Flash Photolysis of Vanadium Oxide Trichloride Vapour. Some New Electronic Transitions of VO

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Flash photolysis of $VOCl_3$ vapour under adiabatic conditions yielded in absorption the visible $C^4\Sigma^- - X^4\Sigma^-$ band system of VO, together with eight new, diffuse u.v. spectra of widely varying intensity, in the range 2300—3800 Å. A comparison is made with the known u.v. transitions of the analogous molecule TaO. No trace of a reported u.v. system near 4000 Å, attributed to matrix isolated VO, was observed. Ground and excited state vanadium atoms were detected, and both photolytic and pyrolytic decomposition modes of $VOCl_3$ are postulated.

EARLIER studies of the electronic transitions of the emitting VO molecule were based on flame,[1] arc,[1,2] and stellar[3] spectra. They revealed the existence of at least two definite and distinct band systems, now described as $C^4\Sigma^- - X^4\Sigma^-$, in the visible, and $B^4\Pi - X^4\Sigma^-$ in the near-i.r.[4] (0·6—0·9 μm) regions, respectively. It is still not certain[5] whether a third group of bands in the i.r.[6] (1—1·5 μm) constitutes a new system or is to be associated with the B–X transition, nor has the lower state of this group of bands been positively identified. The first two systems mentioned were shown to have their lower states in common but it was not known from the emission studies whether this was the ground state or not. Then Richards and Barrow[7] used a carbon tube furnace at 1873 K to obtain some bands of the B–X and C–X systems in absorption. They made a rotational analysis which confirmed the (common) ground state as being $^4\Sigma^-$, and not $^2\Delta$ as previously suggested.[2] A claim[8] made before Richards and Barrow's work[7] that the ground state of VO had been identified is obviously an error, since the reference quoted relates to the ground electronic state of BaO.

Additional confirmation that the lower state of the emission systems was the ground state was found by Weltner and McLeod[9] who obtained the corresponding absorption spectra of VO isolated in a neon matrix at 4 K. These workers also observed four weak, sharp bands attributed to an additional VO system lying between 3798 and 4185 Å. This system, referred to as being D–X, has never been reported as seen in the gas phase. An e.s.r. study[10] of VO in an argon matrix at 4 K yielded independent proof that the ground state was $^4\Sigma^-$, as did some *ab initio* calculations by Carlson and Moser,[11] although the possibility of a $^2\Sigma^-$ state could not be entirely ruled out here.

The present investigation had originally been undertaken to determine whether a relatively intense $C^4\Sigma^- - {}^4\Sigma^-$ system could be detected in absorption, thus establishing the lower state as the ground state. It was made superfluous in this respect, though, by the work of Richards and Barrow[7] and was then later extended with the following objects: (1) to investigate discrepancies in band head data and molecular constants reported by various authors;[2,8,12] (2) to detect in the gas-phase bands of the new matrix absorption system[9] near 4000 Å; (3) to see if any additional absorption systems could be observed. A different experimental approach from that of previous workers was used, in that the VO was formed by the flash photolysis of $VOCl_3$ vapour.

EXPERIMENTAL

A conventional flash photolysis apparatus was used, having photoflash and spectroflash $1/e$ durations of 35 and 9 μs, respectively. The quartz reaction vessel was 45 cm long and used in conjunction with a Hilger and Watts glass/quartz spectrograph (Type E742), although for part of the time a medium quartz spectrograph (E498) was employed. $VOCl_3$ (British Drug Houses Ltd.) was fractionated on a conventional vacuum line and stored at 77 K. Contamination was avoided by using all-metal Hoke valves instead of greased taps. British Oxygen Co. oxygen-free nitrogen was used without further treatment. The Ilford HP3 photographic plates had a usable spectral response under flash conditions from 2100 to 6550 Å. Wavelength calibrations were made with a D.C. iron arc and Hartmann diaphragm. Low pressures of nitrogen were measured with an all-glass spoon gauge and higher pressures with a mercury manometer. The pressure of $VOCl_3$ was not measured directly, but was controlled by adjusting the temperature of the liquid in a reservoir attached to the reaction vessel. Preliminary experiments showed that a temperature of 250 K was suitable. At this temperature the vapour pressure of $VOCl_3$ can be calculated to be *ca.* 146 N m^{-2}, using the known[13] boiling point and latent heat of vaporisation.

RESULTS

It was found in preliminary experiments that the vapour of $VOCl_3$ has a high extinction coefficient throughout the whole u.v. region, but absorbs much less strongly in the

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visible. In particular, the absorption continuum has a maximum near 3350 Å and is very intense below 2600 Å. Flash photolysis (a nominal 1350 J) of VOCl$_3$ vapour under adiabatic conditions, that is with no foreign gas present at all, revealed the presence of numerous transient absorption spectra (Plate). The addition of nitrogen, even at pressures below 1 kN m^{-2}, had an adverse effect on the intensity of the transients and so the isothermal work was discontinued. No bands of ClO were observed under any conditions.

The spectra resulting from adiabatic flash photolysis may conveniently be arranged into four groups. (i) *The* VO *C–X bands.*[6] Altogether, 27 bands of this extensive system, lying between 4630 Å and the limit of the plate response (near 6550 Å) were detected, some of them possibly for the first time in absorption because ground electronic state vibrationally excited levels ($v'' \leqslant 3$) were appreciably populated. Excitation of still higher v'' levels almost certainly occurred but the relevant transitions lie beyond 6550 Å. The bands showed rotational structure,[2,8] with the band head measurements being in fairly good agreement (± 3 cm^{-1}) with Mahanti's arc bands.[2]

(ii) *Transitions in the u.v. region.* A number of new absorption systems lying between 2300 and 3800 Å were observed, but not the *D–X* bands of Weltner and McLeod [9] near 4000 Å. It is of interest to note that a similar unexplained discrepancy [14] was found in a comparison of the gas phase and matrix spectra of TaO near 4500 Å. The transient u.v. and visible spectra were present at low intensity during the early part of the photolysis flash, reached maximum intensity after about 300 μs delay, long after the termination of the flash, and had decayed to zero intensity by one ms. For the most part, the u.v. absorptions appeared to be diffuse, although it was not possible to decide unambiguously whether this diffuseness was real, or apparent and caused by the overlapping of bands. The absorptions near 3545 and 3740 Å did exhibit some incipient structure but closer examination showed some of the heads to be false, arising from overlapping VI transitions. A summary of the wavelengths and overall appearance of the u.v. systems is given in Table 1(*a*). The bands of the 3545 Å system are listed separately in Table 1(*b*). They are indeed rather diffuse but on balance appear to be slightly degraded to longer wavelengths.

TABLE 1

(*a*) Characteristics of the u.v. band systems produced when VOCl$_3$ is flash photolysed (1350 J)

Approximate band width (Å)	Band centre		Visual intensity [a] (0—10)
	Å	cm^{-1}	
12	2375	42,110	1
25	2430	41,150	10
35	2645	37,810	2
160	2990	33,440	10
65	3110	32,150	8
65	3275	30,530	2
40	3545	28,210	2
80	3740	26,740	2
	(Weak continuum 2445—2900 Å?		0)

[a] On this scale the *C–X* bands near 5100 Å have an intensity of *ca.* 3.

(*b*) Band heads in the 3545 Å system. Other heads are present but are too weak or diffuse to be measurable

λ_{air} (± 1 Å)	ν_{air} (cm^{-1})	λ_{air} (± 1 Å)	ν_{air} (cm^{-1})
3522·3	28,390	3565·0 [b]	28,050
3534·7	28,290	3568·8 [b]	28,020
3550·1 [b]	28,170	3573·5	27,980
3558·0 [b]	28,110		

[b] These bands are considerably more intense than the others.

(iii) *Post photolysis continuum.* This feature extended from *ca.* 3900 Å to shorter wavelengths. The absorption was relatively weak from *ca.* 2800 to 3100 Å, but particularly intense between 3200 and 3600 Å with a maximum near 3350 Å, and it first appeared a few ms after the photoflash. It was very prominent after *ca.* 30 s and had decayed by a considerable extent after 5 min.

(iv) *Atomic transitions.* A large number of absorption lines of atomic vanadium appeared throughout the entire wavelength region under investigation, many of them originating from excited atoms. In the absence of a spectroscopic flash some atomic emissions were recorded. The atomic spectra were not investigated further beyond the observations that (*a*) they could be detected on the zero delay exposure, especially the lines at 3183·99 and 3185·41 Å, (*b*) they reached a maximum concentration during the period of the photolysis flash, (*c*) the excited atoms had largely relaxed by about 115 μs, and (*d*) the ground-state atoms eventually disappeared between 700 μs and 1 ms.

DISCUSSION

The Mechanism of VOCl$_3$ *Decomposition.*—It appears that more than one process is involved in production of the carriers of the transient spectra, and a complete elucidation of the mechanism would necessarily constitute a separate, detailed study. However, a few general comments may be made. The formation of vanadium atoms at zero delay time, and at maximum concentration during the photolysis flash period, suggests that this process is probably photolytic rather than pyrolytic. On the other hand, photolysis could not cause a great deal of decomposition since direct rupture of the V–O bond [6] would involve absorption of light of wavelengths <2000 Å, that is in a region where light input to the reaction vessel is low. An alternative possibility involves reaction between two electronically excited VOCl$_3$ molecules. The participation of such energy-rich molecules in the flash photolytic decomposition of CrO$_2$Cl$_2$ has been established by Wild and his co-workers,[15] although they did not report the detection of chromium atoms, nor of CrO.

As the vanadium atom concentration diminishes, the intensity of the transient u.v. and visible spectra increases, a result which could superficially be attributed to the combination of V and O atoms to form, for example, VO, provided sufficient undecomposed VOCl$_3$ was present to act as a third body. A more probable explanation of the build-up of transient species, though, would be the progressive pyrolysis of VOCl$_3$ caused by the temperature rise resulting from the adiabatic conditions. The transition metal oxides, MO, are exceedingly

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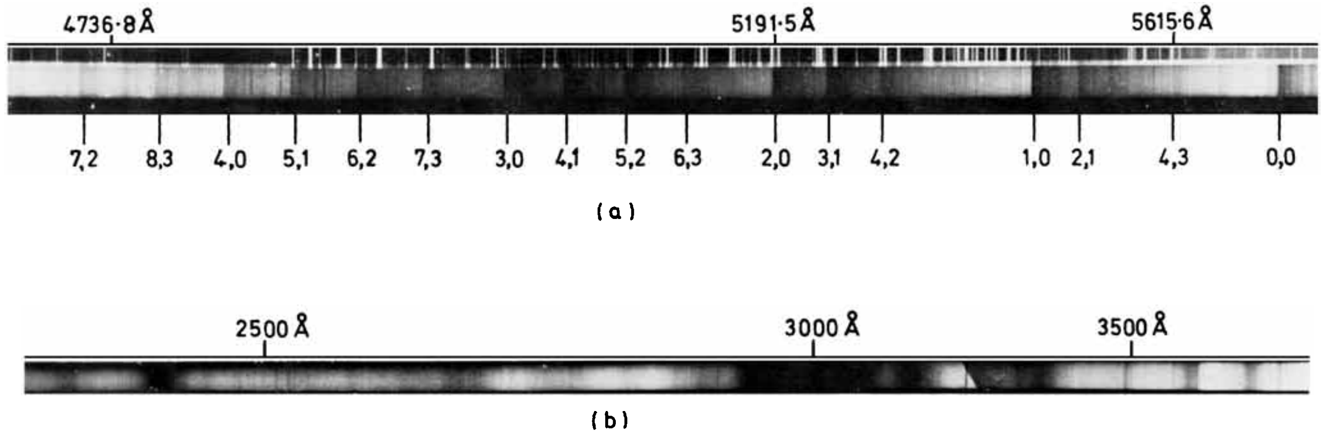


PLATE. Transient absorption spectra observed during the adiabatic flash photolysis of vanadium oxide trichloride vapour at a pressure of 146 Nm^{-2}. Photoflash energy 1350 J; delay time 186 μs. The comparison spectrum is an iron arc. (a) Part of the VO C–X system showing some of the bands originating from excited v'' levels; (b) U.v. spectra ascribed to VO and atomic vanadium.

stable [16] and the VO molecule in particular has been reported to be thermally stable in the gas phase at 2073 K. If the $VOCl_3$ were to decompose in the above manner, then presumably any $VOCl_2$ or VOCl present would be similarly unstable. The appearance of the VO visible band system at delay times as short as 10 μs shows also the presence of a possible second mode of direct photolysis, $VOCl_3 + h\nu \longrightarrow VO + Cl_2 + Cl$.

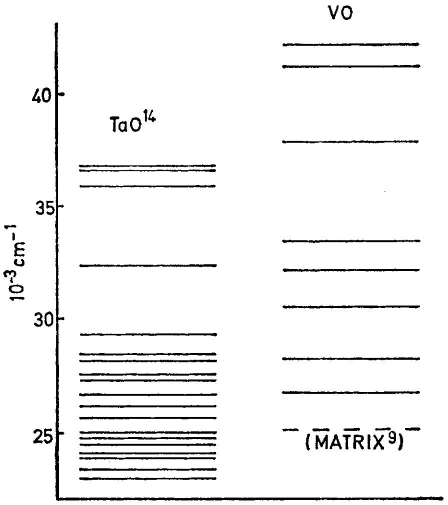
Identification of the Transient Species.—It has already been stated that the numerous bands beyond 4630 Å arise from the VO *C–X* transition.[7] That VO is truly the carrier has been established by Mahanti.[2] The two additional VO band systems in the i.r. region [5] were not detected in the present work since they lay beyond the long wavelength limit of the plates.

The previously unreported u.v. transients cannot be positively identified but on balance are attributable to VO. A supporting argument is that the transient molecular spectra, including the *C–X* bands, rise and decay at about the same rate. It is highly improbable that a mixture of two or more species, for example VO, VOCl, $VOCl_2$, and possibly V_2 as well would behave in this manner. In any case, the postulated pyrolytic origin of VO precludes the presence of the other species. The generally diffuse, apparently continuous nature of most of the u.v. bands may be more apparent than real, and caused by the fairly modest resolving power (*ca.* 25,000) of the spectrograph. A similar situation exists in the example of TiCl,[17] the spectrum of which has been examined under high resolution [18] when the seemingly diffuse, narrow continua were shown to have an extremely complex vibrational and rotational structure.

The post-photolysis continuum cannot easily be explained. If it is a light-scattering phenomenon caused by particles of V_2O_5 or metallic vanadium, it is difficult to see how the unusual wavelength dependence arises. On the other hand it is possible that a slow reaction is occurring to give a temporary build-up of a strongly absorbing product which then gradually decomposes into final products. Certainly neither $VOCl_3$ nor chlorine is responsible for the 3350 Å absorption maximum in spite of their each having a band in this region, since they could only be present at far too low a pressure.

Classification of the Observed Transitions.—Since the u.v.-bands attributed here to VO could obviously be classified into two categories *viz*, very intense and relatively weak [Table 1(*a*)], it is tempting to attribute them to fully allowed and to semi-forbidden transitions, respectively. However, such assignments could only be reliably checked after a suitable high-resolution study. The possibilities also exist that the weaker bands belong to V_2, or to doublet-doublet transitions of VO. Doublet states could arise from $O(^3P) + V(^6D)$, the latter excited state being only 2112 cm^{-1} above the vanadium atom ground state.

Kasai [10] has proposed a M.O. scheme for VO, closely similar to that of Weltner and McLeod [19] for the not too different molecule TiO, in which the highest occupied levels (σ_n and δ) are essentially non-bonding and derived from the vanadium 4*s* and 3*d* levels, respectively. Details of higher energy orbitals in diatomic molecules containing a transition-metal atom are not generally available,[20] owing to the dearth of experimental data and the difficulty of making precise M.O. calculations. The ordering of the last three electrons in ground state VO was long in doubt but it has now been firmly established [10,11] that the state is $\sigma\delta^2$, $^4\Sigma^-$. The M.O. scheme of Kasai [10] may be used as a basis for assigning some of the observed spectra. For example, the *B–X* i.r. system is consistent with $\sigma\delta^2 \rightarrow \sigma\delta\pi^*$, and the slightly more energetic *C–X* visible system with $\sigma\delta^2 \rightarrow \sigma\delta\sigma^*$. In both cases there is spin conservation, and as the transitions are of the non-bonding to anti-bonding type, an increase in internuclear separation would be expected, in agreement with the observed degradation of the bands to longer wavelengths. Attempts to correlate the numerous other spectra observed in this work with specific electron configurations would scarcely be profitable without a fuller knowledge of the transitions.[20] However, details of numerous electronic states of the related molecule TaO are known,[14] and a comparison of these with the new ultraviolet spectra of VO is shown in the Figure.



A comparison of the electronic levels of TaO[14] with those of VO found in the present work. The broken line indicates a level observed only in matrix studies [9]

Molecular Constants of the $X^4\Sigma^-$ State. The desirability of using a technique such as flash photolysis for producing ground-state transition-metal oxides MO with the rotational fine structure less developed has been pointed out by Barrow,[16] and the present work shows not only that $VOCl_3$ is a suitable precursor in this instance but that the u.v. regions of interest are delineated.

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Band heads of the visible C–X system obtained in absorption in the present work are not listed here since they are in good agreement with the emission band head data of Mahanti [2] and there is no doubt that the relationship [2]

$$\nu = 17501{\cdot}3 + [863{\cdot}5(v' + \tfrac{1}{2}) - 5{\cdot}4(v' + \tfrac{1}{2})^2] - [1012{\cdot}7(v'' + \tfrac{1}{2}) - 4{\cdot}9(v'' + \tfrac{1}{2})^2]$$

does predict band head positions adequately (±2 cm^{-1}) for $v'' < 9$ and $v' < 9$. On the other hand, the currently accepted molecular constants, based on a revised analysis by Lagerqvist and Selin [8] (Table 2) do utilise band origin determinations but only involve the (2,0), (1,0), (0,0), (0,1), and (0,2) bands. They do not predict the band head frequencies even approximately (errors of 50 cm^{-1} or so) when higher values of v' are concerned. The discrepancy here lies not so much in the fact that the head-to-origin separations are by no means negligible (about 4 cm^{-1}, by calculation) but that Lagerqvist and Selin's upper state constants are stated by them [8] to be not so accurate because of perturbations. If their $\omega_e x'$ value of $\sim$6·6 cm^{-1} be replaced provisionally with Mahanti's [2] value of 5·4 cm^{-1} then the observed band heads and the calculated origins agree within 7 cm^{-1} or better, depending on v'. It is obviously desirable that a more extended rotational study of the VO visible bands be made, using high resolution.

TABLE 2

Molecular constants associated with the VO C–X transition. Values are in cm^{-1} units. A comparison of the two sets of figures is made in the final part of the Discussion

Constant	ω_e''	$\omega_e x''$	B_e''	α_e''	ω_e'
Mahanti [2]	1012·7 [a]	4·9 [a]	0·3876	0·0024	863·5 [a]
L. and S. [8]	1011·6	4·97	0·5480	0·0034	865·9

Constant	$\omega_e x'$	B_e'	α_e'	T_e'
Mahanti [2]	5·4 [a]	0·3349	0·0027	17,501·3
L. and S. [8]	$\sim$6·6	0·4953	0·0035	17,492·2

[a] In agreement with values found in this work.

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