*Inorg. Chem.* **1985**, *24*, 4293–4298

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# Cocondensation Products of Molybdenum Trioxide Vapor with Methanol, Water, and Tetrahydrofuran

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*Received March 12, 1985*

Cocondensation reactions of $MoO_3$ vapor with methanol, $H_2O$, and tetrahydrofuran (THF) at −196 °C are reported. The cocondensates have all been studied by using infrared spectroscopy and thermal gravimetric analysis (TGA). The methanol cocondensate was shown to be $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$, residual unreacted $MoO_3$, and physisorbed $CH_3OH$. Photolysis of a slurry of the methanol cocondensate in methanol under dioxygen selectively gave dimethoxymethane. The conversion was catalytic with 55 turnovers over an 18-day period. The water cocondensate was a new molybdenum trioxide dihydrate, different from the known yellow monoclinic $MoO_3{\cdot}2H_2O$. The THF cocondensate was an amorphous solid with a bulk composition of 0.57 mol of THF/mol of $MoO_3$. Water and THF in a mole ratio of 20:1 and traces of propene, butadiene, acetaldehyde, acetone, and furan were observed when the THF cocondensate was heated to 170° C in dioxygen. Additional heating in $O_2$ to 410 °C yielded $CO_2$ and water. A solution of the THF cocondensate in wet THF containing 18-crown-6 exposed to air gave crystals of the seven-coordinate peroxomolybdenum complex, $[MoO(O_2)_2(H_2O)_2]{\cdot}18\text{-crown-}6{\cdot}H_2O$, after 35 days. Additional studies showed the peroxomolybdenum was formed from reaction of molybdenum oxide with $H_2O_2$ formed in situ from α-hydroperoxytetrahydrofuran.

## Introduction

Cook and Timms[1] recently reported on the cocondensation reaction between $MoO_3$ vapor and various small molecules. Cocondensation reactions between $MoO_3$ vapor and various ligands are of interest to us because of the relationship between the proposed active catalytic sites on supported molybdate catalysts and the sites available on $MoO_3$ vapor. Solid $MoO_3$ is coordinated by oxygen in a distorted octahedral array,[2] while four-coordinate molybdenum has been proposed as the active catalytic site in the molybdate catalysts supported on silica[3,4] and in the alumina-supported catalysts with low molybdenum content.[5,6] $MoO_3$ vapor consists of a mixture of cyclic trimers, tetramers, and pentamers with the trimer dominant.[7] The structure of the trimer is a planar ring with $D_{3h}$ symmetry and four-coordinate molybdenum. A comparison of the coordination about the molybdenum for the proposed active catalytic sites on the molybdate catalysts and that on the $MoO_3$ trimer is shown in Figure 1. The close geometrical relationship between molybdenum in the proposed active catalytic site and molybdenum in gaseous $MoO_3$ vapor suggested that possible catalytic precursors might be trapped during cocondensation. This may lead to observation of catalytic products during warm-up. Alternatively, subsequent photolytic or thermal studies of the cocondensation products may lead to new insights concerning catalytic pathways.

Here we report the results of cocondensation of methanol, water, and tetrahydrofuran with $MoO_3$ vapor. Additional studies involving the cocondensation products are also reported.

## Experimental Section

**Materials.** Tetrahydrofuran (THF) (J. T. Baker) was freshly distilled over sodium/benzophenone prior to use. The water used was Millipore (Milli-Q) reagent grade deionized water with a resistivity greater than 10 MΩ/cm. All other starting materials were commercially available.

**Physical Measurements.** IR spectra were recorded on a Mattson Sirius 100 FT-IR instrument at 2-cm$^{-1}$ resolution. Solid samples were run as KBr pellets or Nujol mulls. Gas samples were run in a cell with a 10-cm path length between NaCl plates. NMR were recorded in suitable solvents on a Varian FT-80A spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E9 EPR spectrometer at room temperature. Gas chromatography/mass spectral (GC/MS) data were obtained with a Varian MAT GmbH CH7 Massenspektrometer at an ionization potential of 70 eV interfaced with a Varian 1200 gas chromatograph equipped with a flame ionization detector. Columns used were 5% Carbowax 20M on 100/120 Supelcoport or 100/120 Porapak QS. Routine GC runs were performed on a Hewlett Packard 5710A GC equipped with a thermal conductivity detector. Powder X-ray diffraction patterns were obtained on a Norelco 3600 automated X-ray powder diffractometer using Cu Kα radiation at 45 kV and 40 mA equipped with a single-crystal graphite monochromator. $MoO_3$ was identified by comparison with the JCPDS powder diffraction file.

**Thermogravimetry (TGA).** Analysis was carried out on a Mettler Model TA 2000C simultaneous differential scanning calorimeter and thermogravimetric analyzer. All samples were heated at a rate of 5 °C/min under dioxygen. The residue in all cases after analysis was identified as $MoO_3$ by X-ray powder diffraction.

**Cocondensation Reactions.** The cocondensation reactions were carried out in a 2-L Pyrex reaction vessel evacuated to $10^{-4}$ torr. The vessel was immersed in liquid nitrogen to allow $MoO_3$ vapors and ligand to be cocondensed on the walls. Condensation apparatus of this type, used in metal atom chemistry, have been described elsewhere.[8,9]

Molybdenum trioxide powder (99% pure) was sublimed by resistive heating from a 10-mm-diameter, 45-mm-long niobium tube.

$MoO_3$ vapor was cocondensed with methanol, water, and tetrahydrofuran in a mole ratio of 1:10 to 1:50 depending on the ligand involved. The cocondensate was warmed to room temperature, and all volatiles including excess reactant ligand were pumped off and handled on a high-vacuum line. The reactor was then filled with either dry nitrogen or argon and taken into an inert atmosphere glovebox (Vacuum Atmospheres Model He-493-2), where the solids were physically removed for further study.

**$MoO_3$ + Methanol.** Molybdenum trioxide (4.57 g, 31.7 mmol) was cocondensed at −196 °C with $CH_3OH$ (20.0 g, 625 mmol). When the mixture was warmed to 20 °C in the dark, 15.67 g of volatiles were recovered, which were shown by GC analysis to be unreacted $CH_3OH$ (15.3 g, 478 mmol) and water (0.37 g, 21 mmol), along with a gray-green solid (5.01 g). IR (KBr): 3300 (w, br), 2931 (w), 2830 (w), 1619 (w), 1453 (m), 1390 (m) cm$^{-1}$; below 1200 cm$^{-1}$ a broad unresolved peak. $^1H$ NMR ($D_2O$): δ 3.74 ($OCH_3$), 5.13 (HDO). All manipulations after cocondensation were done in the dark.

The TGA curve for the methanol cocondensate is given in Figure 2. A weight loss of 5% was observed between 40 and 90 °C, corresponding primarily to the loss of physisorbed methanol. A weight loss of 11% was observed at ca. 100 °C, corresponding primarily to loss of two adducted methanol molecules from $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$ (**1**). The methoxide groups (9%) were lost at ca. 225 °C. The above analysis shows the methanol cocondensate contained 78% **1**, 18% unreacted $MoO_3$, and 4% physisorbed methanol (see Discussion).

**$MoO_3$ + $H_2O$.** Molybdenum trioxide (4.21 g, 29.2 mmol) was cocondensed at −196 °C with water (25.0 g, 1390 mmol) giving a bright

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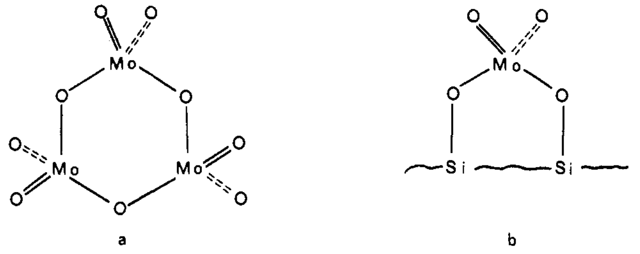

**Figure 1.** (a) Structure of $MoO_3$ trimer.[7] (b) Proposed structure of silica-supported molybdate catalysts.[3]

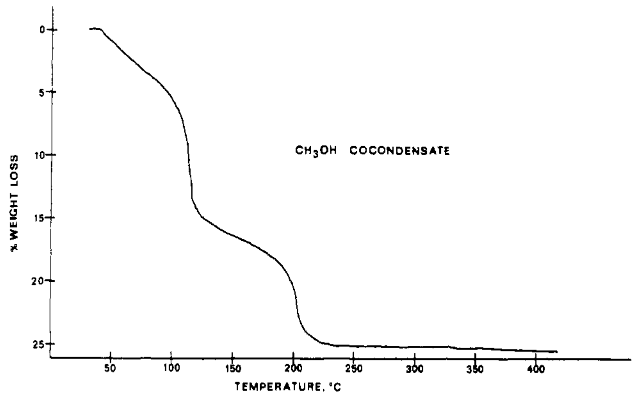

**Figure 2.** TGA curve in $O_2$ for the methanol cocondensate.

yellow solid. As the cocondensate warmed, the solid slowly turned blue. Once the water melts, a blue solution and a blue solid are observed. The excess water was removed by evacuation, leaving a blue solid. IR (Nujol): 3300 (w, br), 1620 (w), 954 (m), 875 (s), 721 (s), 696 (s), 683 (s), 631 (s), 557 (s) cm$^{-1}$. The blue $H_2O$ cocondensate was shown by X-ray powder diffraction to be amorphous.

TGA curves for both (a) the blue $H_2O$ cocondensate and (b) yellow $MoO_3 \cdot 2H_2O$[10] are shown in Figure 3. A weight loss of 15% was observed at ca. 120 °C for the $H_2O$ cocondensate, which corresponds to approximately 1.5 $H_2O$ lost/$MoO_3$ present. A second weight loss of 5% was observed at ca. 220 °C, which is consistent with approximately 0.5 $H_2O/MoO_3$. On the basis of total weight loss, the blue $H_2O$ cocondensate was identified as 97% $MoO_3 \cdot 2H_2O$ (**2**) and 3% unreacted $MoO_3$.

The $H_2O$ cocondensate (0.65 g) was stirred with 50 mL of anhydrous $CH_3OH$ for 3 days in the dark. A white solid (0.74 g), shown by spectroscopy to be **1**, was recovered after filtration.

**$MoO_3$ + Tetrahydrofuran (THF).** Molybdenum trioxide (4.89 g, 34.0 mmol) was cocondensed at −196 °C with freshly distilled THF (22.3 g, 309 mmol). When the mixture was warmed to 20 °C, unreacted THF and a green solid were recovered. IR (KBr): 3450 (m, br), 2976 (m), 2877 (m), 1620 (m), 1460 (m), 1395 (w), 1345 (vw), 1023 (m), 969 (s) cm$^{-1}$; below 950 cm$^{-1}$ a broad unresolved peak. NMR ($D_2O$): $\delta$ 1.85 ($CH_2$), 3.70 ($OCH_2$).

The TGA curve for the THF cocondensate is given in Figure 4. There are two regions of weight loss. One weight loss occurred at ca. 130 °C (13%), with a second weight loss at ca. 380 °C (9%). The total weight loss of 22% analyzes as 0.57 mol of THF present per mol of $MoO_3$.

The THF cocondensate was heated in dioxygen from 20 to 170 °C. GC/MS analysis of the volatile products trapped at −130 °C showed water and THF, with traces of propene, butadiene, acetaldehyde, acetone, and furan. GC/MS analysis of the volatile products obtained by additional heating of the sample in dioxygen from 170 to 410 °C showed $CO_2$ and $H_2O$. The residue from this heating was shown to be $MoO_3$ by X-ray powder diffraction.

The THF cocondensate (0.68 g) was stirred with excess $CH_3OH$ for 12 h. After filtration, 0.68 g of a white solid was recovered. TGA indicated the white solid was a mixture of 93% $Mo_2O_5(OCH_3)_2 \cdot 2CH_3OH$ (**1**) and 7% unreacted $MoO_3$. IR (KBr): 3300 (m, br), 2931 (m), 2831 (m), 1453 (m), 1390 (m), 1103 (m), 1013 (s), 946 (s), 931 (s), 902 (s), 793 (s), 775 (s) cm$^{-1}$.

**$[MoO(O_2)_2(H_2O)_2] \cdot 18$-crown-6·$H_2O$ (3). Method A.** A green homogeneous solution was obtained after addition of 1.4 mL of $H_2O$ to a slurry of the THF cocondensate (0.49 g) in 100 mL of THF. This solution turned yellow 30 min. after saturation with dioxygen in the presence of light. 18-crown-6 (0.91 g, 3.42 mmol) was added to this solution. Thirty-five days later, air-stable, yellow crystals of **3** (0.91 g, 1.84 mmol) were obtained. The crystals were soluble in $H_2O$, ethanol, dimethyl sulfoxide, THF, and acetone. IR (KBr): 3500 (m, br), 2899 (m), 1469 (w), 1350 (m), 1285 (w), 1103 (vs), 962 (s), 868 (m), 735 (m) cm$^{-1}$; NMR ($D_2O$) $\delta$ 3.65 (s), 4.73 (s). Anal. Calcd for $MoC_{12}H_{30}O_{14}$: Mo, 19.4; C, 29.2; H, 6.1; O, 45.3. Found: Mo, 19.5, C, 28.5; H, 5.7; O, 46.3.

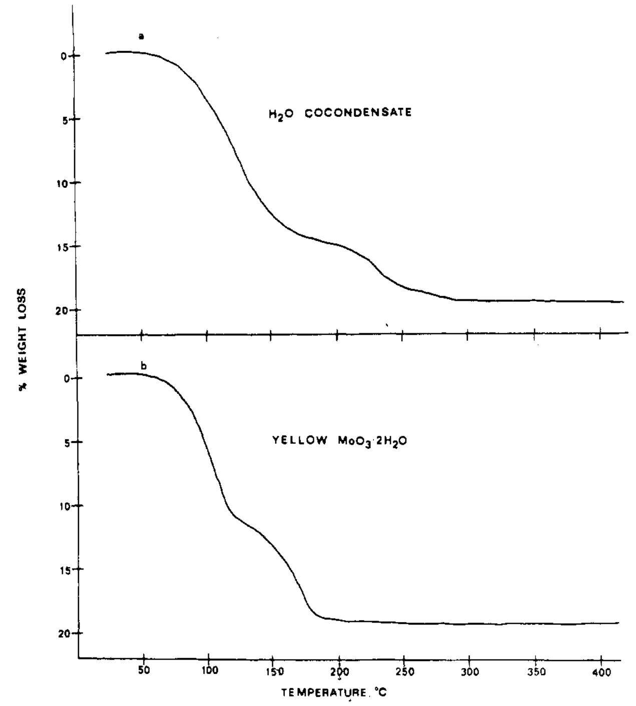

**Figure 3.** TGA curve in $O_2$ for (a) the $H_2O$ cocondensate and (b) yellow $MoO_3 \cdot 2H_2O$.[10]

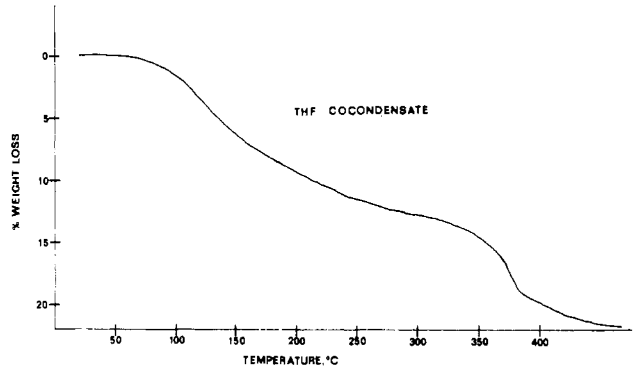

**Figure 4.** TGA curve in $O_2$ for the THF cocondensate.

**Method B.** A 6.4% $\alpha$-hydroperoxytetrahydrofuran in wet THF (10.0 mL) solution was added to the THF cocondensate (0.21 g) under argon. A yellow homogeneous solution was observed immediately. The yellow solution sat for 16 h, after which time 18-crown-6 (0.23 g, 0.87 mmol) in THF (5.0 mL) was added. Rapid formation of a yellow precipitate was observed. After filtration 16 h later, crystals of **3** (0.32 g) were recovered.

**Method C.** Upon addition of 0.8 mL of 30% $H_2O_2$ to a slurry of the THF cocondensate (0.51) g in dry THF, a yellow homogeneous solution was immediately observed. After exposure to air, 18-crown-6 (0.23 g, 0.87 mmol) was added to the yellow solution. Immediate precipitation of **3** was observed. The solution was filtered after 15 h with recovery of 0.21 g of **3**.

*Caution*! Hydroperoxide solutions are known to be unstable to both heat and shock so extreme caution must be taken to avoid an explosion.[11]

**$\alpha$-Hydroperoxytetrahydrofuran.** 2,2′-Azobis(2-methylpropionitrile) (AIBN) (0.1 g) was dissolved in 50 mL of THF containing 2.0 mL of

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[10] A sample of yellow $MoO_3 \cdot 2H_2O$ together with its TGA curve was kindly supplied by E. M. McCarron of the E. I. du Pont de Nemours and Co., Inc.

[11] Shanley, Edward S. In "Organic Peroxides"; Swern, Daniel, Ed.; Wiley-Interscience: New York, 1972; Vol. III, Chapter V.

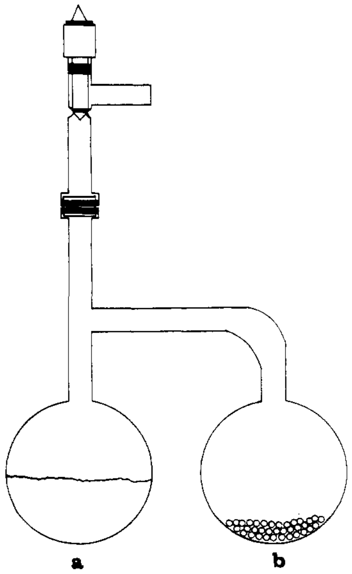

**Figure 5.** Schematic of the vessel used to lower the activity of water in the photolysis of methanol with the methanol cocondensate. Bulb a contains the reaction slurry and bulb b contains 4A molecular sieves.

$H_2O$. The solution was saturated with oxygen and set aside in a well-lighted, warm area of the laboratory. Iodometric titration after 2 weeks indicated the solution contained 2.1% THFOOH. The solution was concentrated to a 6.4% solution of THFOOH by solvent removal under vacuum.

**Photolysis. $CH_3OH$.** The methanol cocondensate (0.71 g) was photolyzed with $CH_3OH$ (20.0 g, 624 mmol) under 1 atm of dioxygen with a Hanovia L (694A) 450-W 837 medium-pressure Hg lamp. After photolysis the volatile components were collected and identified as unreacted $CH_3OH$, $H_2O$, $CH_3OCH_2OCH_3$, and trace amounts of $HCOOCH_3$ by GC/MS.

To determine the catalytic activity of the methanol cocondensate, a stirred slurry of the methanol cocondensate (0.053 g) in anhydrous methanol (20.0 g, 624 mmol) was photolyzed in the vessel shown in Figure 5. The basic design of the flask was used by DeKock and co-workers as the flask connected to an inert-atmosphere Soxhlet extractor.[9] The double-bulb flask was connected to a J. Young Acton Type POR/10-mm/RA valve by a Fischer-Porter Solv-Seal Teflon joint. The slurry was frozen with liquid nitrogen, evacuated, and warmed to room temperature under vacuum three times, and then while at room temperature it was put under 1 atm of dioxygen. Aliquots of the mixture were taken at approximately 3-day intervals and analyzed by GC to monitor formation of dimethoxymethane (DMM). Upon removal of each aliquot the mixture was again freeze-thawed and put under a fresh atmosphere of dioxygen. Fifty-five turnovers were observed after 18 days with a still active catalyst.

**$CD_3OD/CH_3OH$.** A slurry of the methanol cocondensate with 3.0 mL of $CH_3OH$ and 2.9 mL of $CD_3OD$ was photolyzed for 8 days. GC/MS analysis of the products showed approximately 1% conversion to DMM, with the following isotopic isomers observed: $CH_3OCH_2OCH_3$, $CD_3OCH_2OCH_3$, $CD_3OCD_2OCH_3$, $CD_3OCH_2OCD_3$, $CH_3OCD_2OCH_3$, and $CD_3OCD_2OCD_3$.

**Spin-Trapping Experiment.** *N-tert*-Butyl-$\alpha$-phenylnitrone (PBN) and $\alpha$-(1-oxo-4-pyridyl)-*N-tert*-butylnitrone (POBN) were used as obtained from Aldrich. The $WO_3$ powder was prepared by heating $WO_3$·$2H_2O$ at 500 °C for 60 h in air. Mixtures to be irradiated were dispersed ultrasonically with a Bransonic 12 apparatus for 4 min. In all experiments the concentration of PBN and POBN was approximately 0.03 M. The $WO_3$ and $MoO_3$ mixtures irradiated were approximately 10% metal oxide by weight. The aqueous solution of the methanol cocondensate contained approximately 10% cocondensate by weight.

EPR spectra were recorded on a Varian E9 spectrometer in a 0.1-mm Pyrex capillary tube suspended in the EPR cavity. All spectra were recorded at room temperature.

Illumination was performed in the cavity of the spectrometer through its grid by irradiation with a tungsten–halogen lamp from a Standard Model 750C projector (750 W) operated at 110 V. The UV component of the light was filtered out by the Pyrex sample tube (cutoff 330 nm).

## Results and Discussion

**$MoO_3$ Cocondensed with $CH_3OH$.** Cook and Timms[1] identified the methanol cocondensate as $MoO_3$·$2CH_3OH$ on the basis of its IR spectrum. With the recent work of McCarron, Staley, and Sleight[12] (MSS) we are now able to identify the $MoO_3$ and $CH_3OH$ cocondensate as $Mo_2O_5(OCH_3)_2$·$2CH_3OH$ (**1**), unreacted $MoO_3$, and physisorbed methanol. MSS prepared **1** by stirring yellow $MoO_3$·$2H_2O$ with absolute methanol. Kraus and Huber[13] had previously prepared **1**, but had formulated it as $MoO_3$·$2CH_3OH$.

Cook and Timms[1] report traces of $CO_2$ and $H_2CO$ were given off during warm-up of the cocondensate. We took care to prevent exposure of the cocondensate to light during warm-up, and no evidence of $CO_2$ or $H_2CO$ was observed. However GC analysis showed 0.49 mol of $H_2O$ formed/mol of $MoO_3$ deposited, which corresponds to the reaction shown in eq 1. The formation of a

$$4CH_3OH + 2MoO_3 \rightarrow Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH + H_2O \quad (1)$$

stoichiometric amount of water is direct evidence for the dehydration of methanol to produce **1** as formulated by MSS.[12] The thermogravimetry curve and IR spectrum of the cocondensate confirm the identification of **1**.

The TGA curve for the cocondensate is shown in Figure 2. Comparing the TGA curve of the methanol cocondensate with the curve reported by MSS[12] shows that the transition temperatures are identical and the percent weight loss at each transition is similar. Although the theoretical weight loss of 16% is observed between 30 and 140 °C for both the methanol cocondensate and **1** from MSS,[12] the methanol cocondensate shows only an additional 9% weight loss on heating to 225 °C. The theoretical value for this weight loss for **1** is 11.55%. This difference may be explained by two factors: (a) physisorbed methanol is released between 40 and 90 °C for the cocondensate; (b) some unreacted $MoO_3$ is present in the sample. These effects are easily corrected for by assuming that all of the sample is present as $MoO_3$ at the end of the TGA run. This was shown by X-ray powder diffraction analysis. The second weight loss then corresponds to one of three possible reactions as shown by MSS[12]

$$Mo_2O_5(OCH_3)_2 \rightarrow 2MoO_3 + CH_3OCH_3 \quad (2)$$

$$Mo_2O_5(OCH_3)_2 + {}^1/_2O_2 \rightarrow 2MoO_3 + CH_3OH + H_2CO \quad (3)$$

$$Mo_2O_5(OCH_3)_2 + O_2 \rightarrow 2MoO_3 + 2H_2CO + H_2O \quad (4)$$

all of which involve weight loss between $Mo_2O_5(OCH_3)_2$ and $MoO_3$. This analysis shows a typical sample to be 78% **1** and 18% unreacted $MoO_3$ with 4% physisorbed methanol. Sample composition depends on sample history; for example, prolonged evacuation times will leave less physisorbed methanol.

IR absorptions at 2931 and 2830 $cm^{-1}$ corresponding to C–H stretches indicate the methoxy groups are bridging two molybdenum atoms.[14] The $CH_3$ deformation band at 1453 $cm^{-1}$ is also consistent with a bridging methoxy group. For nonbridging methoxy groups, the stretching absorptions are at 2955–2965 and 2845–2854 $cm^{-1}$ and the $CH_3$ deformation is at 1467 $cm^{-1}$.[14]

The physisorbed methanol, presumably attached to the unreacted $MoO_3$, is revealed by an IR absorption located at 1390 $cm^{-1}$. This absorption decreases markedly in intensity when a sample of the methanol cocondensate is evacuated for a period of 20 h at ambient temperature. The 1350–1370 $cm^{-1}$ feature is due to the OH bending mode in liquid, gaseous, and chemisorbed methanol.[12,15] The presence of adventitious water is shown by absorptions at 3300 and 1619 $cm^{-1}$.

**Photolysis of the Methanol Cocondensate.** MSS[12] report irradiation of solid **1** under vacuum yields $H_2CO$ and $CH_3OH$ in nearly equal amounts. They found the effective wavelength for UV irradiation to be below 300 nm.

We find that photolysis of a slurry of the methanol cocondensate in methanol with Pyrex-filtered light (cutoff 330 nm) yields di-

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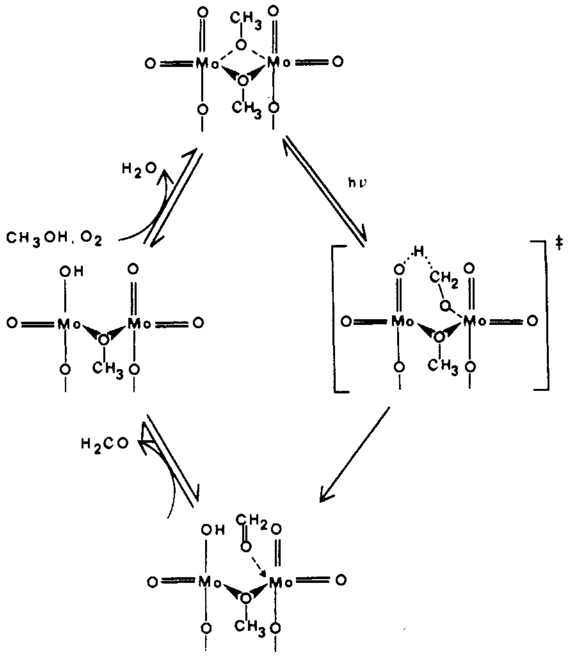

**Figure 6.** Proposed mechanism for photolysis of methanol with the methanol cocondensate. Dotted line is 3-center 2-electron O–H–C bond.

methoxymethane (DMM). Apparently formaldehyde is produced by the photooxidation of the methanol, which in the acidic methanol solution immediately undergoes acetal formation to form DMM.

$$H_2CO + 2CH_3OH \xrightarrow{H^+} CH_3OCH_2OCH_3 + H_2O \quad (5)$$

The photooxidation is catalytic with 55 turnovers after 18 days. At this time, the catalyst was still active.

A proposed mechanism for the catalytic photon-assisted partial oxidation of methanol to formaldehyde is shown in Figure 6. This mechanism incorporates the experimental observations and the results of a recent molecular orbital calculation by Anderson and Ray.[16] They recently used molecular orbital theory to explain the photoactivation of methoxy groups coordinated to unsaturated Mo(VI) centers located at edge surfaces of layered structure $MoO_3$ and on the surface of the $Mo_8O_{24}(OCH_3)_4^{4-}$ anion.

Anderson and Ray[16] show that when the methoxy group has a geometry such that the Mo–O–C angle is 160° and the H–O–Mo angle is 158°, a transition state with a 3-center C–H–O $\sigma$ bond is obtained. Their calculations show that, upon promotion of an electron from the O 2p band to the Mo 4d band, the activation energy of the hydrogen transfer is reduced by nearly one-half. Photoexcitation of an electron from the OH $\sigma^*$ orbital activates the hydrogen-transfer process by increasing the net bond order by $^1/_2$ in the transition state. The result of the hydrogen transfer is coordinated $OH^-$ and $H_2CO$ and reduced molybdenum oxide.

The $H_2CO$ is then desorbed from the reduced molybdenum oxide. Reoxidation to Mo(VI) by oxygen is followed by replacement of the hydroxy group by a methoxy group from methanol with formation of water. This completes the catalytic cycle.

This mechanism is further supported by the results of an ab initio quantum chemical calculation recently reported by Allison and Goddard.[17] They report the thermodynamically favorable catalytic site involves two adjacent surface dioxo units while a single-site single-step reaction is not thermodynamically favorable.

Evidence indicating the hydrogen abstraction is irreversible was shown by photolysis of a mixture of $CH_3OH$ and $CD_3OD$. Upon photolysis, isotopic isomers of DMM were found, but no evidence of hydrogen scrambling was observed. The methyl and methylene units were either fully hydrogenated or fully deuterated, with the following isomers observed: $CH_3OCH_2OCH_3$, $CH_3OCH_2OCD_3$, $CH_3OCD_2OCD_3$, $CD_3OCD_2OCD_3$, $CH_3OCD_2OCH_3$, $CD_3OCH_2OCD_3$. Isomers showing hydrogen scrambling such as $CD_2HOCH_2OCH_3$ were not observed.

Significantly higher turnover rates were observed when the photolysis was carried out in the vessel shown in Figure 5. Bulb a contained the reaction mixture, while bulb b contained only freshly dried 4A molecular sieves. The molecular sieve selectively traps water from above the reaction mixture, lowering the concentration of water vapor in the flask. The concentration of water is then lowered in the reaction mixture. Photocatalysis without decreasing the water concentration consistently gave only 3–5 turnovers after 2 weeks.

This is consistent with the observations of Pernicone[18] on the effect of water in the oxidation of methanol to formaldehyde over thermal iron–molybdate catalysts. Pernicone reports that excess water inhibits the oxidation of methanol and poisons the catalyst.

An alternate mechanism consisting of abstraction of hydrogen from chemisorbed methanol giving the $\cdot CH_2OH$ free radical was ruled out. A search for $\cdot CH_2OH$ free radicals using the spin-trapping agents PBN and POBN gave a null result. Irradiation of a control experiment containing a suspension of aqueous tungsten oxide and methanol readily gave the expected EPR signals of the $\cdot CH_2OH$ spin-trapped adduct.[19] During the spin-trapping experiments the growth of a Mo(V) signal was seen after irradiation of a methanol slurry of the methanol cocondensate as expected for the above proposed mechanism shown in Figure 6. Mo(V) is slow to reoxidize to Mo(VI).

The nature of the spent photocatalyst is not clear. A $g$ value of ca. 1.95 was observed, characteristic of reduced molybdenum. TGA of the spent catalyst shows a loss of weight over a broad region from 80 to 160 °C. This loss is similar to, but not as sharp as, that for the first methanol from compound **1**. Completely absent in the TGA of the spent catalyst is any evidence of loss of a methoxy group. This argues that the methoxy group is necessary for photocatalysis as shown by the mechanism in Figure 6.

Photocatalytic oxidation of organic compounds with heteropoly anions of molybdenum and tungsten have been reported.[20,21] Oxidation of 2-propanol to form acetone[20,21] and ethanol to form acetaldehyde[20] were reported, but no discussion of methanol was given.

**$MoO_3$ Condensed with $H_2O$.** Codeposition of molybdenum trioxide with water yielded a bright yellow solid at −196° C, which slowly turned blue as the cocondensate warmed. The blue color arises from the formation of trace amounts of molybdenum(V). The nature of the reducing agent is unclear. A thermogravimetric analysis of the $H_2O$ cocondensate is shown in Figure 3 and compared with the TGA of the known yellow monoclinic dihydrate, $MoO_3 \cdot 2H_2O$.[10] The overall weight loss from 30 to 400 °C is 20%, which corresponds to 1.93 mol of $H_2O$/mol of $MoO_3$. This is consistent with 97% $MoO_3 \cdot 2H_2O$ and 3% $MoO_3$. The first weight loss occurs at ca. 120 °C and corresponds to the loss of 1.5 water molecules while the second weight loss occurs at ca. 230 °C and corresponds to the loss of 0.95 water molecule. This contrasts sharply with the yellow monoclinic dihydrate, which loses one water molecule at ca. 110 °C and the second water molecule at ca. 170 °C.

The crystal structure of the yellow monoclinic dihydrate, $MoO_3 \cdot 2H_2O$, is known.[22] It consists of layers of corner-shared $MoO_6$ octahedra with two classes of water molecules. These are

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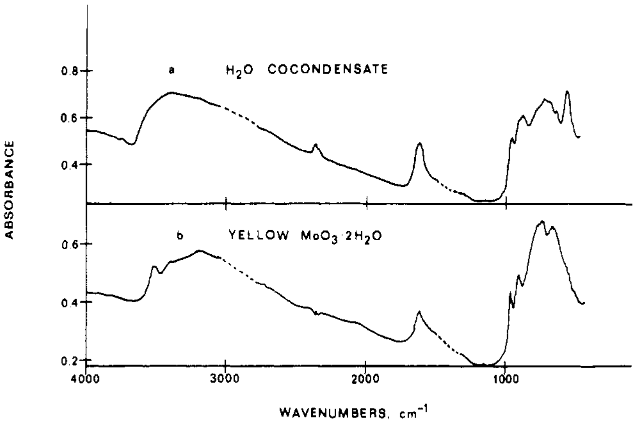

**Figure 7.** IR for (a) the $H_2O$ cocondensate and (b) yellow $MoO_3{\cdot}2H_2O$. Broken lines are regions of Nujol absorption.

the water molecules between layers and the water molecules coordinated to a Mo atom. These two classes of water molecules are reflected in the TGA, with the layer water molecules lost at 110 °C while the coordinated water molecules are lost at 170 °C. The TGA of the blue dihydrate indicates similar classes of water molecules. Here, however, assuming a similar layer structure, it appears that 1.5 water molecules are present in the layers while 0.5 water molecule is coordinated to the Mo atoms. Each type of water molecule is more tightly bound in the blue dihydrate than in the yellow monoclinic dihydrate as shown by the temperature at which the water molecules are lost. In the case of the layered molecules this may reflect an increase in hydrogen bonding. The IR spectrum in the hydrogen stretching region (see below) supports this supposition.

A comparison of the infrared spectra taken in a Nujol mull of the yellow monoclinic dihydrate and the blue dihydrate is given in Figure 7. These results show two clearly different compounds. The yellow monoclinic dihydrate shows a sharp O–H stretching frequency at 3510 $cm^{-1}$ and a sharp H–O–H bending frequency at 1617 $cm^{-1}$. The blue dihydrate shows a broad absorption in the O–H region from 3100–3600 $cm^{-1}$ with an intense sharp H–O–H bend at 1620 $cm^{-1}$. The broad absorption in the O–H stretching region is indicative of significant hydrogen bonding. Distinguishing features also occur in the Mo–O stretching region with the yellow dihydrate showing sharp features at 966, 905, 748, and 666 $cm^{-1}$, while the blue dihydrate shows features at 954, 875, 721, 696, 683, 631, and 557 $cm^{-1}$.

The blue dihydrate is similar to the yellow dihydrate in that it can be converted easily to $Mo_2O_5(OCH_3)_2{\cdot}2CH_3OH$ (**1**) when stirred with anhydrous methanol. MSS[12] reported the synthesis of **1** from yellow $MoO_3{\cdot}2H_2O$ and anhydrous methanol. We observed quantitative conversion of the blue dihydrate to **1** under the same conditions.

The molybdenum(VI) oxide dihydrate formed in this study adds to the already rich family of molybdenum trioxide hydrates. These include the yellow monoclinic dihydrate, two monohydrates, yellow monoclinic $MoO_3{\cdot}H_2O$ and white triclinic $MoO_3{\cdot}H_2O$, and a white hemihydrate. All of these previously known hydrates, with the exception of the yellow monohydrate, were prepared by very slow precipitation from nitric acid solution. The yellow monohydrate is prepared by controlled thermal decomposition of the yellow dihydrate. Here we report rapid entry to a new dihydrate through codeposition.

**$MoO_3$ Condensed with THF.** Cocondensation of molybdenum trioxide with THF yielded a gray-green amorphous solid. The presence of THF in the cocondensate is shown by the IR absorptions at 2976 and 2877 $cm^{-1}$ (C–H stretch) and 1460 $cm^{-1}$ (C–H bend). These absorptions are unchanged from the absorptions in free THF. The shift of the absorption for the C–O–C stretch (1070 $cm^{-1}$ in free THF) to 1023 $cm^{-1}$ indicates the THF is bound through oxygen to the molybdenum.

The $^1H$ NMR spectrum of a filtered $D_2O$ solution of the THF cocondensate showed only resonances for THF. The percent THF observed in the $^1H$ NMR spectrum was consistent with the THF cocondensate analysis by TGA, which is discussed below.

This interaction of the THF oxygen with molybdenum is expected, as it would be the first step in hydrodeoxygenation (HDO). Furimsky[23] studied the HDO of THF by using supported commercial $MoO_3$ and CoO on alumina catalyst under hydrogen in a flow reactor at 400 °C. He observed THF conversion to a mixture of water and hydrocarbon products including propene, 1-butene, *cis*- and *trans*-2-butenes, butadiene, and butane. Furimsky did not observe any organic oxygen containing products such as furan. He suggested that under his reaction conditions, with heating in hydrogen, HDO of THF dominates over its dehydrogenation.

The THF cocondensate was heated in a stream of oxygen, with an exothermic transition occurring at 130 °C. Water and THF in a mole ratio of 20:1 were recovered along with traces of propene, butadiene, acetaldehyde, acetone, and furan. The presence of the organic oxygen-containing products such as furan, along with the absence of any saturated hydrocarbons, suggests that under these reaction conditions, with heating in oxygen, dehydrogenation of THF dominates over its HDO.

The TGA curve for the THF cocondensate is shown in Figure 4. The overall weight loss from 20 to 500 °C corresponds to 0.57 mol of THF/mol of $MoO_3$. There are two transition temperatures. The first transition occurs at 130 °C, and as discussed above, the primary products were THF and water, with trace amounts of propene, butadiene, acetaldehyde, acetone, and furan. The second transition occurs at 380 °C with $CO_2$ and water as the products.

**$[MoO(O_2)_2(H_2O)_2]{\cdot}$18-crown-6$\cdot H_2O$ (3).** To a slurry of the THF cocondensate in dry THF under argon was added the minimum water needed to give a clear green solution. This green solution slowly turns blue in the absence of oxygen at room temperature. However upon exposure to oxygen and light the green solution turns yellow. Attempts to obtain crystals from the yellow solution were unsuccessful until 18-crown-6 was added as a precipitating agent. Initially the addition of 18-crown-6 appeared to be unsuccessful, but after 3 weeks X-ray quality crystals of **3** were obtained. The X-ray structure analysis unexpectedly showed the presence of a seven-coordinate diperoxomolybdenum moiety.[24] The molybdenum atom is surrounded by two peroxo ligands and a water molecule forming the equatorial plane of a distorted pentagonal bipyramid. Another water molecule and an oxide ligand form the apices of the bipyramid. The 18-crown-6 molecule is held by hydrogen bonds between the oxygen atoms on the ether ring and water molecules. The apical water is hydrogen bonded to two oxygen atoms of the ether ring, as is a "free" water molecule sitting above the crown ether. The equatorial water molecule is hydrogen bonded to one of the oxygens on the 18-crown-6 ring and to the "free" water molecule on another molecule of **3**.

The initial synthesis of **3** did not include a strong oxidizing agent, so the presence of the peroxide ligands was not anticipated. Because the direct activation of dioxygen molecules by molybdenum centers has not been reported and THF is known to readily form peroxides in the presence of oxygen, $\alpha$-hydroperoxytetrahydrofuran was suspected as the source of the peroxo ligands. Further evidence for involvement of $\alpha$-hydroperoxytetrahydrofuran was the amount of time (more than 3 weeks) required to obtain **3**. Therefore a solution containing 6.4% $\alpha$-hydroperoxytetrahydrofuran was added to the THF cocondensate. A yellow solution was obtained to which addition of 18-crown-6 caused immediate precipitation of **3**, confirming the role of $\alpha$-hydroperoxytetrahydrofuran.

**3** could not be obtained from peroxide-free yellow solutions of the THF cocondensate in THF. Addition of 18-crown-6 caused immediate precipitation of a yellow-green compound, which gave a negative permanganate test for peroxo ligands. **3** was also not obtained when *tert*-butylhydroperoxide was substituted for $\alpha$-

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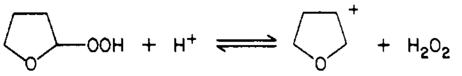
hydroperoxytetrahydrofuran. Again a yellow-green compound was obtained, which did not contain peroxides. However, addition of 30% $H_2O_2$ to a slurry of the THF cocondensate in THF again yielded a yellow solution to which addition of 18-crown-6 caused immediate precipitation of **3**.

The above results suggest the following interpretation. $MoO_3$ behaves as a free radical initiator for THF, leading to formation of $\alpha$-hydroperoxytetrahydrofuran in the presence of $O_2$. Because these solutions are acidic, pH ca. 2, the tetrahydrofuran-substituted peroxide is in equilibrium with $H_2O_2$ as shown in eq 6. The peroxo


(6)

ligand addition to the Mo then occurs through the reaction of the $H_2O_2$ with the molybdenum oxide species in solution.

The counterpart to eq 6 for *tert*-butylhydroperoxide is eq 7.

$$(CH_3)_3COOH + H^+ \rightleftharpoons (CH_3)_3C^+ + H_2O_2 \qquad (7)$$

That **3** does not occur upon the addition of *tert*-butylhydroperoxide implies the equilibrium for eq 7 must lie far to the left under our reaction conditions. This is apparently due to the instability of the *tert*-butyl cation under these conditions. Therefore in this case, without in situ $H_2O_2$ formation, **3** is not observed.

While the synthesis of a number of diperoxomolybdenum(VI) complexes have been reported by reacting oxomolybdenum(VI) complexes with $H_2O_2$,[25] we are aware of only one report of a diperoxomolybdenum(VI) complex synthesized without the addition of $H_2O_2$. This is the formation of diperoxo(tetraphenylporphinato)molybdenum(VI), $(O_2)_2Mo(TPP)$, from the reaction of *cis*-dioxo(tetraphenylporphinato)molybdenum(VI), $O_2Mo(TPP)$, with 2-propanol recently reported by Ledon, et al.[26] In his report, Ledon proposes that $O_2Mo(TPP)$ abstracts a hydrogen atom from the alcohol to form a free radical. The alcohol free radical interacts with dioxygen to form the alkylperoxide, which is in equilibrium with $H_2O_2$. Again, in situ $H_2O_2$ formation leads to a Mo peroxo complex.

**Acknowledgment.** The authors thank Robert Brown at the Albany Bureau of Mines for his assistance with the thermogravimetric analyses and Robert McCune at the Albany Bureau of Mines for his assistance with the X-ray powder diffraction analyses. Thanks are extended to Dr. A. B. Anderson for providing a copy of ref 16 prior to publication.

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# Reactions of Gold(I) Compounds with Carbon Monoxide To Form Gold Clusters and Fulminates

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*Received April 2, 1985*

Au(I) compounds of the type $AuPPh_3X$, where X is a weak coordinated ligand like $NO_3^-$, $ClO_4^-$, $BF_4^-$, or $OAc^-$, react with carbon monoxide to form gold clusters of the type $Au_9(PPh_3)_8X_3$. The carbon monoxide is transformed to $CO_2$, probably via initial binding to gold. A precursor of the gold clusters could be detected in a $AuPPh_3NO_3$ matrix. When $CH_2Cl_2$ is used as a solvent, carbon monoxide and $AuPPh_3NO_3$ or $Au_9(PPh_3)_8{}^{3+}$ give a complicated reaction resulting in the formation of fulminates. In this way $AuPPh_3CNO$ and $Au_{11}(PPh_3)_8(CNO)_2{}^+$ are synthesized. Key in the formation of fulminate is the reaction of a reactive intermediate, probably $AuPPh_3NO$, with $CH_2Cl_2$. $^{13}$CO-labeling experiments confirm the origin of the carbon in the fulminate to be $CH_2Cl_2$.

## Introduction

Recently we described reactions of isocyanides with gold clusters, resulting in the synthesis of $Au_9(PPh_3)_6(i\text{-}PrNC)_2{}^{3+}$, the first gold cluster containing isocyanide ligands.[1] Since carbon monoxide and isocyanide are quite similar electronically, we decided to investigate reactions of gold(I) compounds and gold clusters with CO.

Only two gold–CO compounds are known today, Au(CO)Cl[2] and $Au_2(CO)Cl_4$,[3] but they are unstable in the presence of moisture even at room temperature. As this paper will show, weak coordination of CO to gold is responsible for the rapid reduction of gold compounds to gold clusters. Gold clusters are normally synthesized by using $NaBH_4$ as reducing agent[4] or by means of gold evaporation into a phosphine solution.[5] The introduction of CO as a reducing agent is very interesting in this respect, since CO has been shown to be very mild and selective.

During reduction experiments with CO we discovered the formation of gold–fulminato (Au–CNO) compounds. The formation of the fulminate is due to a complicated reaction involving $CH_2Cl_2$, which was used as solvent. Gold fulminate compounds are very rare. Two types are known, namely the bis(fulminato) complex $Au(CNO)_2{}^-$[6,7] and its oxidized form $Au(CNO)_2X_2{}^-$ (X = Br, I).[8] $Na[Au(CNO)_2]$ is obtained by reacting $AuCl_3$ with ethanol and nitric acid, analogous to the preparation of mercury fulminates.

## Experimental Section

**Instrumentation.** C, H, and N analyses were carried out in the microanalytical department of the University of Nijmegen. The other analyses were measured by Dr. A. Bernhardt, Elbach über Engelskirchen, West Germany. Molecular weights were determined by using a Knauer

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