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Oxy–Methoxy Compounds of Hexavalent Molybdenum

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The compounds $Mo_2O_5(OCH_3)_2$ and $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$ have been prepared by the reaction of methanol with $MoO_3{\cdot}2H_2O$. The presence of methoxy groups is established by chemical analysis, infrared spectra, and decomposition studies. The methoxy groups reduce Mo^{6+} with thermal, UV, or X-ray energy; formaldehyde is liberated as the solid phase changes from white to blue.

Introduction

Molybdenum trioxide has a layer structure and might be considered a good candidate for intercalation chemistry. However, MoO_3 actually is not very reactive at temperatures near room temperature. The hydrate $MoO_3{\cdot}2H_2O$, on the other hand, is relatively reactive and may, therefore, be used as a reagent to prepare a variety of new compounds.[1,2]

We have been particularly interested in the reaction of $MoO_3{\cdot}2H_2O$ with methanol because of its relevance to methanol oxidation to formaldehyde over MoO_3 and molybdate catalysts. In this laboratory, surface reactions between methanol and MoO_3 have been studied and related to the catalytic reaction.[3] Since methoxy groups are found to readily form on the MoO_3 surface at room temperature, we were interested in comparing this surface chemistry with the chemistry of bulk compounds of Mo^{6+} containing methoxy groups.

Previous studies of the reaction between methanol and $MoO_3{\cdot}2H_2O$ indicated the formation of two compounds. The first reported compound (I) was formulated as a molybdenum methyl ester, $MoO_2(OCH_3)_2$,[4] but in a later study, this formulation was refuted in favor of molybdenum trioxide–methanol (1/2), $MoO_3{\cdot}2CH_3OH$.[5] A second compound (II), $MoO_3{\cdot}CH_3OH$,[6] was subsequently reported. We also find two compounds but formulate them as $Mo_2O_5(OCH_3)_2.2CH_3OH$ (**1**) and $Mo_2O_5(OCH_3)_2$ (**2**).

Experimental Section

Canary yellow $MoO_3{\cdot}H_2O$ was prepared by literature procedures.[7] All other starting materials were commercially available. Routine carbon and hydrogen analyses were carried out by Galbraith Laboratories. Powder X-ray diffraction patterns were obtained on a Philips APD-3600 diffractometer using Cu Kα radiation with Si as the internal standard. Powder patterns for both $Mo_2O_5(OCH_3)_2$ and $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$ are given in Table I.

$Mo_2O_5(OCH_3)_2$. Five grams of $MoO_3{\cdot}2H_2O$ was stirred under reflux in 75 mL of absolute methanol. After ca. $^1/_2$ h, the formation of the white $Mo_2O_5(OCH_3)_2$ was noted. The reaction was allowed to proceed for 24 h. The product was then filtered and washed with absolute methanol under a dry nitrogen atmosphere in the dark. Care must be taken to avoid exposure of the dried powder to either water vapor or ultraviolet radiation. Anal. Calcd for $Mo_2O_5(OCH_3)_2$: C, 7.19; H, 1.80; H/C = 3.0. Found: C, 7.15; H, 1.81; H/C = 3.04.

$Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$. Five grams of $MoO_3{\cdot}2H_2O$ was stirred with 75 mL of absolute methanol at 0 °C. After 24 h, the white product was filtered and washed with cold methanol in a dry, dark atmosphere, care being taken to avoid exposure to both water vapor and sunlight. Anal. Calcd for $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$: C, 12.07; H, 3.55; H/C = 3.5. Found: C, 12.28; H, 3.60; H/C = 3.52.

Table I. *d* Spacings (in Å) with Relative Intensities for $Mo_2O_5(OCH_3)_2$ and $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$ and Those Reported for "$MoO_3{\cdot}CH_3OH$"[6]

$MoO_5(OCH_3)_2$	$Mo_2O_5(OCH_3)_2{\cdot}$ $2CH_3OH$	"$MoO_3{\cdot}CH_3OH$"
7.31 (100)	7.88 (100)	7.86 (s)
4.73 (60)	5.78 (48)	5.54 (m)
3.84 (40)	4.82 (20)	[5.48 (m)] (?)
3.76 (25)	4.69 (37)	4.65 (m)
3.27 (5)	4.23 (28)	4.19 (m)
3.22 (40)	3.93 (17)	3.90 (m)
3.17 (20)	3.75 (2)	
3.10 (40)	3.58 (31)	3.54 (m)
2.86 (20)	3.48 (21)	3.44 (m)
	3.41 (7)	
	3.28 (7)	
	3.09 (24)	
	3.06 (56)	3.06 (m)
	2.91 (7)	

Table II. Analysis of the Residues of the Thermal Decomposition of $Mo_2O_5(OCH_3)_2$

dec temp, °C	residue[a]	H content, % of residue	phases after annealing under vacuum at 500 °C[a]	O/Mo[b]
450	Mo_4O_{11}, $2MoO_2$	0	unchanged	2.50
350	Mo_4O_{11}, $2MoO_2$	0	unchanged	2.50
250	amorphous	0.28	Mo_4O_{11}, MoO_2	2.60
150	amorphous	0.33	Mo_4O_{11}, trace MoO_2	2.75

[a] As determined by X-ray diffraction. [b] From TGA performed on vacuum-annealed residues heated in O_2 to 650 °C ($MoO_{3-x} + (x/2)O_2 \rightarrow MoO_3$).

Deuteration. Deuterted samples of the molybdenum oxy–methoxy compounds were prepared by reacting $MoO_3{\cdot}2H_2O$ with CD_3OD under the conditions given above.

Hydrolysis. The reaction of either $Mo_2O_5(OCH_3)_2$ or the methanol adduct with water gave the compound $MoO_3{\cdot}^1/_2H_2O$ as determined by thermogravimetry coupled with mass spectrometry (see below). Anal. Calcd: H, 0.65. Found: H, 0.73.

Thermogravimetry. Analysis was carried out on a Du Pont 951-990 instrument at a heating rate of 5 °C/min. TGA curves in oxygen for both (a) $Mo_2O_5(OCH_3)_2$ and (b) $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$ are given in Figure 1. For the methanol adduct (b), a 16.0% weight loss occurred at ca. 100 °C, giving compound a. For both compounds, the methoxide groups are lost at ca. 225 °C. The residue in both cases was MoO_3, as determined by powder X-ray diffraction (% MoO_3: for (a) 86.23 (calcd), 86.0 (found); for (b) 72.35 (calcd), 72.5 (found)).

A TGA curve for the hydrolysis product, $MoO_3{\cdot}^1/_2H_2O$, is given in Figure 1. The weight loss under vacuum, which occurred at ca. 260 °C, was 6.1% (calcd 5.88%). The residue was MoO_3 as determined by powder X-ray diffraction.

Infrared Studies. Neat pellet samples of $Mo_2O_5(OCH_3)_2$ were prepared for infrared studies by pressing 10 mg of powder in a 1.0 cm diameter die at 6000-lb pressure. The pellets were mounted in

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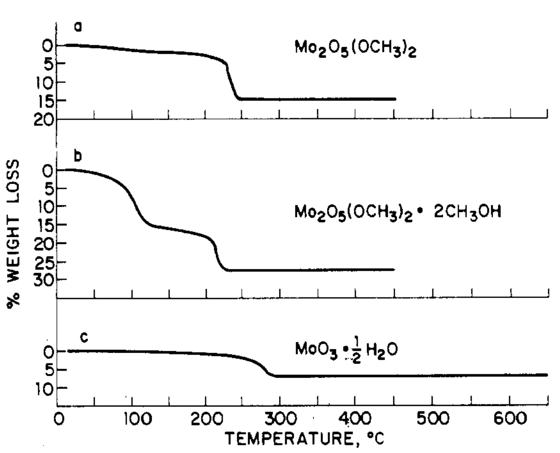

Figure 1. TGA curves for (a) $Mo_2O_5(OCH_3)_2$ under O_2, (b) $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$ under O_2, and (c) $MoO_3{\cdot}{}^1/_2H_2O$ under vacuum.

a cylindrical open-ended quartz oven inside a metal vacuum system. Two thermocouples were positioned inside the oven next to the sample to monitor temperature. Transmission infrared spectra of the sample were taken before and after evacuation and after heating to various temperatures.

Gas Evolution Studies. Analyses of the methoxide thermal decomposition products were performed on a Du Pont 21-491 gas chromatography/mass spectrometry instrument. Powdered samples were loaded into a 120 Pyroprobe unit under a flowing He stream and flashed (20 °C/ms) to the temperatures indicated in Table II.

For the photolysis studies, pellet samples were prepared and mounted in a quartz oven in a vacuum system as for the infrared studies. The pellets were located in line with a sapphire window and at a distance 20 cm from the ionizer region of an Extranuclear quadrupole mass spectrometer. A Bausch and Lomb 150-W xenon arc lamp was used for UV irradiation.

Results

The reaction of $MoO_3{\cdot}2H_2O$ and methanol proceeds as shown in eq 1 and 2. The methanol adduct (b) loses methanol

$$2MoO_3{\cdot}2H_2O + 2CH_3OH \xrightarrow{60°C} \underset{a}{Mo_2O_5(OCH_3)_2} + 5H_2O \qquad (1)$$

$$2MoO_3{\cdot}2H_2O + 4CH_3OH \xrightarrow{0\ °C} \underset{b}{Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH} + 5H_2O \qquad (2)$$

at ~100 °C, giving the simple methoxide (a). TGA curves for these compounds are given in Figure 1. The unindexed powder patterns for these two compounds are compared with the earlier work of Adams and Fowler[6] in Table I.

Hydrolysis of the methoxide to the hemihydrate (eq 3) takes

$$Mo_2O_5(OCH_3)_2 + 2H_2O \rightarrow 2MoO_3{\cdot}{}^1/_2H_2O + 2CH_3OH \qquad (3)$$

place on contact with water vapor. On the basis of its powder X-ray diffraction pattern, this hemihydrate is identical with $MoO_3{\cdot}{}^1/_2H_2O$ which slowly precipitates from concentrated nitric acid solution.[8,9] As such, the hydrolysis of $Mo_2O_5(OCH_3)_2$ affords a simpler and less time-consuming preparative route to the hemihydrate. TGA data for the hemihydrate is also presented in Figure 1.

The infrared spectra of $Mo_2O_5(OCH_3)_2$ show methoxy groups which are removed by either heating or UV irradiation. A spectrum taken in air at 25 °C is shown in Figure 2. The general increase in the base line above 1200 cm^{-1} results from

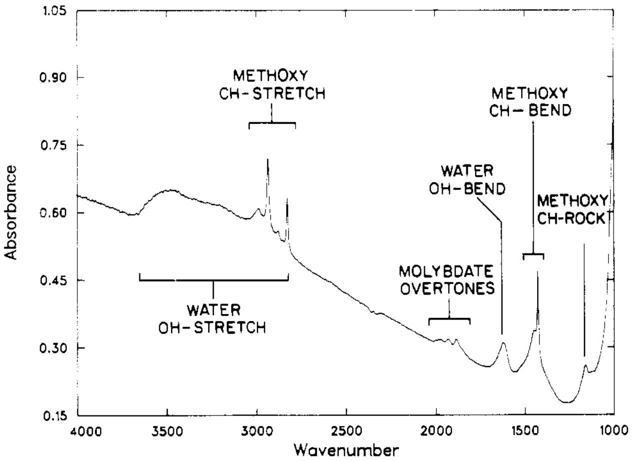

Figure 2. Mid-infrared spectrum of a neat pellet sample of $Mo_2O_5(OCH_3)_2$ obtained in transmission. The general increase in base line with wavenumber is due to light scattering by the sample.

light scattering due to the relatively large particle size. Assignments of the features in this spectrum can be made on the basis of our previous work on methanol adsorption on MoO_3.[10] The OH-bend feature at 1625 cm^{-1} and the broad OH-stretch feature extending from 2700 to 3700 cm^{-1} indicate the presence of adventitious water picked up on exposure to room air (eq 3). The sharply rising absorption going off scale below 1100 cm^{-1} is the beginning of MoO-stretch features, which continue below 1000 cm^{-1} (not shown). The pair of sharp CH-stretch features at 2827 and 2937 cm^{-1} and the broader pair at 2878 and 2988 cm^{-1} indicate the presence of two different methoxy groups. This is also indicated by the two CH-bend features at 1430 (sharp) and 1450 (broad) cm^{-1}. The feature at 1165 cm^{-1} can be assigned to a methyl CO stretch. A CO-stretch feature may also be hidden under the MoO-stretch features below 1100 cm^{-1}. The weak bands in the range 1850–2000 cm^{-1} are overtones of the MoO-stretch vibrations.

The thermal decomposition of $Mo_2O_5(OCH_3)_2$ was studied as a function of temperature. At all temperatures, only four gaseous products were detected: dimethyl ether, formaldehyde, methanol, and water. The relative ratios of these four components were observed to vary as a function of decomposition temperature, and while not quantitative, a correlation between decomposition temperature and product distribution was apparent. The GC/MS analysis showed that the relative amount of dimethyl ether to formaldehyde increased with decreasing decomposition temperature. Since dimethyl ether production does not involve reduction of molybdenum, this observation is in agreement with the analysis of the solid residues presented in Table II; namely, the state of reduction of the molybdenum in the bulk residue is less at the lower decomposition temperatures, as shown by an increase in the O/Mo ratio. Additionally, the lower temperatures favor the formation of amorphous hydrogen bronzes. The decomposition of these bronzes is observed to be extremely sharp, taking place at 325 °C with loss of water to yield crystalline products (mixtures of Mo_4O_{11} and MoO_2).

The photodecomposition of $Mo_2O_5(OCH_3)_2$ yields CH_2O and CH_3OH in nearly equal amounts. The blue residue is amorphous to x rays. Insertion of UV cutoff filters shows that the effective wavelength for the UV irradiation is below 300 nm.

Experiments analogous to those described above were performed on deuterated samples with similar results, the notable difference being a shift in the thermal product dis-

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tribution toward increased dimethyl ether production and consequently higher O/Mo ratios for the bulk residues relative to those for nondeuterated samples under equivalent decomposition conditions.

Discussion

Lack of single crystals has prevented structure determinations of $Mo_2O_5(OCH_3)_2$ and $Mo_2O_5(OCH_3)_2 \cdot 2CH_3OH$. Nonetheless, the chemical analyses, IR data, and decomposition behavior demonstrate the presence of methoxy groups in these compounds.

Infrared spectra of $Mo_2O_5(OCH_3)_2$ (Figure 2) show methoxy groups which are removed by heating or UV irradiation. The positions of the sharp CH_3-stretching features at 2937 and 2827 cm^{-1} and the sharp CH_3-bending feature at 1430 cm^{-1} closely agree with positions of features of methoxy groups on MoO_3 surfaces produced by reaction with methanol.[10] The broader CH_3-stretching features at 2988 and 2878 cm^{-1} and the broader CH_3-bending feature at 1450 cm^{-1} are all at higher wavenumber positions, closer to the values for methanol.[11] However, the positions of these broader peaks do not agree in detail with the peak positions for gaseous or condensed methanol[11] or with the positions observed for chemisorbed intact methanol in our previous work.[10] A more likely explanation for the broader CH_3 features in Figure 2 is that they are due to a second kind of surface-methoxy group. Further evidence for a second kind of surface-methoxy group may be taken from the appearance of the feature at 1165 cm^{-1} in Figure 2. This peak position corresponds to that of a CH_3-rocking mode in gaseous or condensed methanol.[11] No peak at this position was observed for chemisorbed intact methanol or the surface-methoxy group in our work on MoO_3. Presumably, this mode is weak for those species. Its enhanced intensity in the present work suggests that a new type of methoxy group is present. Evidence against the presence of intact methanol molecules in the present work is the lack of an OH-bending feature at 1350–1370 cm^{-1} as is observed for gaseous, condensed, and chemisorbed methanol. The features present in Figure 2 are thus most readily interpreted as due to the presence of two types of methoxy groups. Possibly these are bridged and terminal structures analogous to those described for the isopolymolybdate anion $[Mo_8O_{24}(OCH_3)_4]^{4-}$, by McCarron and Harlow,[2] but the present evidence does not allow us to assign which is which.

The thermal decomposition revealed the following products: methanol, formaldehyde, dimethyl ether, and water. All the observed products can be accounted for by three simple thermal decomposition pathways for $Mo_2O_5(OCH_3)_2$ (eq I–III). Pathway I is a non-redox process involving a methyl transfer between methoxy groups. No C–H bonds are broken. On the other hand, pathways II and III are both of the redox type and both involve the breaking of C–H bonds.

$$Mo_2O_5(OCH_3)_2 \longrightarrow 2MoO_3 + (CH_3)_2O \qquad (I)$$

$$Mo_2O_5(OCH_3)_2 \longrightarrow Mo_2O_5 + CH_3OH + CH_2O \qquad (II)$$

$$Mo_2O_5(OCH_3)_2 \longrightarrow [H_2Mo_2O_5] + 2CH_2O$$

$$\hookrightarrow 2MoO_2 + H_2O \qquad (III)$$

All three decomposition pathways are assumed to operate simultaneously, but with different activation energies. In contrast, the photolysis of $Mo_2O_5(OCH_3)_2$ appears to proceed solely via pathway II, as witnessed by the generation of roughly equal amounts of methanol and formaldehyde. This observation is consistent with the established disproportionation pathway for photochemically generated methoxy radicals[12]

$$2CH_3O\cdot \rightarrow CH_3OH + CH_2O$$

Insight into the factors governing the operation of the individual thermal decomposition pathways as a function of temperature can be gained by a study of the bulk decomposition residues. The solid products were identified by X-ray diffraction and quantified by TGA, and this allowed for a semiquantitative determination of the relative magnitudes of the three pathways. For example, if the rates of decomposition for the three pathways at a given temperature were equal, the resulting solid phase would have the overall composition Mo_2O_5.[13] The actual correlation between decomposition temperature and the solid residue formed is given in Table II. Indeed, for decomposition at temperatures above the hydrogen bronze decomposition temperature (325 °C), the residue always has the oxygen-poor composition Mo_2O_5.[13] But at lower decomposition temperatures, amorphous hydrogen bronzes richer in oxygen ($O/Mo < 2.5$) are produced.

This trend of increasing oxygen content with lower decomposition temperature for the solid residue can be seen as a result of the fact that C–H bond breaking is rate limiting. As the energy available for C–H bond breaking (pathways II and III) decreases with decreasing temperature, the oxygen content of the residue rises ($O/Mo \rightarrow 2.75$) as the decomposition proceeds increasingly via the non-redox-type pathway I. In fact, in a gross demonstration of the kinetic isotope effect, the thermal decomposition of $Mo_2O_5(OCD_3)_2$ at temperatures below ~200 °C yields primarily MoO_3 and $(CD_3)_2O$ (pathway I), confirming that the rates of the decomposition reactions of the redox type (pathways II and III) are limited by the breaking of C–H (C–D) bonds.

The molecular products obtained on thermal decomposition of $Mo_2O_5(OCH_3)_2$ are very similar to those obtained in the thermal decomposition of methoxy groups on the surface of MoO_3. The primary difference is that the decomposition of $Mo_2O_5(OCH_3)_2$ produces significant quantities of dimethyl ether, whereas this product is nearly absent on the thermal decomposition of the surface methoxy species on molybdenum trioxide. However, the steady-state catalytic reaction of methanol on MoO_3 can produce significant quantities of dimethyl ether under low-conversion conditions where the surface concentration of methoxy groups is expected to be highest. Thus, there is, in fact, a good correlation between the catalytic products over MoO_3 and the thermal decomposition of $Mo_2O_5(OCH_3)_2$ with regard to dimethyl ether formation.

At higher temperatures, the methoxy groups begin to decompose, liberating formaldehyde. The hydrogen left behind may combine with remaining methoxy groups, liberating methanol, or it may be utilized in the formation of a hydrogen molybdenum bronze, with the bronze decomposing sharply at about 325 °C. In either case, two electrons are left behind in Mo 4d levels for every molecule of formaldehyde produced. It can be concluded that methoxy decomposition occurs in essentially the same manner in $Mo_2O_5(OCH_3)_2$ as on the MoO_3 surface.

Registry No. **1**, 88916-50-1; **2**, 86727-41-5; MoO_3, 1313-27-5; $MoO_3 \cdot {}^1/_2H_2O$, 62267-35-0.

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(13) The phase, $H_{2x}Mo_2O_{5+x}$, is amorphous. It decomposes according to $H_{2x}Mo_2O_{5+x} \rightarrow [Mo_2O_5] + xH_2O$, with $3[Mo_2O_5] \rightarrow Mo_4O_{11} + 2MoO_2$. The decomposition occurs very sharply at 325 °C (DSC exotherm) with violent liberation of H_2O. Hence, at decomposition temperatures above 325 °C, only Mo_4O_{11} and 2 MoO_2 are observed.