novel superoxovanadium species **A** alongside free CO_2. Isotopic substitution experiments involving ^{18}O and comparison of the IR spectrum of **A** with that of the known oxovanadium species $[VO_2Cl_2]^-$ and $[VO_2F_2]^-$ indicate that **A** is the superoxide $[VO_2(\sigma\text{-}O_2)]$. The ^{16}O–^{18}O isotopic shift for $\nu_{asym}(VO_2)$ of **A** gives an upper limit of *ca.* 115° for the OVO bond angle of the dioxo moiety of **A**; the intensity ratio of the bands arising from ν_{sym} and $\nu_{asym}(VO_2)$ suggests a value of 108 ± 5° for this angle. The reaction is initiated by loss of CO from $[V(CO)_6]$ to form $[V(CO)_5]$; a step which is shown to be photochromic, and proceeds *via* at least one oxocarbonyl intermediate.

Photo-oxidation of metal carbonyls in low-temperature matrices containing O_2 has proved to be a convenient way to generate *molecular* metal oxides. Examples include CrO_2 from $[Cr(CO)_6]$,[1] a mixture of MoO_2 and MoO_3 from $[Mo(CO)_6]$,[2] WO_3 and the hitherto unknown peroxodioxo species $[WO_2(\eta^2\text{-}O_2)]$ from $[W(CO)_6]$,[2] $[Fe(\eta^2\text{-}O_2)]$ and FeO_3 from $[Fe(CO)_5]$,[3] Mn_2O_7 from $[Mn_2(CO)_{10}]$[4] and $[Re_2O_7]$ from $[Re_2(CO)_{10}]$.[5] In some of these systems it has proved possible to observe intermediate oxocarbonyl species where CO and oxygen (in one form or another) are bound to the metal. Thus more-or-less complete reaction mechanisms have been proposed for the photo-oxidation of $[M(CO)_6]$ (M = Cr, Mo or W),[6-8] $[Fe(CO)_5]$[3] and $[Re_2(CO)_{10}]$.[5] Some trends emerge from these studies, *e.g.* in Group 6 it appears, as expected, that the +VI oxidation state is more readily achieved at the bottom of the group than at the top. However, in many cases it seems that the appearance of certain product or intermediate compounds may simply reflect their photochemical properties, for example how closely their absorption bands overlap with the output from the photolysis source. This might explain why $[Re_2(CO)_{10}]$ is less readily oxidised than is $[Mn_2(CO)_{10}]$, a result which would be unexpected on a simple argument of thermodynamic stability. One mononuclear binary carbonyl whose matrix photo-oxidation has not so far been looked at is $[V(CO)_6]$. There is a particular interest in studying the chemistry of $[V(CO)_6]$ since it is unique amongst simple metal carbonyls in being a paramagnetic 17-electron compound.

Oxovanadium species exhibit an extremely complex chemistry. Vanadium has four principal oxides: V_2O_5, V_2O_4, V_2O_3 and VO, alongside a number of other phases of intermediate composition. Also well known are the cations $[VO_2]^+$ and $[VO]^+$ (the widespread vanadyl ion), and a wide range of vanadate species which are formed *via* extremely complex equilibria in acidic or alkaline solution. Of particular interest to the current work is the known propensity of vanadium to form peroxo complexes, where the metal is in the +V oxidation state.[9] These are formed by the addition of H_2O_2 to aqueous solutions of vanadium(V); in neutral or alkaline conditions the orthovanadate ion $[VO_2(\eta^2\text{-}O_2)_2]^{3-}$ is produced, whereas in strongly acid solution the peroxovanadium cation $[V(\eta^2\text{-}O_2)]^{3+}$ predominates. There is an impetus provided to studies of vanadium oxides because of the important uses which these compounds find. These include catalysis (V_2O_5 finds immense use as the catalyst in the conversion of SO_2 to SO_3 in the Contact process for sulfuric acid production) and use as battery materials.[10] Oxovanadium compounds are also of interest in bioinorganic chemistry.[11,12]

Against this background we commenced our investigation of the photo-oxidation of $[V(CO)_6]$ in O_2-doped Ar matrices. Our aims were threefold. First to characterise any oxide products of the reaction; we hoped that it might prove possible to make novel oxo or peroxo compounds of vanadium in this way. Secondly, to attempt to elucidate the mechanism of the photo-oxidation process, or at least to identify key intermediates in the reaction. Thirdly, to compare our results with those previously obtained for diamagnetic metal carbonyls.

Experimental

The matrix-isolation apparatus used at Reading has been described elsewhere.[1,4,13] Matrices were deposited by slow-spray-on; the vapour over a sample of $[V(CO)_6]$ held at 0 °C being co-condensed with premixed gaseous samples of O_2 and Ar. As $[V(CO)_6]$ is extremely photosensitive all of the glass part of the spray-on apparatus was coated with aluminium foil in order to minimise the risk of reaction prior to deposition. The matrix support was a CsI window cooled to *ca.* 20 K using an Air Products Displex 202 OSP closed-cycle refrigerator. IR spectra were recorded using a Perkin-Elmer model 983 spectrometer which gave a typical resolution and accuracy not exceeding 0.5 cm^{-1}.

The matrix gases Ar (stated purity 99.998%) and $^{16}O_2$ (stated purity >99.6%) were used as supplied by Aldrich. Hexacarbonylvanadium was used as supplied by Strem. Samples of $^{18}O_2$ (isotopic purity 98%) and of 'scrambled' $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ (containing 55% of the isotope ^{18}O) were used as supplied by Merck, Sharp and Dohme. An Applied Photophysics 150 W high-pressure xenon lamp was used as the photolysis source. Narrow-band interference filters were employed with wavelengths of maximum transmission at 337, 365 or 436 nm and band passes of *ca.* 20 nm.

A sample of $[V(CO)_6]$ partially enriched in ^{13}CO was prepared by photolysis of the vapour over a sample of $[V(CO)_6]$ containing the elements in their natural abundance with ^{13}CO gas in a 2 l bulb. Separation of the enriched sample was achieved by pumping the contents of the bulb slowly through a glass spiral immersed in liquid nitrogen.

Results and Discussion

When a matrix composed of [V(CO)$_6$], O$_2$ and Ar in the approximate proportions 1:200:1000 is subjected to broad-band UV/VIS photolysis for 1 h the IR absorption bands due to the parent hexacarbonyl at 1976, 596 and 438 cm^{-1} [14] are seen to decay and disappear. At this stage of photolysis the only IR bands present are at 2343.0, 2137.5, 1129.0, 969.5, 960.0, 660 and 563.5 cm^{-1}. The two high frequency bands may be identified with matrix-isolated CO$_2$ [ν_{asym}(OCO)] [15] and CO [ν(CO)] [16] respectively. The three features seen between 900 and 1200 cm^{-1} are in a region commonly associated with ν(M=O) (M = transition metal) or ν(O–O) stretching vibrations of oxo-metal species.[17] In particular the position of the band at 1129.0 cm^{-1} is highly suggestive of the ν(O–O) vibration of a σ-co-ordinated (superoxo) O$_2$ unit.[18–20] Although it is often not possible to make an unequivocal assignment to σ-O$_2$ or to η^2-O$_2$ (peroxo) on the basis of band *position* alone this feature appears to be at too high a wavenumber for assignment to a peroxo unit.[17] The band at 563.5 cm^{-1} is in a region associated with ν(M–O) vibrations of co-ordinated O$_2$ units. The band at 660 cm^{-1} may be assigned to the bending mode of free CO$_2$.[15]

The position and relative intensities of the bands at 969.5 and 960.0 cm^{-1} [$I_{969.5}:I_{960.0} \approx 1:3$] are reminiscent of ν_{sym}- and ν_{asym}-(O=V=O) vibrations of the non-linear VO$_2$ unit in the anionic vanadium(v) species [VO$_2$Cl$_2$]$^-$ [21] and [VO$_2$F$_2$]$^-$ [22] which show ν_{sym}- and ν_{asym}-(O=V=O) vibrations at 970 and 959 cm^{-1}, and at 970 and 962 cm^{-1} respectively. They are also quite close to the positions of ν(V=O) modes of the neutral vanadium(v) species [VO$_2$Cl] which shows ν_{sym}- and ν_{asym}-(O=V=O) vibrations at 855 and 990 cm^{-1}.[23] Neither of the features correspond to a band at 1031 cm^{-1} reported to arise from the ν_{asym}(O=V=O) vibration of matrix-isolated VO$_2$.[24,25] Thus we may conclude that the matrix photo-oxidation of [V(CO)$_6$] by molecular O$_2$ leads to one or two oxide products, neither of which are VO$_2$. Since there are no ν(CO) bands of co-ordinated CO groups seen in the IR spectrum at this stage we may conclude that any such product is a binary oxide species.

In order: (*i*) to determine whether a single, or two distinct oxide products are formed; (*ii*) to characterise such products; (*iii*) to probe the mechanism of reaction we carried out the following series of experiments. First, progressively to irradiate the matrix for different periods of time so as to search for reaction intermediates, to monitor the build up of products and to determine whether or not the bands at 1129, 969.5, 960.0 and 5635 cm^{-1} all arise from a single product. Secondly, to search for any photoselectivity shown by the system by utilising narrow-band optical filters. Thirdly, to examine the effect of varying the concentrations of the initial matrix ingredients, in particular to look for any effect of varying the O$_2$:Ar ratio. Fourthly, to utilise isotopic substitution with ^{18}O in order to confirm the identity of the oxide product or products.

In Fig. 1 is illustrated graphically the temporal behaviour of IR bands when an O$_2$-doped Ar matrix containing 20% O$_2$ is subjected to broad-band UV/VIS irradiation; the region 850–1150 cm^{-1} of the infrared spectra is illustrated in Fig. 2. Hexacarbonylvanadium is found to be extremely photosensitive. Photolysis for 2 min causes a substantial diminution (*ca.* 20%) in the size of IR absorptions arising from this molecule, and these bands decay to 50% of their original intensity after *ca.* 5 min photolysis. After short photolysis times (*ca.* 2 min) new, rather weak, bands are seen to appear at 1954.5 and 1946.5 cm^{-1}. These bands may be assigned to the binary carbonyl [V(CO)$_5$], which has previously been generated by the reaction of V atoms with CO at cryogenic temperatures[25] or by photolysis of matrix-isolated [V(CO)$_6$].[26] Pentacarbonylvanadium is reported to show IR absorptions at 1952 and 1943 cm^{-1} in a CO-doped Ar matrix.[25] Thus our values for an O$_2$-doped Ar matrix would seem to be quite reasonable. As shown in Fig. 1 the concentration of [V(CO)$_5$] within the matrix decreases upon prolonging the period of photolysis and the compound has disappeared after photolysis for 20 min. When all of the [V(CO)$_6$] is consumed, the intensity of bands arising from oxide products ceases to increase (see Figs. 1 and 2).

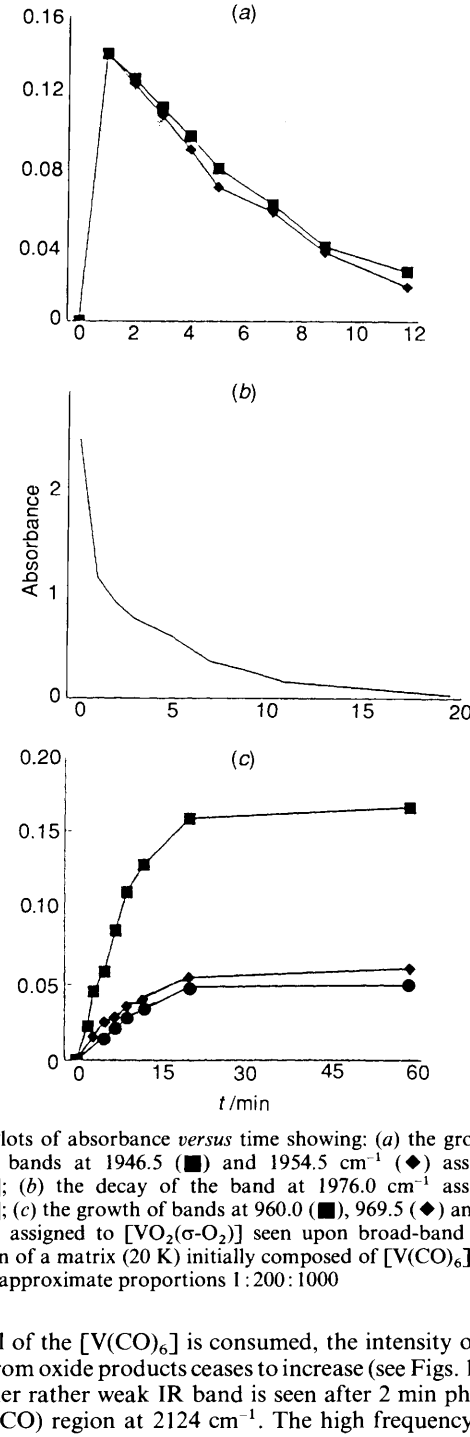


Fig. 1 Plots of absorbance *versus* time showing: (*a*) the growth and decay of bands at 1946.5 (■) and 1954.5 cm^{-1} (◆) assigned to [V(CO)$_5$]; (*b*) the decay of the band at 1976.0 cm^{-1} assigned to [V(CO)$_6$]; (*c*) the growth of bands at 960.0 (■), 969.5 (◆) and 1129.0 cm^{-1} (●) assigned to [VO$_2$(σ-O$_2$)] seen upon broad-band UV/VIS irradiation of a matrix (20 K) initially composed of [V(CO)$_6$], O$_2$ and Ar in the approximate proportions 1:200:1000

Another rather weak IR band is seen after 2 min photolysis in the ν(CO) region at 2124 cm^{-1}. The high frequency of this absorption is suggestive of an oxocarbonyl species where the metal centre is in a high oxidation state.[6,7,17] This feature too decays upon prolonged photolysis. It disappears after 20 min irradiation. Its growth and decay characteristics are matched (see Figs. 1 and 2), by a band at 946 cm^{-1}. These bands may be assigned to an intermediate **Y**. The only other feature which appears to arise from an intermediate species is a weak band at 923 cm^{-1} assigned to an intermediate **Z**. It is not clear from this experiment alone whether or not the bands at 946 and 923 cm^{-1} belong to the same compound [Fig. 3(*a*)]. The 'product' bands at 1129.0, 969.5, 960.0 and 563.5 cm^{-1} show no diminution in intensity, even after prolonged periods of broad-band photolysis.

The effect of varying the O$_2$:Ar ratio from 5% O$_2$ through to 100% O$_2$ was not marked. The same IR features were seen whatever concentration of O$_2$ was used. Nor did their relative intensities vary much, although it did prove possible to show

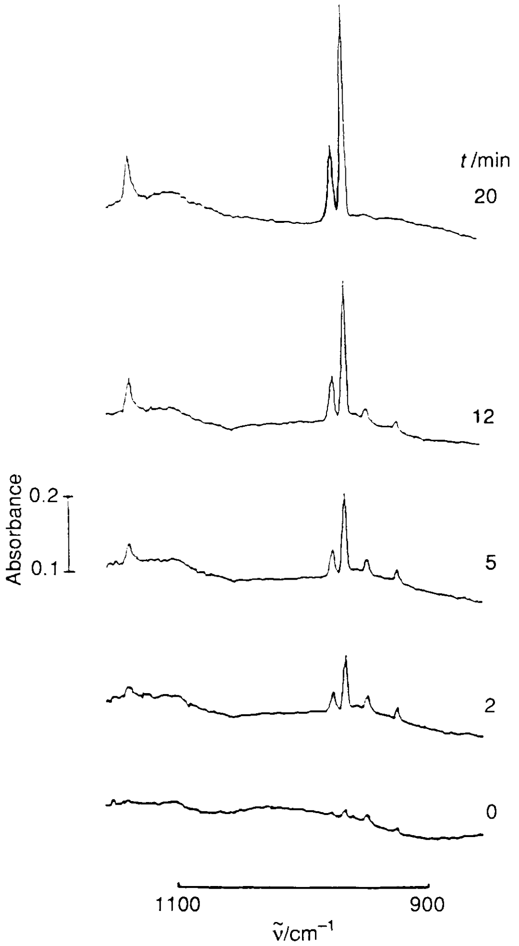


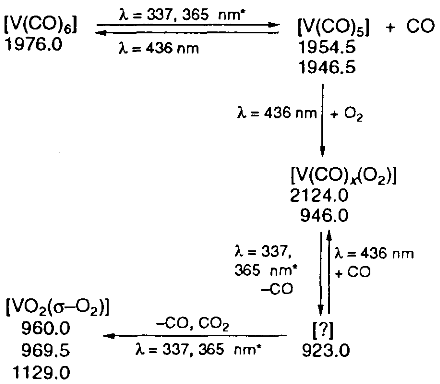
Fig. 2 The region 850–1150 cm^{-1} of the infrared absorption spectrum of a matrix (20 K) initially composed of [V(CO)$_6$], O$_2$ and Ar in the approximate proportions 1:200:1000 upon progressive broad-band UV/VIS photolysis

Table 1 Behaviour of IR absorption bands seen upon photolysis of [V(CO)$_6$] in 20% O$_2$-doped Ar matrices

	Time of photolysis[b]/min					
ν[a]/cm^{-1}	0	2	5	10	20	Origin
2343.0		app	inc	inc	inc	CO$_2$[c]
2137.5		app	inc	inc	inc	CO[d]
2124.0		app	dec	dis	—	**Y**[e]
1976.0	app	dec	dec	dec	dis	[V(CO)$_6$][f]
1954.5		app	dec	dec	dis	[V(CO)$_5$][g]
1946.5		app	dec	dec	dis	[V(CO)$_5$][g]
1129.0		app	inc	inc	inc	**A**[h]
969.5		app	inc	inc	inc	**A**[h]
960.0		app	inc	inc	inc	**A**[h]
946.0		app	dec	dis	—	**Y**[e]
923.0		app	dec	dis	—	**Z**[i]
596.0	app	dec	dec	dis	—	[V(CO)$_6$][f]
563.5		app	inc	inc	unc[j]	**A**[h]
438.0	app	dec	dec	dis	—	[V(CO)$_6$][f]

[a] ± 1 cm^{-1}. [b] app = Appears, dis = disappears, unc = unchanged in intensity, inc = increased in intensity, dec = decreased in intensity. [c] Ref. 15. [d] Ref. 16. [e] Oxocarbonyl intermediate, not fully characterised. [f] Ref. 14. [g] Ref. 25. [h] **A** = [VO$_2$(σ-O$_2$)] (see text). [i] Unidentified intermediate. [j] Weak band, therefore difficult to discern small changes in intensity.

that the bands at 923 and 946 cm^{-1} probably do not belong to the same molecule. It is also certain from these experiments that the bands at 969.5 and 960.0 cm^{-1} belong to a common product since their intensity ratio remains constant at $I_{969.5}:I_{960.0}$ = 1:2.9(±0.1). Similarly, the band at 1129.0 appears to belong to the same product as that at 969.5 since the intensity ratio $I_{1129.0}:I_{969.5}$ is constant, within the limits of experimental error, at 1:2.8(±0.2). Thus we may assign the bands at 1129.0, 969.5 and 960.0 cm^{-1} to a common product, **A** (Table 1). Not unexpectedly, the reaction proceeds rather more rapidly when higher O$_2$ concentrations are used: complete oxidation of [V(CO)$_6$] takes about 90 min in a 5% O$_2$-doped Ar matrix, as opposed to *ca.* 20 min in a 20% O$_2$-doped Ar matrix.



Scheme 1 Steps denoted * are also initiated by broad-band UV/VIS photolysis

The effect of irradiating the matrix with light of different wavelengths is perhaps of more interest. Narrow-band UV irradiation at λ = 337 nm causes production of the same intermediates and products as does broad-band irradiation but the reaction is enormously decelerated; after photolysis for 1 h under these conditions there has been only a relatively small decline in the intensity of absorptions arising from [V(CO)$_6$] (*ca.* 35%) and only extremely weak features are seen in the region 900–1200 cm^{-1}. However, if the reaction is first initiated by between 2 and 5 min broad-band irradiation and then narrow-band photolysis is employed some interesting features are seen [Figs. 3(*b*)–3(*d*)]. Irradiation at λ = 436 nm of a matrix which has previously been subjected to broad-band photolysis for 2 min causes the concentration of [V(CO)$_5$] to decline and that of [V(CO)$_6$] to increase, presumably by reaction (1), thus demonstrating that the interconversion of

$$[V(CO)_5] + CO \xrightarrow{\lambda\, =\, 436\ \mathrm{nm}} [V(CO)_6] \qquad (1)$$

matrix-isolated [V(CO)$_5$] and [V(CO)$_6$] is photochromic. There is also an increase in the concentration of **Y**. These bands assigned to **Y** decline in intensity, however, when UV light at a wavelength of 337 or 365 nm is used to irradiate the matrix. Under the same conditions the concentration of **A** rises and there is some conversion of [V(CO)$_6$] to [V(CO)$_5$]. None of [V(CO)$_5$], **Y** or **Z** are ever built up in high yield; never more than *ca.* 10% of the yield of **A** judging by the relative intensities of their IR absorptions. Their yield is not greatly increased by filtered photolysis, implying that they show rather wide absorption bands. This assertion is backed up by the finding that the concentration of **A** increases irrespective of whether visible or near UV light is used to irradiate the matrix [Fig. 3(*b*)]. There is no sign of any other oxocarbonyl intermediate in any of our experiments. It is now possible to propose the outline reaction mechanism which is shown in Scheme 1.

In order to identify positively the product of the reaction it is necessary to turn to experiments utilising the isotope ^{18}O. Three such experiments were performed: (*i*) where the matrix initially contained [V(CO)$_6$], ^{18}O$_2$ and Ar in the approximate proportions 1:100:1000; (*ii*) where the matrix initially contained [V(CO)$_6$], ^{16}O$_2$, ^{18}O$_2$ and Ar in the approximate proportions

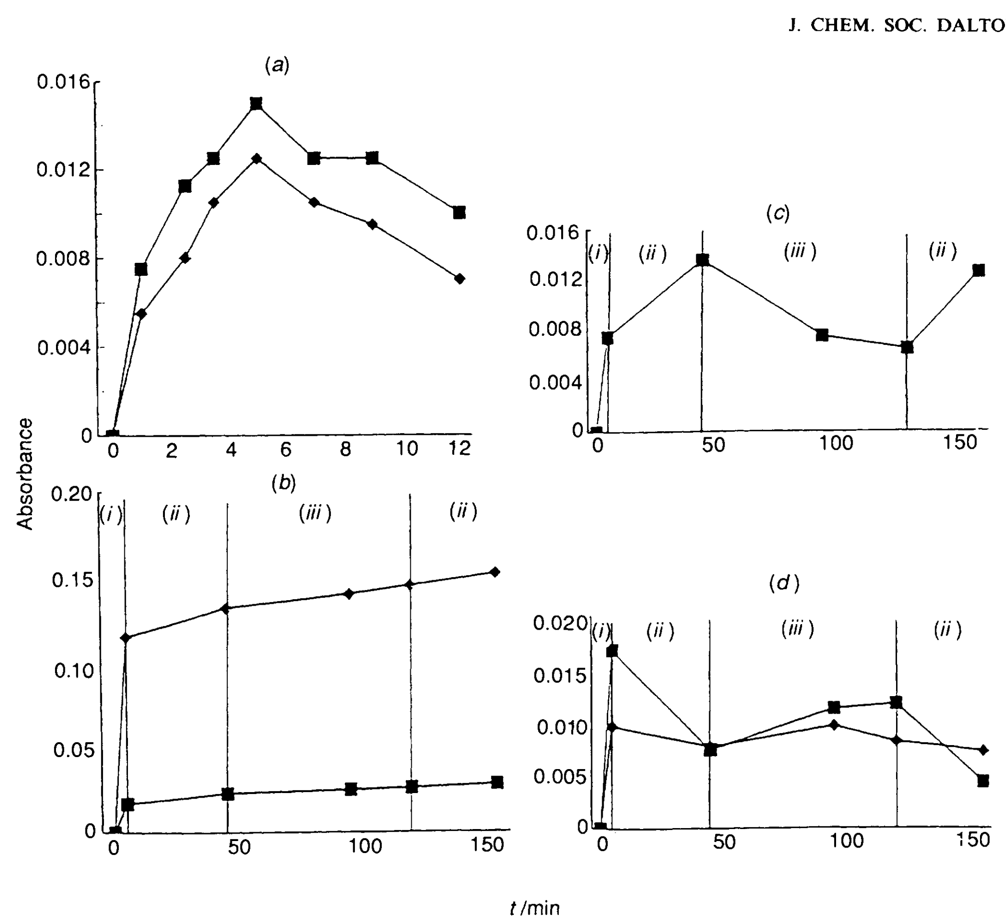


Fig. 3 Plots of absorbance *versus* time showing: (*a*) the growth and decay of bands of **Z** at 923 cm^{-1} (■) and **Y** at 946 cm^{-1} (◆) upon broad-band photolysis; (*b*) the growth of bands of **A** at 1129 (■) and 960 cm^{-1} (◆) upon narrow-band photolysis; (*c*) the growth and decay of the band at 1946.5 cm^{-1} of [V(CO)$_5$] upon narrow-band photolysis; (*d*) the growth and decay of bands of **Y** (■) at 946 cm^{-1} and **Z** (◆) at 923 cm^{-1} upon narrow-band photolysis. The matrices used for these experiments were initially composed of [V(CO)$_6$], O$_2$ and Ar in the approximate proportions 1 : 200 : 1000 and were held at a temperature of 20 K; (*i*) broad-band irradiation, (*ii*) λ = 365 nm, (*iii*) λ = 436 nm

Table 2 Behaviour of IR absorption bands assigned to photoproduct **A** upon isotopic substitution with ^{18}O

ν^a/cm^{-1}						
$^{16}O_2$	$^{18}O_2$	$^{16}O^{18}O$	Δ^b/cm^{-1}	R^c	ρ^d	Assignment
1129.0	1064.5	1097.0	64.5	0.9429	0.99	ν(O–O)
969.5	929.0	931^e	40.5	0.9582	1.90	$\nu_{sym}(VO_2)$
960.0	921.5	957^e	38.5	0.9599	0.15	$\nu_{asym}(VO_2)$
563.5	539.5	f	24.0	0.9574	—	ν(V–O)

^{a} ±0.5 cm^{-1}. ^{b} $\Delta = \nu(^{16}O_2) - \nu(^{18}O_2)$, ±1.0 cm^{-1}. ^{c} $R = \nu(^{18}O_2)/\nu(^{16}O_2)$, ±0.0008. ^{d} $\rho = [\nu(^{16}O_2) - \nu(^{16}O^{18}O)]/[\nu(^{16}O_2) - \nu(^{18}O_2)]$. ^{e} Approximate values; exact positions difficult to measure owing to band overlap. ^{f} Not observed.

1 : 50 : 50 : 1000; (*iii*) where the matrix initially contained [V(CO)$_6$], $^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$ and Ar in the approximate proportions 1 : 25 : 50 : 25 : 1000.

Upon substituting $^{16}O_2$ by $^{18}O_2$ the bands at 1129.0, 969.5, 960.0, 946.0 and 563.5 cm^{-1} shift to 1064.5, 929.0 (sh), 921.5, 906.5 and 539.5 cm^{-1} respectively. These isotopic shifts are listed in Table 2, while the spectra are illustrated in Fig. 4. The shift of 64.5 cm^{-1} in the band at 1129.0 cm^{-1} is almost exactly as calculated (64.6 cm^{-1}) for a ν(O–O) vibration of a co-ordinated O$_2$ group.[17] The shift of 24.0 cm^{-1} in the band at 563.5 cm^{-1} is likewise close to the shift calculated (24.4 cm^{-1}) for a ν(V–O) vibration of a co-ordinated O$_2$ unit and thus confirms the identity of this moiety as V(η^2-O$_2$) or V(σ-O$_2$). The shift of 38.5 cm^{-1} in the band at 960.0 cm^{-1} is consistent with this feature arising from the ν_{asym}(OVO) vibration of an O=V=O unit with an upper limit for the bond angle of 115°.[27] This bond angle is very close to that calculated from the intensity ratio I_{asym} : I_{sym} for this species;[28] the measured ratio of 2.9(±0.1) : 1 would give a bond angle of 108 ± 5°. This value may be compared with the OVO angle of 107.1(3)° in the vanadium(v) complex [PMePh$_3$]$^+$[VO$_2$Cl$_2$]$^-$ as determined by single-crystal X-ray diffraction.[21] The shift of 40.5 cm^{-1} in the band at 969.5 cm^{-1} is consistent with this band arising from the ν_{sym} mode of such a unit.[1] Thus the identity of this moiety is almost certainly a non-linear dioxovanadium unit, *i.e.* VO$_2$. The shift of 39.5 cm^{-1} in the band at 946.0 cm^{-1} is consistent with this intermediate oxocarbonyl species also containing a dioxo unit with a bond angle of *ca.* 120°. Unfortunately it was not possible to build up **Z** in a large enough quantity to perform any isotopic substitution experiments on this intermediate.

The experiment utilising a mixture of $^{16}O_2$ and $^{18}O_2$ serves to confirm these isotopic shifts. Moreover the fact that no additional features are seen (see Fig. 4) demonstrates that the product is formed from reaction with just two O$_2$ molecules. Had more than two O$_2$ molecules been involved we would expect to see features arising from 'scrambled' isotopomers containing both ^{16}O and ^{18}O.

The classical way to distinguish, using vibrational spectroscopy, between σ- and η^2-co-ordinated O$_2$ units is to prepare the species containing the three oxygen isotopomers $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$. Observation of a single band arising from the mixed isotopomer is taken as evidence of σ-co-ordination, while η^2-co-ordination should give rise to *two* bands from this isotopomer because of the two different possible modes of ligation of σ-$^{16}O^{18}O$, *i.e.* M–$^{16}O^{18}O$ and M–$^{18}O^{16}O$,[17,29] although the splitting between the two bands can be small. Thus in the cobalt(II) porphyrin [Co(tpp)(O$_2$)] (H$_2$tpp = 5,10,15,20-tetra-

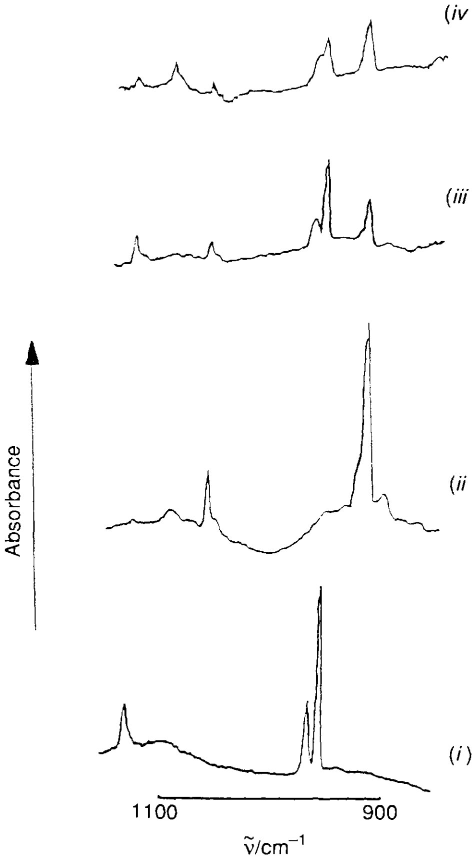
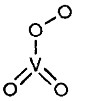


Fig. 4 The region 850–1150 cm^{-1} of the infrared absorption spectra of matrices (20 K) after broad-band UV/VIS photolysis for 20 min: (*i*) initial matrix composition $[V(CO)_6]$:$^{16}O_2$:Ar = *ca.* 1:100:1000; (*ii*) initial matrix composition $[V(CO)_6]$:$^{18}O_2$:Ar = *ca.* 1:100:1000; (*iii*) initial matrix composition $[V(CO)_6]$:$^{16}O_2$:$^{18}O_2$:Ar = *ca.* 1:50:50:1000; (*iv*) initial matrix composition $[V(CO)_6]$:$^{16}O_2$:$^{16}O^{18}O$:$^{18}O_2$:Ar = *ca.* 1:25:50:25:1000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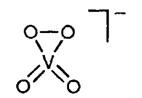
B

phenylporphyrin) the $^{16}O^{18}O$ adduct (where the O_2 unit is bonded in side-on fashion) exhibits bands at 1252 and 1241 cm^{-1} arising from the two isotopomers. In the iron analogue $[Fe(tpp)(O_2)]$ the separation between the corresponding two bands is less than 3 cm^{-1}.[17] As shown in Fig. 4, although there appears to be only one band arising from the $^{16}O^{18}O$ isotopomer of A the feature is quite broad, so that it is not possible to distinguish unequivocally between peroxo (η^2) and superoxo (σ) ligation of the O_2 unit on the basis of this spectrum alone. This central band is, however, symmetrically disposed between the two outer features which result from the $^{16}O_2$ and $^{18}O_2$ isotopomers. The asymmetry parameter ρ[1,6] = 0.99, confirming that these features do indeed arise from ν(O–O) of a co-ordinated O_2 unit.[1,6] The bands arising from the dioxo part of **A** containing the three O_2 isotopomers $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ are likewise not straightforward to interpret. However, the pattern can be fitted to the expected pair of highly unsymmetrical triplets[1,6] where $\rho(\nu_{asym})$ = *ca.* 0.15 and $\rho(\nu_{sym})$ = *ca.* 1.90, such that the bands are strongly overlapping and individual components cannot be resolved. The two triplets would be expected to be highly unsymmetrical since ν_{sym}- and ν_{asym}-(O=V=O) are very close in energy (9 cm^{-1}) and since $\nu_{sym} > \nu_{asym}$ then $\rho(\nu_{sym}) > 1$ and $\rho(\nu_{asym}) < 1$. Although by no means completely certain this is the only reasonable interpretation which can be placed on the spectral data. A *trioxo* unit is extremely unlikely for a vanadium compound and the ^{16}O–^{18}O isotopic shift and band position[30] are not consistent with a monoxo unit. When $[V(CO)_6]$ partially enriched in ^{13}CO was utilised in place of natural-abundance $[V(CO)_6]$ as the starting material the band of **Y** at 2124 cm^{-1} was seen to give way to a pair of bands at 2124 and 2077 cm^{-1}. This finding serves to identify the band as arising from a ν(CO) vibration and suggests that **Y** contains a monocarbonyl unit.

Taken together these results provide a body of evidence that the product of photo-oxidation of $[V(CO)_6]$ in matrices containing O_2 is either the anionic species $[VO_2(\eta^2\text{-}O_2)]^-$,**B** or the neutral species $[VO_2(\sigma\text{-}O_2)]$ **A**.

We may summarise briefly the evidence in favour of each formulation. The remarkable correspondence between the IR spectra of the VO_2 part of the product with the IR spectra of the VO_2 parts of the vanadium(v) anions $[VO_2Cl_2]^-$ [21] and $[VO_2F_2]^-$ [22] suggests a close structural and electronic similarity between the three species and thus provides persuasive, though not conclusive, evidence in favour of the anion. Against this is the wavenumber (1129.0 cm^{-1}) of the ν(O–O) vibration, a value which is extremely high for a peroxo (η^2) unit but entirely typical for a superoxo σ unit.[17] Furthermore we see no sign of any cationic counterpart to an anionic product in any of our experiments. It seems unlikely that an infrared silent cation such as O_2^+ has been formed. Thus we may conclude that the product of photo-oxidation of $[V(CO)_6]$ in O_2-doped matrices is the neutral molecule $[VO_2(\sigma\text{-}O_2)]$ **A**. It is shown that the reaction is initiated by loss of a CO group from $[V(CO)_6]$ to yield $[V(CO)_5]$[25] and proceeds *via* two detectable intermediates **Y** and **Z**. Intermediate **Y** is probably $[V(CO)O_2]$; the nature of **Z** remains unclear. It shows no co-ordinated CO groups and appears not to be VO_2.[24]

We may compare briefly the result of photo-oxidation of $[V(CO)_6]$ with that of other binary carbonyls. The observation that $[V(CO)_6]$ is oxidised to the +v oxidation state when $[Cr(CO)_6]$ is not oxidised to the +vi state *possibly* reflects the greater ease with which the V^V oxidation state is reached.[31] It is perhaps not surprising to find that vanadium oxide species, in the presence of O_2, give rise to a product like **A** which contains co-ordinated O_2 as well as a dioxo unit. This finding is entirely in line with the known behaviour of high-valent vanadium oxo species in the presence of H_2O_2 in solution.[9] It is also of interest that the paramagnetic $[V(CO)_6]$ yields a product which contains a σ-co-ordinated O_2 unit, a behaviour which stands in contrast to the known chemistry of diamagnetic mononuclear metal carbonyls under similar conditions.[1–3,6–8]

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