Vapour Transport of Dioxygenyl Salts

By **Michael J. Vasile** * and **Warren E. Falconer**, Bell Laboratories, Murray Hill, New Jersey 07974, U.S.A.

The species present in the vapour phase over solid dioxygenyl salts have been examined using modulated molecular-beam mass spectrometry and electric deflection. All the dioxygenyl salts studied ($O_2Nb_2F_{11}$ + O_2NbF_6, $O_2Sb_2F_{11}$, O_2SbF_6, $O_2Ta_2F_{11}$, O_2BiF_6, O_2RuF_6, O_2RhF_6, and O_2PtF_6) decomposed upon vaporization. The salts of Ru, Rh, and Pt yield O_2 and the corresponding hexafluoride, which can reversibly reform the salt if conditions are such that hexafluoride does not first decompose. The remainder of the salts studied decomposed to O_2, F_2, and MF_5.

A PRIORI, one might expect ionic complexes to attain considerable stabilization in the crystalline solid state and consequently to melt or vaporize only at high temperature, possibly above temperatures of extensive dissociation or decomposition of the complex. Dioxygenyl compounds are usually formulated as $O_2^+A^-$, where most of the known A^- are hexafluoro-anions. This implies extensive charge transfer from molecular oxygen, and, hence, reduced probability of sublimation, or of melting and evaporation. However, the large electron affinities of the metal hexafluorides might be sufficient to stabilize the ion pairs as free molecules through Coulombic interactions. Bartlett and Lohmann[1] observed that O_2PtF_6 could be moved *in vacuo* above 90 °C without decomposition, apparently by sublimation. Edwards *et al.*[2] found similar behaviour for O_2PtF_6, O_2RuF_6, and O_2RhF_6, but dioxygenyl salts with group V hexafluoro-anions could not be transferred by heating *in vacuo*. In accord with this latter observation, Young *et al.*[3] have presented evidence that O_2SbF_6 decomposes into O_2, F_2, and SbF_5 above 100 °C.

Mass spectra of dioxygenyl salts of those metals that form strongly oxidizing hexafluorides (Ru, Rh, and Pt), obtained at the lowest temperatures giving adequate signals, appeared to be those of the corresponding hexafluoride admixed with oxygen.[2] By contrast mass spectra of the dioxygenyl salts of elements that form pentafluorides with a high affinity for F^-, obtained under comparable conditions, resemble those of the corresponding pentafluoride with some oxygen and fluorine present.[2] This suggested that thermal decomposition to the pentafluoride occurs, and indeed, after prolonged heating at higher temperatures, the O_2^+ ion disappears from the mass spectrum leaving a fragmentation pattern characteristic of the metal pentafluoride alone. Within the first group of salts, the mass spectra of O_2PtF_6 remained invariant with increasing temperature to 138 °C, while O_2RuF_6 and O_2RhF_6 showed a transition to pentafluoride spectra at 70 and 60 °C. This behaviour is compatible either with the latter samples containing some of the less volatile pentafluoride as an impurity, or with decomposition in the molecular-beam source to form pentafluoride.

Since the electron-impact mass spectrum of a dioxygenyl salt might be very similar to the composite spectrum of the salt's components, these mass spectral data were inadequate to determine whether dioxygenyl compounds were transported intact in the gas phase. Therefore, we constructed a modulated molecular-beam apparatus with a mass-spectrometer detector and electric-deflection capability.[4] Modulation of the molecular beam permits one to distinguish by neutral flight times whether ions are fragments from a common progenitor, or whether a given fragment ion arises from different neutrals, possibly dissociation products, in the beam source.[5,6] Electric deflection by inhomogeneous electric fields discriminates between polar and nonpolar molecules in the beam, and is especially sensitive for near symmetric tops exhibiting first-order Stark effects.[7]

Strong focusing effects would be observed for O_2MF_6 compounds if they were intact in the molecular beam since the molecules would be quite polar. Furthermore, for O_2MF_6 units, the O_2^+ signal should be in phase with the MF_n^+ ($n = 0 \longrightarrow 6$) signals in the mass spectrum. On the contrary, if decomposition to O_2 and MF_6 (or $MF_5 + \frac{1}{2}F_2$) occurs in going to the vapour phase, these components will be independent of each other in the molecular beam, will therefore exhibit no polarity, and will show a large phase or time of flight difference due to the difference in molecular weights.

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[7] W. E. Falconer, A. Buchler, J. L. Stauffer, and W. A. Klemperer, *J. Chem. Phys.*, 1968, **48**, 312.

EXPERIMENTAL

All dioxygenyl salts used in this study were synthesized as previously described.[2] Samples were stored and loaded into effusion sources in a dry box (helium atmosphere; O_2, H_2O concentrations <1 p.p.m.). Molecular beams from Monel effusion sources were modulated by mechanical chopping in a differentially pumped source chamber. After traversing a path of 70 cm through a region in which an inhomogeneous quadrupolar electric field could be applied, the components were ionized by impact with 70 or 100 eV electrons, and the resultant ions mass analysed with a quadrupole mass filter.[4] Mass spectra were first obtained at effusion source temperatures just high enough to obtain adequate signal levels. Subsequent spectra were taken at higher temperature.

Three types of experiments were performed. (1) For each dioxygenyl salt, the molecular beam was tested for polar species and the phase relationship of each of the ions in the mass spectrum was established. (2) Representative samples were vaporized in a two-segment Monel system which connected to the gas source of the molecular-beam apparatus through a U-tube or straight collection tube maintained at dry-ice temperature (see Figure). The collection tube and gas source were extensively prefluorinated. These experiments showed if detectable pressures of O_2 or MF_6 exist in what is essentially a sublimation of the dioxygenyl salt. The collection tube segment was raised to room temperature and gas evolution was monitored. The vapour-transferred material in the tube was then either heated above room temperature or returned to the dry box and recovered for analysis. (3) O_2RuF_6 was vapour transferred in a quartz vessel with a central cold finger. The transfer temperature and the temperature of collection were varied to determine the conditions necessary for transfer as unchanged O_2RuF_6 or with decomposition to RuF_5.

RESULTS AND DISCUSSION

Focusing and phase-angle results for the dioxygenyl salts studied are summarized in the Table. In each case, the O_2^+ signal was out of phase with MF_n^+ ($n = 0 \longrightarrow 6$) signals at all source temperatures. If the O_2^+ and MF_n^+ peaks in the mass spectrum were to result from the electron-impact cracking of a single species, there would be no phase-angle difference in the synchronous detection of the modulated molecular beam. In test spectra of perfluorotri-n-butylamine, all the fragment ions, which vary in mass from 69 to 502 a.m.u., had phase angles within a 2° spread. A calculation of the mass difference required to produce a 3° difference in phase angles between O_2 and a heavier molecule originating from a source under true effusive conditions at 100 °C yields 12 a.m.u., or a molecular weight of 44. A similar calculation based on O_2 and PtF_6 at 87 °C predicts a phase-angle difference of 37°, while 25° was observed. Thus we conclude that the O_2^+ and MF_n^+ ions have different neutral progenitors, O_2 and either MF_5 or MF_6, formed by dissociation in the effusion source. Departures from true effusive flow from the molecular beam source are responsible for the disparity in the predicted and observed phase difference.

Dioxygenyl salt	Effusion source temp. (t/°C)	Phase difference (°) $\phi MF_n^+ - \phi O_2^+$
$O_2NbF_6 + O_2Nb_2F_{11}$ *	62	40
$O_2Sb_2F_{11}$	77—85	37
O_2SbF_6	82—85	31
$O_2Ta_2F_{11}$	100	23
O_2BiF_6	100	30
	121	28
O_2RuF_6	42	30
	55	34
	77	45
O_2RhF_6	15	28
	36	23
O_2PtF_6	87	25

* Mixture. † All non-polar.

Refocusing of the neutral beam species could not be achieved for any of the dioxygenyl salts tested. In this apparatus, ClO_3F, $\mu = 0{\cdot}024$ D,[8] could readily be refocused; 2% of the straight-through beam intensity was recovered with 20 kV applied to the quadrupole rods. Significantly larger refocusing was obtained for molecules with larger dipole moments, *e.g.* 40% of the unobstructed beam for ReO_3F ($\mu = 0{\cdot}85$ D)[9] at 5 kV. Signal to noise limits the minimum refocusing observable to 1% of the unobstructed beam. An undissociated ion pair such as $O_2^+MF_6^-$ would be expected to exhibit strong refocusing. Assuming that 40% refocusing would be obtained from such a species, then as little as 3% of the undissociated dioxygenyl salt in the molecular beam would show a refocusing effect above the noise level.

The dioxygenyl salts in the Table apparently vaporize with dissociation according to the following equations:

$$O_2MF_6 \longrightarrow O_2 + MF_6 \quad M = Ru, Rh, Pt \qquad (1)$$

$$O_2MF_6 \longrightarrow O_2 + \tfrac{1}{2}F_2 + MF_5 \quad M = Sb, Bi \qquad (2)$$

$$O_2M_2F_{11} \longrightarrow O_2 + \tfrac{1}{2}F_2 + M_2F_{10},MF_5 \quad M = Nb, Sb, Ta \qquad (3)$$

The fact that O_2PtF_6 can be transferred *in vacuo* and prepared by mixing O_2 and PtF_6 at a pressure of *ca.* 25 Torr at room temperature[1] shows that the reverse of reaction (1) proceeds readily.

In an on-line transport experiment with O_2PtF_6 using a Monel U-tube held at dry-ice temperature as a collector, a small oxygen signal could be detected, but no PtF_6. The sample was heated in stages from ambient to 74 °C, and with each temperature increment a momentary increase in the oxygen signal was obtained. A similar effect could be obtained by closing valve A (Figure) for a short period of time. The sample was heated until the oxygen signal disappeared. The sample container was isolated and the U-tube temperature was raised in steps. Oxygen evolution was observed at -15 °C, without the complementary PtF_6 spectrum. At 70—74 °C vigorous oxygen and PtF_6 evolution was observed. Similar behaviour was obtained in an experiment using a straight collection tube maintained at -78 °C. The straight tube was brought

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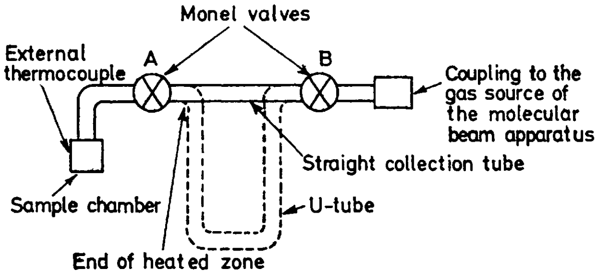
[8] L. Frenkel, W. Smith, and J. J. Gallagher, *J. Chem. Phys.*, 1966, **45**, 2251.

[9] J. F. Lotspeich and A. Javan, *J. Chem. Phys.*, 1959, **31**, 633.

to room temperature, returned to the dry box, and a dark red solid was recovered from it. This solid was determined to be O_2PtF_6.

These manipulations were repeated with O_2RhF_6, O_2RuF_6, O_2SbF_6, and $O_2Ta_2F_{11}$. Strong oxygen signals were found for O_2SbF_6 and $O_2Ta_2F_{11}$ with the collection tubes held at -78 °C, and no further oxygen evolution occurred when the collection tubes were brought to room temperature. For $O_2Ta_2F_{11}$, white solid TaF_5 was recovered from the collection tube. The condensate in the O_2SbF_6 experiment was SbF_5, which is readily vaporized at room temperature.



Apparatus used for on-line vapour-transfer experiments. All segments are independently demountable and made entirely of Monel. Heating of the sample chamber, valve A, and collection tube up to the point indicated was achieved by closely wound Nichrome resistance wire in glass sleeving

From O_2RuF_6 no evidence of RuF_6 was obtained, but moderately strong O_2 signals were observed as the sample temperature was increased from 25 to 100 °C. A relatively strong O_2 signal was observed when the U-tube cold trap was brought to room temperature, but no evidence of RuF_6 was observed. With a straight collection tube, a substantial amount of green RuF_5 was recovered from the section of the straight tube in which the temperature gradient to -78 °C occurred. A much smaller amount of dark red solid O_2RuF_6 was recovered from the part of the tube which was held at -78 °C. Essentially the same results were obtained for a parallel experiment involving O_2RhF_6 (maximum sample temperature = 35 °C) with the exception that the bulk of the RhF_5 recovered remained in the sample chamber.

The results of the collection-tube experiments show that the reverse of reaction (1) occurs only under conditions that preserve the MF_6 molecules and prevent their decomposition into MF_5 or lower fluorides.

O_2RuF_6 Was transferred in a quartz vessel at 45 and at 90 °C to a central finger cooled with liquid nitrogen. The transfer was virtually complete, without decomposition, and the material collected on the cold finger was O_2RuF_6. With the transfer being from 55 °C to a room temperature surface, however, considerable gas was evolved and the material recovered was green RuF_5.

The vapour transport of those dioxygenyl salts that can be recovered is analogous to that of ammonium chloride. NH_4Cl is known to vaporize as NH_3 and HCl.[10] We have examined the gas phase in equilibrium with NH_4Cl using the techniques described in this paper. The beam obtained from a Monel effusion source at 154 °C gave two components, NH_3 and HCl, with a 4° phase-angle difference between the monitored ions NH_3^+ and $H^{37}Cl^+$. Ideally, one calculates an expected phase-angle difference of 5°. The two components showed different focusing behaviour, characteristic of NH_3 and HCl respectively. In an on-line transfer experiment, almost no gas was observed in the mass spectrometer, and NH_4Cl was recovered essentially quantitatively from the straight collection tube.

CONCLUSION

It is clear from these experiments that the dioxygenyl compounds examined dissociate upon vaporization. The apparent sublimation of O_2PtF_6, O_2RuF_6, and O_2RhF_6 is in reality independent vapour transport of O_2 and MF_6, followed by recombination of the components on or near a cold surface.

We acknowledge W. A. Sunder for synthesizing the dioxygenyl salts, W. A. Kaiser for design of the refocusing field, F. A. Stevie for performing many of the experiments, and W. Klemperer for pointing out the parallelism between the transport of dioxygenyl compounds and that of ammonium chloride.

[4/1588 *Received*, 30*th July*, **1974**]

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[10] R. S. Mulliken, *J. Phys. Chem.*, 1952, **56**, 801 and references contained therein.