The Reactivity of Molybdenum and Tungsten Trioxide Vapours towards Organic and Inorganic Compounds at −196 °C

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Vapours of molybdenum and tungsten trioxides, prepared by heating the solid oxides under vacuum, have been reacted with organic compounds and some inorganic halides at −196 °C. Complexes of the trioxides are formed with pentane-2,4-dione, acetone, formic acid, and methanol, but the oxides fail to bring about metathesis or isomerisation of olefins. Oxygen–halogen exchange reactions occur between the trioxides and BCl_3, $SiCl_4$, and HCl; PCl_3 is oxidised. The reactivity of the condensed vapours of both oxides at −196 °C is markedly higher than the reactivity of the normal solid oxides at room temperature.

Most metal oxides dissociate when they evaporate, giving oxygen and the vapour of the metal or of a lower oxide.[1] Some exceptions to this generalisation occur among the higher oxides of transition metals, *e.g.* OsO_4, Re_2O_7, MoO_3, and WO_3. The volatility of these oxides varies considerably, from OsO_4 which is very volatile at room temperature to WO_3 which evaporates appreciably only above 1 000 °C under vacuum. The temperature required for vaporisation is a reflection of the strength of the bonds broken in the formation of the oxide vapours. We considered the possibility that the chemistry of the vapours of those oxides which evaporate only at fairly high temperatures may be significantly different from that of their solid forms, just as the vapours of many metals are more reactive than their respective solid metals.[2] Accordingly, we have evaporated molybdenum and tungsten trioxides and condensed their vapours at low temperatures with vapours of inorganic and organic compounds, to determine what reactions these trioxide vapours may undergo which are not shown by the normal solid trioxides.

Evaporation of molybdenum and tungsten trioxides is known to yield mixtures of cyclic dimers, trimers, tetramers, and pentamers, with the trimer being predominant.[3] The tungsten trioxide trimer is believed to be a puckered ring with C_{3v} symmetry,[4] whilst the molybdenum trioxide trimer is a planar ring with D_{3h} symmetry.[5] In each of the rings, the metal is four-co-ordinate. In the solid trioxides, tungsten is octahedrally co-ordinated by oxygen and molybdenum is co-ordinated by oxygen in a distorted octahedral array,[6] *i.e.* the co-ordination numbers of the metals in the trioxide vapours are lower than in the solid trioxides. Some dissociation of tungsten trioxide is reported to occur upon evaporation giving W_3O_8 as an additional vapour species.[7] According to mass spectrometric data, the ratio of $(WO_3)_3 : W_3O_8$ is *ca.* 5 : 1 at 1 100 °C.[8] However, our results have given no evidence for a difference in chemistry between condensed $(WO_3)_n$ and any W_3O_8 which may be mixed with it.

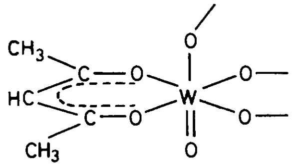
Results and Discussion

In the reactions described below, two experimental conditions were used. In co-condensation reactions, the vapours of the trioxides were condensed with the vapours of other compounds on the walls of a glass reactor cooled in liquid nitrogen, to give a condensate with a trioxide to compound mol ratio of about 1 : 10. The reactor was then warmed to room temperature (r.t.), with continuous vacuum pumping to remove any volatile product and the excess reactant. In sequential-condensation reactions, the trioxide vapours were first condensed on the liquid-nitrogen cooled walls of the glass reactor and then excess of the other compound vapours was condensed on top. The reactor was warmed to r.t. as in the co-condensation reactions.

Reaction of Tungsten and Molybdenum Trioxide Vapours with Organic Compounds.—(*a*) *Pentane*-2,4-*dione.* Co-condensation of MoO_3 vapour and $C_5H_8O_2$ vapour at −196 °C gave an orange condensate but the solid residue left on warming to r.t. was green. The i.r. spectrum and melting point of this green material were almost the same as those of the known compound $[MoO_2(O_2C_5H_7)_2]$ [9,10] which can be formed from MoO_3 and $C_5H_8O_2$ under reflux. Pure $[MoO_2(O_2C_5H_7)_2]$ is yellow but it is known to become green on slight decomposition.[11]

The compound $[WO_2(O_2C_5H_7)_2]$ has been prepared as a pale yellow solid from reaction of WO_2Cl_2 with $C_5H_8O_2$.[12] Unlike $[MoO_2(O_2C_5H_7)_2]$, the compound could not be made directly from solid WO_3 and $C_5H_8O_2$.

We obtained an orange-brown solid at room temperature from the co-condensation reaction of WO_3 and $C_5H_8O_2$ vapours at −196 °C. Its i.r. spectrum showed it was a $C_5H_7O_2$ complex, but the C and H analyses indicated a $WO_3 : C_5H_7O_2$ ratio close to 1 : 1. The ^1H n.m.r. spectrum in CD_3CN showed strong resonances of uncomplexed $C_5H_8O_2$ plus a multiplet at δ 6.0 assigned to the $-CH-$ proton of a co-ordinated $C_5H_7O_2$ group. On heating, the solid decomposed without melting or vaporisation at *ca.* 250 °C. We cannot assign a detailed structure to our product but it may be a polymer of units shown by (1).



(1)

Sequential condensation of either MoO_3 or WO_3 with $C_5H_8O_2$ gave products containing some co-ordination of $C_5H_7O_2$ groups to the metals but the reactions were less efficient than the co-condensation reactions.

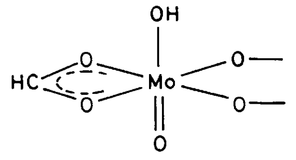
(*b*) *Acetone.* Co-condensation of MoO_3 vapour and acetone gave a pale yellow solid, with a composition approximately $(MoO_3)_{1.8}\cdot Me_2CO$. The solid was not soluble in inert solvents and treatment with 1 mol dm^{-3} NaOH liberated acetone. In the i.r., the solid showed a strong absorption at 1 655 cm^{-1} which we assign to ν(C=O) for acetone co-ordinated to molybdenum by analogy with known ketone complexes of MoO_2Cl_2.[13] Sequential condensation of MoO_3 and acetone gave a product containing very little combined acetone.

Our attempts to co-condense WO_3 and acetone vapours led to an unexpected result. In these experiments the WO_3 was evaporated from an insulated silica crucible wound with resistively heated molybdenum wire (see Experimental section), but the crucible caused appreciable thermal decomposition of acetone vapour. This was evident because the condensate on the reactor walls contained H_2O, CO_2, and allene in addition to unreacted acetone. The formation of allene was found to be independent of the presence of WO_3 in the evaporation crucible, but it was shown to be dependent on the presence of two parts of the evaporation assembly, the alumino-silicate wool insulation and the alumina cement used to coat the molybdenum windings. In the absence of WO_3, acetone vapour was cracked by this assembly at a pressure of of *ca.* 1 Pa and 1 150 °C, to give allene and water, *i.e.* $(CH_3)_2CO \longrightarrow CH_2{=}C{=}CH_2 + H_2O$. We are not aware of other reports of this mode of decomposition of acetone. In the presence of evaporating WO_3, CO_2 was formed in addition to H_2O and allene.

The involatile, blue-grey material on the reactor walls from the WO_3–acetone co-condensation had the approximate composition $(WO_3)_{2.7}{\cdot}Me_2CO$. Its i.r. spectrum was very similar to that of the corresponding molybdenum product in the region 1 700—1 000 cm^{-1}, but the tungsten product showed a strong O–H band at 3 400 cm^{-1} due to reaction with water on the cold surface.

(*c*) *Formic acid.* Very little is reported in the literature on reactions between HCO(OH) and either molybdenum or tungsten trioxide. Salts of the formylated octamolybdate cluster anions, $[Mo_8O_{26}(O_2CH)_2]^{6-}$, have been described recently and in this the unidentate HCO_2^- groups show C–O absorptions in the i.r. at 1 612 and 1 265 cm^{-1}.[14,15]

Co-condensation of MoO_3 vapour and HCO(OH) gave a pale green solid of approximate composition $(MoO_3)_{1.2}{\cdot}HCO(OH)$ plus a little CO_2. The solid was extremely light sensitive and it was prepared and handled in darkened containers to avoid it turning blue. No inert solvent was found for the solid but with water it gave a blue solution. The i.r. spectrum showed very strong bands at 1 570 and 1 345 cm^{-1} assigned to asymmetric and symmetric C–O stretching modes respectively for a bidentate carboxylate group coordinated to molybdenum. Strong, broad bands in the region 960—600 cm^{-1} were assigned to Mo=O and Mo–O stretching modes, while an extremely broad band at around 3 300 cm^{-1} indicated the presence of Mo–OH groups in the product. The results suggest that the product contains the structure (2). The light sensitivity of the product presumably arises from facile elimination of CO_2 and H_2O with reduction of Mo^{VI} to Mo^{V} or Mo^{IV}.



(2)

Sequential condensation of MoO_3 and HCO(OH) gave a solid with similar properties to the co-condensation product, but it contained only half as much combined HCO(OH).

The co-condensation reaction between WO_3 and HCO(OH) vapours was much less efficient than the corresponding reaction using MoO_3. The i.r. spectrum showed the tungsten product to be similar to the molybdenum product but with stronger O–H bands due to some decomposition of HCO(OH) to CO + H_2O during the co-condensation. Unlike the molybdenum product, the tungsten product was not very light sensitive, probably due to the greater stability of W^{VI}.

(*d*) *Methanol.* A pale green, light-sensitive solid was obtained from co-condensation of MoO_3 and CH_3OH vapours of approximate composition $MoO_3{\cdot}2CH_3OH$. Traces of CO_2 and H_2CO were found in the volatiles pumped off during warm-up of the co-condensate. The properties and i.r. spectrum of the solid were similar to those of the compound $MoO_3{\cdot}2CH_3OH$ prepared from $MoO_3{\cdot}2H_2O$ and CH_3OH by Kraus and Huber.[13] The structure proposed for $MoO_3{\cdot}2CH_3OH$ by Kraus and Huber has CH_3OH co-ordinated through oxygen to six-co-ordinate molybdenum(VI) with weak hydrogen bonding to Mo=O groups.

The co-condensation reaction between WO_3 and CH_3OH vapours gave a grey solid of approximate composition $WO_3{\cdot}CH_3OH$. The i.r. spectrum showed a very broad O–H band at 3 400—2 800 cm^{-1} suggesting more extensive hydrogen bonding than in the molybdenum product. Otherwise the spectra for the two products were very similar.

(*e*) *Olefins.* The well known ability of tungsten in high oxidation states to bring about metathesis of olefins prompted us to co-condense WO_3 vapour and olefins. With hex-1-ene there was no reaction. All the alkene was recovered unchanged and solid WO_3 was left on the walls of the reactor.

With WO_3 vapour and styrene, we also found no evidence of metathesis but all the olefin was polymerised. The i.r. spectrum of the brown solid product in the range 3 000—1 000 cm^{-1} was extremely similar to that of a film of polystyrene. Absorptions in the W=O and W–O stretching regions were broader and weaker than the polystyrene bands. The observed polymerisation could have been caused by the condensing WO_3 vapour acting as an acid catalyst although it is also possible that free radicals, formed by thermal decomposition of traces of the styrene vapour, caused the effect.

Halogen Exchange Reactions of Molybdenum and Tungsten Trioxide Vapours.—Exchange reactions of the general type shown by equation (i), where M is a metal and E is an element

$$MO_n + EX_m \longrightarrow MO_{n-1}X_2 + EOX_{m-2} \quad \text{(i)}$$

in Groups 3B—6B, are thermodynamically favourable in many cases, although the reactions are often slow except at elevated temperatures. Thus, solid tungsten trioxide reacts with boron tribromide above 150 °C [16] according to equation (ii).

$$3\ WO_3(s) + 4\ BBr_3(g) \longrightarrow 3\ WOBr_4 + 2\ B_2O_3 \quad \text{(ii)}$$

We have studied reactions of molybdenum and tungsten trioxide vapours with several inorganic halides at −196 °C. The reactions with BCl_3 are especially efficient, with volatile $(BOCl)_3$ being formed along with the metal oxohalides. Under co-condensation conditions, MoO_3 and BCl_3 gave a product from which MoO_2Cl_2, and probably a little $MoOCl_4$, could be sublimed. The purple sublimate, richer in chlorine than MoO_2Cl_2, may have contained some of the purple 1 : 1 complex of MoO_2Cl_2 and $MoOCl_4$. Only MoO_2Cl_2 was sublimed from the sequential-condensation product.

The co-condensation reaction of WO_3 and BCl_3 gave a dark red solid, soluble in organic solvents, from which $WOCl_4$ and WO_2Cl_2 were liberated in equal amounts by vacuum sublimation. The sequential-condensation reaction gave the same products in only slightly lower yield. Thus, the reaction between WO_3 and BCl_3 can be represented approximately by equation (iii).

$$2\ WO_3(g) + 3\ BCl_3(g) \xrightarrow[\text{warm to } 25^\circ\text{C}]{\text{co-condense } -196\ ^\circ\text{C}} WOCl_4 + WO_2Cl_2 + (BOCl)_3 \quad \text{(iii)}$$

Molybdenum and tungsten trioxide vapours reacted less efficiently with $SiCl_4$ than with BCl_3. The approximate compositions of the products were $(MoO_3)_{10}{\cdot}SiCl_4$ and $(WO_3)_5{\cdot}SiCl_4$, respectively. On heating the solids under vacuum, small amounts of MoO_2Cl_2 and WO_2Cl_2 were liberated. The i.r. spectra of the products were dominated by metal–oxygen bands, although bands around 1 030 cm^{-1} could be assigned to ν(Si–O). We could not discern ν(Si–Cl) bands in the spectrum from either product although the result is not conclusive because they may have been obscured by the broad envelope of Mo–O and W–O bands. However, the products gave no $SiCl_4$ on heating and they were not exceptionally water sensitive, suggesting that they did not contain Si–Cl bonds and that complete oxygen for chlorine exchange had occurred.

Reactions between PCl_3 and solid MoO_3 and WO_3 above 150 °C have been reported in less recent literature.[17] Oxidation of P^{III} to P^{V} and reduction of the metal from oxidation state +6 to +4 were thought to be primary reactions with a further reaction of MoO_2 with $POCl_3$ to give MoO_2Cl_2 and P_2O_5 at higher temperatures.

We have found that the condensed vapour of WO_3 reacts efficiently with PCl_3 but reactions with MoO_3 are less efficient. With both trioxides, sequential-condensation experiments gave more extensive reaction with PCl_3 than co-condensation experiments. We have no good explanation for this observation. Approximate compositions for the products from the most efficient reactions were $(MoO_3)_6{\cdot}PCl_3$ and $WO_3{\cdot}PCl_3$. The solid products were very dark coloured, suggesting reduction of the oxidation state of the metals. No $POCl_3$ was detected in the excess PCl_3 pumped off when the condensates were warmed to r.t. After removing the excess PCl_3, heating the solid products to 400 °C liberated no volatiles. The i.r. spectra of the tungsten products gave evidence for P–O bonds (bands at 1 200 and 1 080 cm^{-1}), W=O and W–O bonds, P–Cl bonds (strong band at 625 cm^{-1}), but no evidence for W–Cl bonds. The results suggest that the reaction between WO_3 and PCl_3 only involves oxygen transfer from W^{VI} to P^{III} giving P^{V} and W^{IV} or W^{V}.

Oxygen–halogen exchange is known to occur in the reaction of HCl with solid MoO_3 at room temperature[13] [equation (iv)]. Species such as $MoO(OH)_2Cl_2$ are thought to be intermediates.

$$MoO_3 + 2\,HCl \longrightarrow MoO_2Cl_2 + H_2O \qquad \text{(iv)}$$

Solid WO_3 is reported to react with HCl only above 400 °C to give WO_2Cl_2.[18] However, we have found that co-condensation of HCl and WO_3 gave extensive reaction. The pale green solid isolated, of approximate composition $WO_3{\cdot}HCl$, showed bands in its i.r. spectrum indicative of –OH, W=O, W–O, and W–Cl groups. Heating the solid to 300 °C under vacuum liberated WO_2Cl_2 and H_2O. Thus, the pattern of this co-condensation reaction seems similar to the pattern of the reaction at r.t. between HCl and solid MoO_3. Little reaction was observed from the sequential condensation of WO_3 and HCl.

Conclusions

Our experiments have shown that the vapours of MoO_3 and WO_3 are considerably more reactive when condensed with other compounds at −196 °C than are the normal solid forms of the trioxides at r.t. The difference in reactivity between the condensed vapour and the normal solid forms is somewhat greater for WO_3 than for MoO_3 as expected from the higher heat of sublimation of WO_3.

In co-condensation reactions, polymerisation of the condensing trimers and tetrameters of the trioxides probably competed with their reactions with other compounds at low temperatures. As a result, products of many of our reactions have been polymeric solids with only part of the metal centres reacted with other compounds. Yields from sequential-condensation reactions have mostly been worse, indicating that more of the available metal sites have been lost during the condensation of the trioxide vapours before other compounds have been added.

The difficulty of being able to make molecular products in high yield somewhat limits the synthetic usefulness of the trioxide vapours. However, we feel that the trioxide vapours may find more important uses in the preparation of molybdenum and tungsten oxide based heterogeneous catalyst systems and our future work will be along those lines.

Experimental

The oxides were evaporated inside a cylindrical glass reaction vessel, 125 mm diameter, 300 mm deep, and evacuated to $<10^{-2}$ Pa. The vessel was partly immersed in liquid nitrogen so that the oxide vapours and the vapours of compounds bled into the reaction vessel could be condensed together on the cold walls. Co-condensation apparatus of this type, used for metal atom chemistry, has been fully described elsewhere.[2]

Molybdenum trioxide (dried powder, 99% pure) was sublimed at *ca.* 650 °C from a 12 mm diameter silica crucible within a resistively-heated molybdenum wire spiral coated with alumina cement and surrounded by alumino-silicate wool insulation (Kaowool, Morgan Refractories); the rate of evaporation was about 10 mmol h^{-1} for a power input of 30 W. Tungsten trioxide was prepared by heating tungstic acid (99% pure) in air to 450 °C, compacting the powder to pellets, and re-heating to 700 °C in air. The crushed pellets were sublimed from a resistively-heated platinum boat at *ca.* 1 150 °C; the evaporation rate was *ca.* 10 mol h^{-1} for a power input of 110 W. In a few experiments, evaporation of WO_3 was carried out from silica crucibles like those used for evaporating MoO_3, but some corrosion of the silica was observed.

Volatile products from reactions of the oxide vapours with compounds on the cold walls of the reaction vessel were pumped out and handled on a high-vacuum line. Solid products were scraped out of the reaction vessel inside a dry nitrogen-filled glove box (Vac Atmospheres) and were characterised mainly by elemental analysis and by i.r. spectroscopy in Nujol and hexachlorobutadiene mulls using a Perkin-Elmer 425 spectrometer. Mass spectra were run on an AEI MS 902 spectrometer.

Reactions.—MoO_3 *vapour* + *pentane*-2,4-*dione*. Molybdenum trioxide (2.0 g, 14 mmol) was condensed over 1 h with $C_5H_8O_2$ (15 g, 147 mmol) to give an orange solid at −196 °C. The only volatile compound liberated on warming to 20 °C was excess $C_5H_8O_2$; a green solid remained, m.p. 180—182 °C {lit. value[9] for $[MoO_2(C_5H_7O_2)_2]$ 184 °C} (Found: C, 35.8; H, 4.3. $C_{10}H_{14}MoO_6$ requires C, 36.8; H, 4.3%). The solid was almost completely soluble in CH_3CN. ^1H n.m.r. (CD_3CN): δ 2.20 (s, 6 H), 5.94 (s, 1 H), plus very small peaks at 5.60, 3.60, and 2.00 assigned to free $C_5H_8O_2$. I.r.: strong bands at (lit. values[9] in parentheses) 1 585 (1 597), 1 495 (1 515), 1 353 (1 364), 1 261 (1 266), 1 020 (1 026), 930 (935), 905 (904), and 798 (800w) cm^{-1}.

Condensation of MoO_3 (2.0 g, 14 mmol) on the cooled walls of the reactor followed by excess $C_5H_8O_2$ gave a yellow solid; pumping away the excess ligand and warming to 20 °C left a green-yellow solid only partially soluble in CH_3CN (Found: C, 31.9; H, 4.0%; i.r. similar to above with broad bands).

WO_3 *vapour* + *pentane*-2,4-*dione*. Tungsten trioxide (2.0 g, 8.6 mmol) was condensed over 1 h with $C_5H_8O_2$ (15 g, 147 mmol) to give a greenish solid at −196 °C. When the WO_3 was evaporated from a platinum boat, excess $C_5H_8O_2$ was the only volatile recovered on warming the condensate to 20 °C, but when the WO_3 was evaporated from a silica crucible, traces of CO_2 and allene were also obtained (see WO_3 + acetone, below). An orange-brown solid remained, almost completely soluble in CH_3CN from which it could be recovered unchanged (Found: C, 18.3; H, 2.2. $C_5H_7O_5W$ requires C, 18.15; H, 2.1%). ^1H n.m.r. (CD_3CN): δ 6.0 (broad multiplet, *ca.* 1 H), 5.60 (s, 1 H), 3.60 (s, 2 H), 2.20 (s, 6 H), 2.1—1.9 (several sharp peaks including proton impurities in solvent). I.r.: 2 955w, 2 900m, 2 830w, 1 705m, 1 577s, 1 530 (sh), 1 512s, 1 453m, 1 415m, 1 351s, 1 270s, 1 182w, 1 020m, 972m, 945s, 910m, 874s, 812s, 780m, 715m, 675m, 600w, 585w, 455m, 380w, 295w, and 290w cm^{-1}.

Condensation of WO_3 vapour followed by excess $C_5H_8O_2$ vapour at −196 °C, gave, on warming to r.t., a yellow solid (Found: C, 4.90; H, 0.8%). I.r.: as above for co-condensed product, but strong, broad poorly resolved regions of absorption at 1 000—550 and 400—300 cm^{-1}.

MoO_3 *vapour* + *acetone*. Molybdenum trioxide (1.9 g, 13.2 mmol) was condensed at −196 °C with dry acetone (10 g, 172 mmol) in 1 h. On warming to 20 °C, acetone was the only volatile recovered; a pale yellow solid remained (Found: C, 11.5; H, 2.0; calc. mol. ratio MoO_3 : Me_2CO based on C, 1.78 : 1). I.r.: 3 400w, br, 2 920m, 2 850w, 1 655s, 1 420m, 1 530m, 1 245m, 1 083w, 960s, 872s, 795s, 720s, 710s, 620s, and 551s cm^{-1}. The solid became blue on exposure to laboratory light. It was insoluble in CH_3CN and $CHCl_3$; 1 mol dm^{-3} NaOH liberated acetone.

Condensation of MoO_3 vapour followed by acetone vapour at −196 °C gave, on warming to room temperature, a yellow solid (Found: C, 3.30; H, 0.90%). I.r.: as above for the co-condensed product but much broader bands.

WO_3 *vapour* + *acetone*. Tungsten trioxide (1.6 g, 6.9 mmol) was evaporated from a silica crucible and condensed with dry acetone (10 g, 172 mmol), at −196 °C. The volatiles liberated on warming the condensate to r.t. were collected and fractionated; small amounts of CO_2 and allene were identified by their i.r. spectra along with unreacted acetone (166 mmol recovered). A blue-grey solid remained at r.t. (Found: C, 5.3; H, 1.2%; calc. mol. ratio WO_3 : Me_2CO based on C, 2.68 : 1). I.r.: 3 400s, br, 2 900w, 2 830w, 1 705s(sh), 1 650ms, 1 618m(sh), 1 410m, 1 353m, 1 225m, 1 140w, 1 080w, 975s, 895s, 805s, 715s, 450m, and 360m,br cm^{-1}.

MoO_3 + *formic acid*. Molybdenum trioxide (1.9 g, 13.2 mmol) was condensed with HCO(OH) (*ca.* 10 g, 217 mmol) at −196 °C. A little CO_2 was pumped off with excess HCO(OH) on warming to 20 °C; the residual solid was pale green (Found: C, 5.5; H, 0.9%; calc. mol. ratio MoO_3 : HCO(OH) based on C, 1.21 : 1). I.r.: 3 300m, br, 2 930m, 1 660m, br, 1 570s, 1 345s, 957s, 910—610s, br, and 280m cm^{-1}. The solid was insoluble in Et_2O and $CHCl_3$ and it turned deep blue in contact with CH_3CN or C_5H_5N.

A similar reaction in which MoO_3 vapour was first condensed at −196 °C followed by excess HCO(OH) also gave a yellow-green solid [Found: C, 2.9; H, 0.7%; calc. mol. ratio MoO_3 : HCO(OH) based on C, 2.55 : 1]. I.r.: 3 300w, br, 1 660m, br, 1 540s, 1 320s, bands below 1 000 cm^{-1} very broad.

WO_3 + *formic acid*. Tungsten trioxide (2.5 g, 10.8 mmol) was condensed with HCO(OH) (*ca.* 7 g, 152 mmol) at −196 °C. The pressure in the reactor rose during the co-condensation through release of a permanent gas believed to be CO. The only volatile pumped off from the condensate on warming to 20 °C was HCO(OH); the solid residue was pale blue [Found: C, 1.7; H, 0.5%; calc. mol. rato WO_3 : HCO(OH) based on C, 2.84 : 1]. I.r.: 3 300s, br, 2 930m, 1 660m, br, 1 569s, 1 356s, 980s, 815s, br, 690s, br, and 300 m, br cm^{-1}.

MoO_3 + *methanol*. Molybdenum trioxide (1.0 g, 6.9 mmol) was condensed at −196 °C with dry CH_3OH (10 g, 312 mmol). On warming to 20 °C a little CO_2 and H_2CO (identified by their i.r. spectra) were liberated along with unreacted CH_3OH; a green solid remained (Found: C, 11.0; H, 3.35%; calc. mol. ratio MoO_3 : CH_3OH based on C, 1 : 1.86). I.r.: 3 300w, br, 2 940w, 2 835w, 1 430w, 1 380w, 1 100w, 1 030m, 985s, 945s, 916s, 900s, 760s, 520s, and 350s cm^{-1}.

WO_3 + *methanol*. Tungsten trioxide (3.0 g, 12.9 mmol) was condensed at −196 °C with a large excess of CH_3OH. A little CO_2 (detected by i.r.) was liberated along with CH_3OH vapour on warming the condensate to 20 °C; there was no H_2CO. The solid residue was blue-grey (Found: C, 3.95; H, 1.3%; calc. mol. ratio WO_3 : CH_3OH based on C, 1.18 : 1). I.r.: 3 300m, br, 2 920w, 1 430m, 1 380w, 1 230w, 1 070w, 970m, 927m, 870m, 818s, broad area of absorption at 800—500, and 330m cm^{-1}.

WO_3 + *hex*-1-*ene*. Tungsten trioxide (3.4 g, 14.7 mmol) was condensed with C_6H_{12} (*ca.* 100 mmol) at −196 °C. The initial condensate was yellow, but on warming to 20 °C only hex-1-ene was liberated and the residual blue-grey solid contained < 1% C.

WO_3 + *styrene*. Tungsten trioxide (2.0 g, 8.6 mmol) was condensed with C_8H_8 (2.1 g, 20 mmol) at −196 °C to give a brown solid which remained unchanged with no liberation of C_8H_8 on warming to 20 °C (Found: C, 47.2; H, 3.8%; mol. ratio WO_3 : C_8H_8 as of reactants, 1 : 2.3). I.r.: 4 000—1 000 cm^{-1} identical to polystyrene film, 1 000—550 cm^{-1} broad area of absorption with sharp polystyrene bands superimposed, and 300m, br cm^{-1}.

MoO_3 + BCl_3. Molybdenum trioxide (1.3 g, 9.0 mmol) was condensed at −196 °C with BCl_3 (10.7 g, 90 mmol) to give an orange condensate which became plum coloured on warming to 20 °C with pumping to remove BCl_3. The recovered BCl_3 deposited B_2O_3 around the vacuum system, showing that it contained unstable $(BOCl)_3$.[19] The purple solid nearly all sublimed on heating to 200 °C under high vacuum. The sublimate, collected on a liquid-nitrogen cooled cold-finger, was first pink, then green, and it became purple at 20 °C (Found: Cl, 38.5. MoO_2Cl_2 requires Cl, 35.7%); its i.r. and mass spectrum showed only peaks expected for MoO_2Cl_2.

Repeating the above experiment using sequential-condensation of MoO_3 and BCl_3 gave a pink solid at 20 °C (Found: Cl, 31.5%) which gave green MoO_2Cl_2 on warming to 100 °C.

WO_3 + BCl_3. Tungsten trioxide (1.0 g, 4.3 mmol) was condensed with BCl_3 (10 g, 8.5 mmol) at −196 °C. The excess BCl_3, removed on warming to 20 °C, contained some $(BOCl)_3$. The residue was an orange solid (Found: Cl, 36.0%) which on heating under vacuum gave an orange-red sublimate at *ca.* 180 °C, identified by i.r. and mass spectra as $WOCl_4$, and a yellow sublimate at *ca.* 300 °C identified as WO_2Cl_2.

Repeating the above experiment using sequential-condensation of WO_3 and BCl_3 gave a pale yellow solid at 20 °C containing <5% Cl.

MoO_3 + $SiCl_4$. Molybdenum trioxide (1.5 g, 10.4 mmol) was condensed at −196 °C with a large excess of $SiCl_4$; the solid obtained at 20 °C after pumping away $SiCl_4$ was yellow and it slowly turned green in daylight (Found: Cl, 8.6%). I.r.: 1 120w, 1 020m, 980m, 950—650 broad area of strong bands, 570w, 380m, and 330m cm^{-1}. Heating to 150 °C under vacuum gave a little MoO_2Cl_2 vapour and a dark solid residue.

WO_3 + $SiCl_4$. Tungsten trioxide (0.5 g, 2.2 mmol) was condensed at −196 °C with a large excess of $SiCl_4$ which was pumped away on warming to 20 °C to leave a white solid (Found: Cl, 10.5%). I.r.: 1 150m, 1 040m, 980—600 area of broad, strong bands, and 325m, br cm^{-1}. The solid decomposed at *ca.* 350 °C under high vacuum liberating a little WO_2Cl_2 vapour.

$MoO_3 + PCl_3$. Molybdenum trioxide (1.7 g, 12 mmol) was condensed on the walls of the reactor at -196 °C and then PCl_3 (10 g, 73 mmol) was condensed on top; PCl_3 was the only volatile recovered on warming to 20 °C; the residual solid was blue-black (Found: Cl, 10.1%). I.r.: 1 270m, 1 183m, 977m, 816s, 720s, br, 600s, and 330m, br cm^{-1}.

Co-condensation of MoO_3 and PCl_3 gave a dark grey solid, after removal of excess PCl_3, containing *ca.* 3.4% Cl. Its i.r. spectrum was similar to the above but the bands at 1 270, 1 183, and 600 cm^{-1} were weaker than in the sequential-condensation product.

$WO_3 + PCl_3$. Tungsten trioxide (2.8 g, 12 mmol) was condensed at -196 °C and then PCl_3 (*ca.* 10 g, 73 mmol) was condensed on top and the condensate warmed to 20 °C with pumping to remove PCl_3. The residual solid was dark green (Found: Cl, 31.5%). I.r.: 1 200m, 1 080s, 990s, 875m, 715s, 625s, and 370s cm^{-1}. The solid darkened on heating to 350 °C but gave off no volatiles.

The product obtained by co-condensation of WO_3 and PCl_3 was grey-black (Found: Cl, 18.8%). I.r.: as above for sequential-condensation product but bands were less sharp.

$WO_3 + HCl$. Tungsten trioxide (2.1 g, 9.0 mmol) was condensed with HCl (90 mmol) at -196 °C. On warming to 20 °C, HCl was the only volatile liberated but *ca.* 10 mmol remained combined with the WO_3 in a pale green solid (Found: Cl, 16.2; H, 0.4. $WO_3{\cdot}HCl$ requires Cl, 13.2; H, 0.5%). I.r.: 3 300w, 1 600m, 970m, 855m, 820—650 area of broad, strong bands, 628s, and 350s cm^{-1}. Heating the solid under high vacuum at 300 °C yielded some water vapour and a yellow-green sublimate of WO_2Cl_2.

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