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Thermal desorption of dimethyl methylphosphonate from MoO₃

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Thermal desorption of dimethyl methylphosphonate from MoO₃

Organophosphonates are used as chemical warfare agents, pesticides, and corrosion inhibitors. New materials for the sorption, detection, and decomposition of these compounds are urgently needed. To facilitate materials and application innovation, a better understanding of the interactions between organophosphonates and surfaces is required. To this end, we have used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to investigate the adsorption geometry of dimethyl methylphosphonate (DMMP) on MoO₃, a material used in chemical warfare agent filtration devices. We further applied ambient pressure X-ray photoelectron spectroscopy (APXPS) and temperature programmed desorption (TPD) to study the adsorption and desorption of DMMP. While DMMP adsorbs intact on MoO₃, desorption depends on coverage and partial pressure. At low coverages under UHV conditions, the intact adsorption is reversible. Decomposition occurs with higher coverages, as evidenced by PCH_x and PO_x decomposition products on the MoO₃ surface. Heating under mTorr partial pressures of DMMP results in product accumulation.

Keywords: ambient pressure X-ray photoelectron spectroscopy; chemical warfare agent simulant; surface science; diffuse reflectance infrared Fourier transform spectroscopy; organophosphonate; temperature programmed desorption

Introduction

Organophosphonates are used as pesticides, corrosion inhibitors, and chemical warfare agents, and their chemistry has consequently been widely studied.¹ In applications, such as decontamination,² sensing,¹ personnel protection,³ and decomposition,¹ metal oxides are frequently used. Undercoordinated metal atoms and hydroxyl groups are the common surface binding sites for the phosphoryl moiety of DMMP.¹ The most stable (010) surface of MoO₃ is oxygen-terminated with no inherent undercoordinated Mo atoms on the surface⁴ and does not easily hydroxylate; thus, this surface contrasts with those previously studied.^{1,5} Here, we continue our previous investigations of the adsorption of dimethyl methylphosphonate (DMMP), a common chemical warfare agent simulant, on

polycrystalline MoO₃.⁶ Our past studies with ambient pressure X-ray photoelectron spectroscopy (APXPS) and density functional theory found evidence for weak, intact adsorption on pristine MoO₃ surfaces at room temperature, while decomposition to methanol upon adsorption was observed for hydroxylated surfaces. In both cases the molecular coverage depended on the DMMP partial pressure.

The current work continues this study by presenting more evidence for intact adsorption using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), a technique that has been used to characterize interactions between DMMP and various other metal oxides.⁷⁻⁹ The DRIFTS experiments are supported by APXPS measurements in which we determine the effect of DMMP pressure and coverage on thermal desorption, focusing on three conditions: (i) after a 4 Langmuir (L, 1×10^{-6} Torr for 1 s) dose of DMMP, (ii) under 10 mTorr of DMMP, and (iii) after extended exposure to 10 mTorr of DMMP. The XPS study of a 4 L dose of DMMP (i) is compared with temperature programmed desorption (TPD). This experimental condition is representative of measurements under traditional surface science conditions where the pressure in the analysis chamber remains below 10^{-8} Torr, and in this case, intact desorption was largely seen. When heating with higher coverages of DMMP under both 10 mTorr (ii) and 10^{-5} Torr (iii), more decomposition products are observed on the surface, including PO_x and PCH_x, but heating under the higher pressure condition results in accumulation of these products on the MoO₃ surface.

Experimental

Diffuse reflectance infrared Fourier transform spectroscopy

MoO₃ nanoparticles (99.94+%, 13-80 nm) were purchased from US Research Nanomaterials, Inc. and mixed with KBr (10% w/w MoO₃) using a mortar and pestle.

The resulting powder was dried in an oven (387 K) and stored in a desiccator until use in DRIFTS experiments. DMMP was purchased from Sigma-Aldrich and used as received. A Harrick Scientific Praying Mantis DRA optical accessory was used with an associated Harrick Scientific high temperature reaction chamber HVC-DRP-5 for the DRIFTS measurements. Before DMMP exposure, MoO₃/KBr powder was loosely packed in an environmental DRIFTS cell and heated to 673 K in 20 mL/min of flowing O₂ for 2 hrs. This step was taken to ensure the mixture was dehydrated and fill oxygen vacancies on the surface of the MoO₃ nanoparticles. The mixture was then cooled to room temperature and the DMMP exposure was performed using a saturator cell, described elsewhere,^{10,11} with argon as the carrier gas. A flow rate of 20 mL/min was used with an estimated DMMP concentration of 90 ppm. IR spectra were collected at 4 cm⁻¹ resolution on a Nicolet iS-50R spectrometer equipped with a liquid N₂ cooled MCT-A detector in 5 min intervals; spectra were averaged over the first minute (100 scans) followed by a 4 min delay.

Ambient pressure X-ray photoelectron spectroscopy

The photoemission spectra were collected at the APXPS end station¹² of beamline 11.0.2¹³ at the Advanced Light Source at Lawrence Berkeley National Laboratory. The preparation and analysis chambers had base pressures better than 5 x 10⁻⁹ Torr. A 0.2 mm diameter aperture in the analysis chamber leads to the differentially pumped electrostatic lens system¹⁴ of the hemispherical electron energy analyser (Phoibos 150, SPECS Surface Nanoanalysis GmbH) that allows for measurements at pressures of up to several Torr in the analysis chamber.

The MoO₃ samples were prepared by cleaning a Mo foil (99.95% Alpha Aesar) via a sputter (1 x 10⁻⁵ Torr Ar⁺, 1.5 keV, 5 mA emission current, 10 min) and anneal cycle (10 min at 1173 K). To oxidize, the foil was heated to 690 K for 10 min followed by

cooling to 373 K in 35 Torr of O₂. DMMP (>97%, Fluka) was degassed by freeze-pump-thaw cycles and introduced into the analysis chamber via a precision leak valve.

The photon energies were selected such that electrons around 200 eV kinetic energy were analyzed, thus providing the same analyzer sensitivity, gas phase attenuation, and similar probing depths for all elements. The photon energies used were 340 eV for P 2p, 435 eV for Mo 3d, 490 eV for C 1s, and 735 for O 1s. The combined beamline and electron energy analyser resolution was better than 350 meV. The interaction of the photon beam with the sample can cause changes to the spectra of MoO₃¹⁵ and DMMP (*i.e.*, beam damage), as we have characterized previously.⁶ Continually changing the irradiated sample area minimized photon beam exposure and the spectra reported here are free from photon-induced damage. During the temperature-dependent measurements, a sufficient amount of time passed until no changes in the spectra were seen (*i.e.*, steady-state conditions). The binding energy in all spectra was calibrated to the Mo 3d_{5/2} peak at 232.5 eV.⁴ A polynomial background was subtracted from all spectra except Mo 3d, where no background was removed. The surface components of the spectra were fit with Voigt functions. Gas phase components were constrained to asymmetric Gaussian functions from fits of the gas phase molecule. The P 2p spin-orbit components were constrained to a binding energy splitting of 0.85 eV, the same full widths at half maximum, and an area ratio of 2:1 for the 2p_{3/2} and 2p_{1/2} components.¹⁶

Temperature programmed desorption

The TPD experiment of DMMP on a MoO₃ thin film was conducted in a UHV chamber with a base pressure of 1 x 10⁻⁹ Torr. The sample was mounted across two copper rods through tantalum clips. To prepare the MoO₃ thin film, the molybdenum foil (99.95% Alpha Aesar) was oxidized under an O₂ pressure of 4 Torr at 673 K for 10 minutes. The oxidation state of molybdenum in the film was confirmed by XPS. Before a TPD

experiment, 4 L of DMMP (degassed by freeze-pump-thaw cycles) were dosed through a leak valve onto the sample at 298 K. Afterwards, the sample was cooled to 170 K to ensure a flat baseline for the desorption spectra. The temperature was then ramped at a rate of 2 K s⁻¹ by passing a DC current through the sample while simultaneously monitoring desorption products by a Hiden 3F/PIC quadrupole mass spectrometer.

Results

DRIFTS data

Our previous studies suggested that DMMP adsorbs largely intact on polycrystalline MoO₃ through an interaction between the phosphoryl oxygen and the terminal oxygen atoms or hydroxyl groups of the molybdenum oxide surface.⁶ To further investigate binding of DMMP on MoO₃, a DRIFTS spectrum of MoO₃ nanoparticles exposed to a stream of DMMP vapor is compared to a spectrum of liquid DMMP (Figure 1). The peaks are assigned according to reference values reported in the literature.⁹ Since surface defects and hydroxylation promote DMMP decomposition, the small band at 971 cm⁻¹ (Figure 1b) suggests the O₂ pre-treatment did not completely remove these sites. However, the similarity in the C–H stretch region of the IR spectra (Figure 1a) indicates that most of the surface-adsorbed DMMP molecules remain intact. Upon adsorption, we observed a large redshift in the P=O stretch (1185 cm⁻¹) with respect to liquid phase DMMP (1244 cm⁻¹), indicating that this group is strongly interacting with MoO₃, similar to what has been reported for DMMP adsorbed on MgO and La₂O₃.⁹ Also, the OCH₃ symmetric stretch (1035 cm⁻¹) of surface-adsorbed DMMP lies between the gas (1050 cm⁻¹) and liquid (1032 cm⁻¹) phase positions, indicating these groups interact with the MoO₃ surface, albeit weaker than the P=O group.

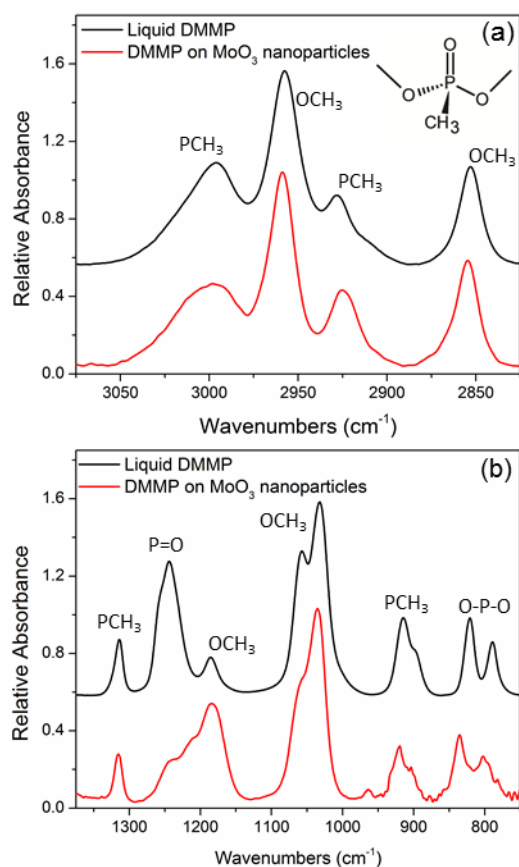


Figure 1. DRIFTS spectra of liquid DMMP (black) and MoO₃ nanoparticles exposed to DMMP (red) in the (a) high and (b) low wavenumber regions. The inset in (a) shows the chemical structure of DMMP.

Low DMMP coverage – heating in vacuum

To probe the surface species during the desorption process, photoemission spectra were collected at increasing temperatures after dosing 4 L of DMMP at 289 K (4×10^{-8} Torr for 100 s). The background pressure after dosing was 2×10^{-9} Torr. The C 1s photoemission spectra in Figure 2a show two peaks: a methyl peak at 284.5 eV and a methoxy peak at 286.2 eV. The spin-orbit splitting of the P 2p peak is apparent in the spectrum at 289 K in Figure 2b, and only one P-containing surface species is present. This spectrum, combined with a methoxy-to-methyl peak area ratio of 2:1 (reflecting the number of functional groups in the intact molecule) is consistent with intact adsorption. Upon heating, the intensities of both the P 2p and C 1s spectra decrease. A small, low-

binding energy shoulder appears in the P 2p spectrum at 323 K and increases in intensity until 423 K. While about 10% of the original amount of P remains at this temperature, all carbon has been removed from the surface within the detection limit.

A gradual decrease in the DMMP components of the O 1s spectra upon heating is also seen in Figure 3a. The O 1s binding energy of the methoxy group is about 532.8 eV. The appearance of the phosphoryl group overlaps with a feature corresponding to a small amount of hydroxyl groups on the surface (~10% of a monolayer, ML). A DMMP coverage of ~15% of a ML is calculated from the intensities of the molecular and oxide components, described previously.^{6,17} At 373 K the O 1s spectrum becomes identical to that of pristine MoO₃. Figure 3b shows the Mo 3d spectra, with a small amount of Mo⁵⁺ indicated by the low binding energy shoulder at ~231.3 eV; we have assigned this peak to surface defects and possibly a lower oxidation state Magnéli phase resulting from our preparation method.⁶ No changes are seen in the Mo 3d spectrum after DMMP dosing and heating.

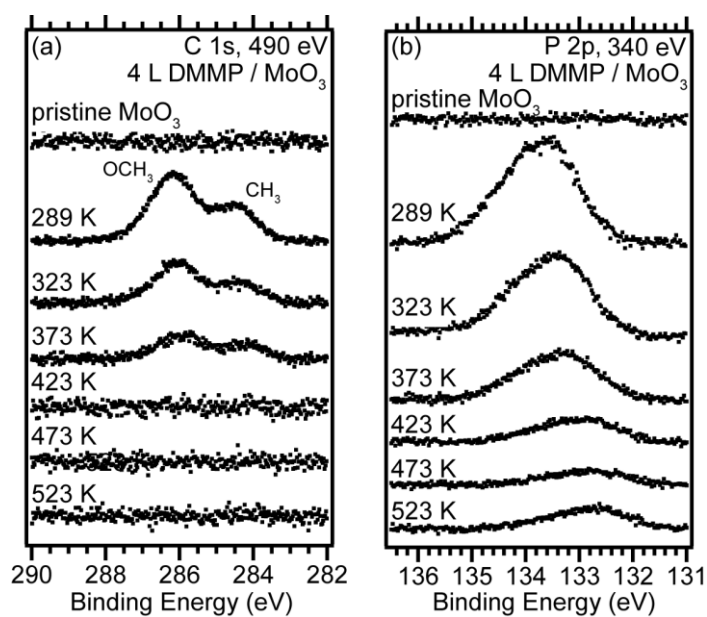


Figure 2. (a) C 1s spectra and (b) P 2p spectra of pristine MoO₃, after exposure to 4 L DMMP, and while subsequently heating at the temperatures listed.

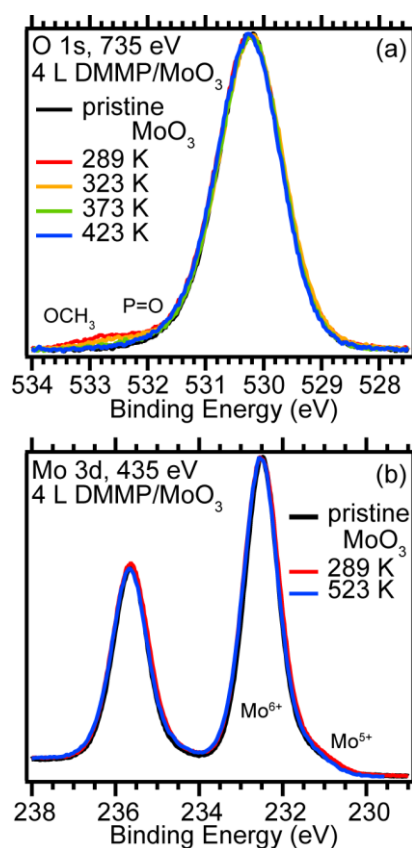


Figure 3. (a) O 1s and (b) Mo 3d spectra of pristine MoO₃, after dosing 4 L of DMMP, and while subsequently heating at the temperatures listed. The spectra are normalized to their maximum intensities.

The gas phase species formed during the heating of a 4 L dose DMMP adsorbed on MoO₃ were studied using TPD. Several DMMP fragments and likely products were monitored, and the results are plotted in Figure 4. The parent ion (124 amu) and another characteristic fragment (79 amu, either PO₃⁺ or PO₂CH₄⁺)^{18,19} of DMMP show that desorption begins just below 250 K and has a maximum around room temperature, suggesting that DMMP does not strongly adsorb to MoO₃. These mass spectrometry signals reach baseline levels again at around 450 K. Signals from methyl (15 amu) and methoxy (31 amu), follow the same trend as the parent ion, suggesting no decomposition. There is no signal from common decomposition products seen in other DMMP decomposition studies, such as methanol (32 amu),²⁰ dimethyl ether (46 amu),^{21,22} methane (16 amu)^{20,21} or H₂,^{20,21} strongly implying intact desorption under these conditions.

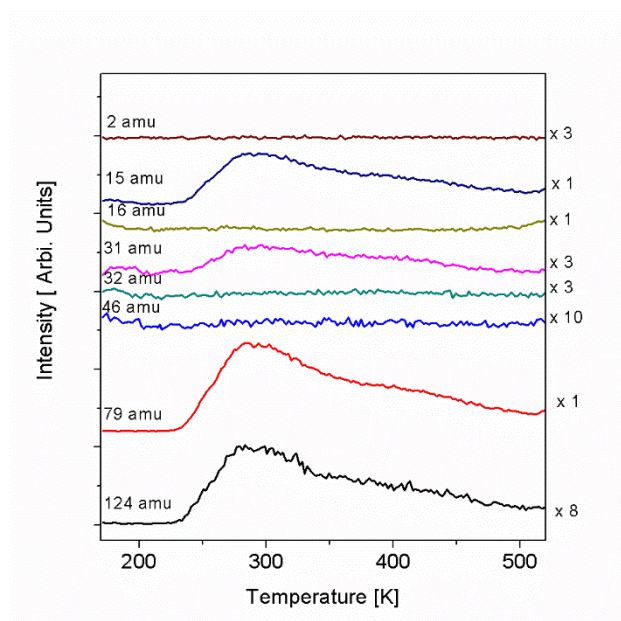


Figure 4. TPD results of 4 L DMMP dosed on MoO₃ at room temperature, cooled to 170 K, and heated with a ramp rate of 2 K s⁻¹.

High DMMP coverage – Heating in 10 mTorr DMMP

To determine how a constant pressure of DMMP and a larger surface coverage affects the surface species during heating, another MoO₃ sample was heated in 10 mTorr of DMMP; the C 1s and P 2p spectra of this study are shown in Figures 5a and 5b, respectively. The intense methoxy peak in the O 1s spectrum in Figure 6a indicates a large coverage (~75% ML). Gas phase peaks contribute to the C 1s, P 2p, and O 1s spectra at slightly higher binding energies than the surface species; these components and the surface species are fit in the room temperature C 1s and P 2p spectra in Figures 6a and 6b, respectively. With increasing temperature, the density of the gas phase molecules in front of the sample decreases; therefore, this contribution decreases until it is undetectable at 423 K.²³ Above 295 K, the large line-width of the surface P 2p peaks combined with their overlap of gas phase components complicates the deconvolution of the P 2p spectra, and fits are not attempted. However, qualitative interpretation of the spectra indicate multiple P species upon heating.

Similar to the case of heating in vacuum, the intensity of the C 1s and P 2p components initially decreases when heated in 10 mTorr of DMMP background vapor (Figure 5). However, methoxy carbon remains on the surface, and the methyl component decreases in binding energy and is assigned as PCH_x. The broad P 2p spectra in Figure 6b show significantly more PO_x at the surface, even at 573 K; PCH_x could contribute to the P 2p peak broadening. Phosphorus-containing species appear to accumulate, as indicated by the intensity increase between 523 K and 573 K. Changes in the substrate are also apparent in the APXPS data. The main peak in the O 1s spectra (see Figure 6a) after heating has broadened towards the higher binding energy side. The Mo⁵⁺ shoulder in the Mo 3d spectrum has become more a more prominent at 573 K, seen in Figure 6b.

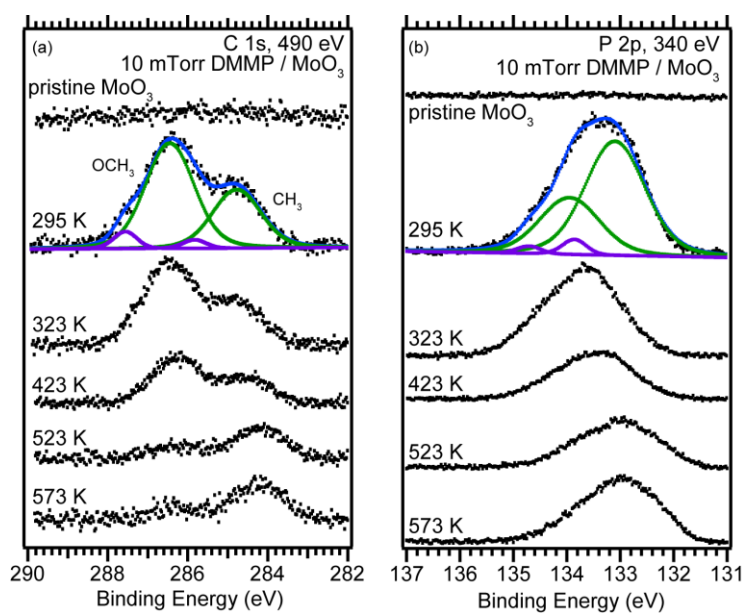


Figure 5. (a) The C 1s and (b) P 2p spectra of MoO₃ collected under a pressure of 10 mTorr DMMP at room temperature and the temperatures listed. Black dots are the data points, the blue line is a fit of surface (green) and gas phase (purple) components of DMMP.

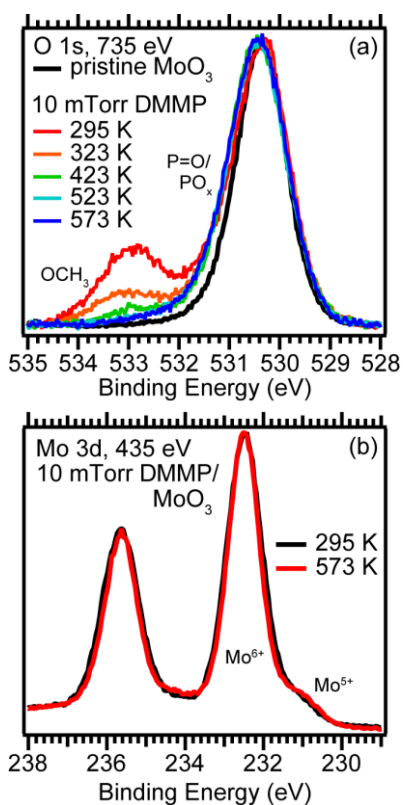


Figure 6. (a) O 1s and (b) Mo 3d spectra of pristine MoO₃ (black) and during exposure to 10 mTorr DMMP at the temperatures listed. All spectra are normalized to their maximum intensities.

High DMMP coverage – Heating in background DMMP pressure

The increase in the amount of decomposition products when heating under a constant pressure of DMMP could be a result of either the initially higher surface coverage or heating in the presence of DMMP vapor. To distinguish between these two options, a MoO₃ film was exposed to 10 mTorr of DMMP at room temperature for at least 3 hours. The chamber was then evacuated to 1 x 10⁻⁵ Torr, the lowest attainable pressure after pumping for one hour due to the high sticking coefficient of DMMP to the analysis chamber. Carbon remains on the surface at 473 K (see Figure 7a), though there appears to be slightly more methoxy than when heating in 10 mTorr of DMMP. Figure 7b shows PO_x and possibly also PCH_x, but in contrast to heating under 10 mTorr of DMMP, there is no significant accumulation of these species with increasing temperature, despite similar time scales of heating.

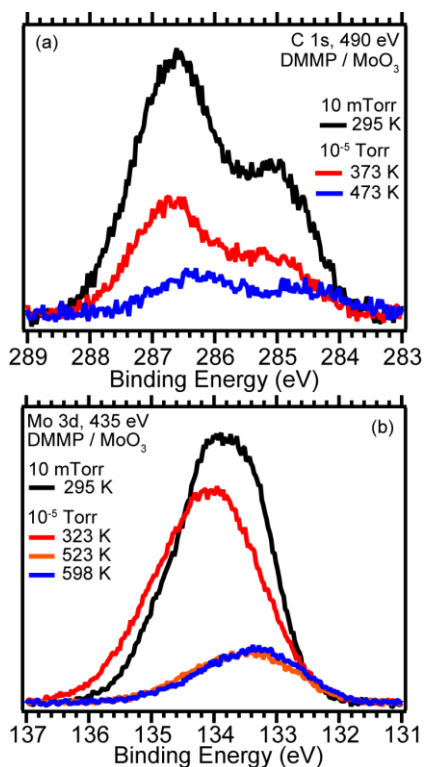


Figure 7. (a) C 1s and (b) P 2p of DMMP on MoO₃ under 10 mTorr of DMMP at 295 K and while heating to the temperatures listed at a background DMMP pressure of 1 x 10⁻⁵ Torr.

Discussion

The DRIFTS results in Figure 1 support our previous suggestion of intact adsorption of DMMP on MoO₃ through the phosphoryl oxygen atom,⁶ as indicated by the red shift in the P=O peak. The studies of the thermally-induced desorption of DMMP presented here further support the notion of weak adsorption at room temperature. The lack of decomposition products in the TPD measurements and the gradual intensity decrease in the P 2p and C 1s XPS results (see Figure 2) suggest that DMMP desorbs intact when heating in vacuum, with complete removal of all carbonaceous components at 423 K. About 10 % of the original P remains on the surface as PO_x; this species begins to form at 323 K and is often seen in studies of DMMP decomposition on metal oxides.^{18,21,20,21} The lack of a resolvable corresponding O 1s component is reasonable considering the small amount of PO_x compared to the bulk oxygen.

In traditional UHV surface science techniques, molecules are commonly dosed at low pressures to study adsorption properties under as clean as possible conditions. While such studies are essential in understanding basic interactions of molecules and surfaces, there is a pressure gap in comparing UHV studies with the reactivity of molecules on surfaces under ambient conditions. Since there is a pressure dependence on the surface coverage, we have studied the desorption process 10 mTorr DMMP, ~10% of the vapor pressure at room temperature.

Mirroring the UHV study, gradual desorption of intact DMMP occurs while heating the MoO₃ under a constant pressure of 10 mTorr of DMMP. More decomposition products are seen in all the photoemission spectra, in contrast to the lower coverage/vacuum study. Above 423 K, a significant amount of methyl groups remain on the surface, most likely as PCH_x, similar to what was observed in previous studies of DMMP on CeO₂.²¹ The presence of Mo-CH_x species is unlikely because Mo-C species

have much lower binding energies, around the range of 282.7 eV²⁴ to 283.2 eV.²⁵ A small amount of methoxy lingers, though it is unclear if this peak is from surface methoxy groups or methoxy-P species. The peak at ~132.5 eV in the P spectra (Figure 5b) at temperatures of 523 K and above indicates PO_x.^{21,21} Significantly more PO_x results in a peak on the high binding energy side of the O 1s spectra in Figure 6a, matching previous results of decomposed DMMP on CeO₂.²¹ Overall, the higher DMMP coverage resulted in more products and their accumulation upon heating in 10 mTorr of DMMP. This could be due to reactions between the adsorbed DMMP molecules. Heating initially high coverages of DMMP on MoO₃ in 10⁻⁵ Torr (*i.e.*, 4 orders of magnitude lower than in the case of heating in 10 mTorr DMMP), results in less accumulation of these decomposition products at high temperatures.

DMMP has been found to adsorb onto several metal oxides, including Al₂O₃,^{5,9,26,27} Fe₂O₃,⁹ MgO,^{5,9} ZnO,⁵ La₂O₃,⁹ SiO₂,^{28,29} TiO₂,^{5,21} CeO₂,^{7,21} and WO₃.⁵ Of these, intact adsorption at room temperature occurs on TiO₂,²¹ CeO₂,²¹ and SiO₂.^{28,29} While intact desorption is observed on SiO₂,²⁸ decomposition is more extensive on TiO₂²¹ and CeO₂²¹ when heating in vacuum after exposure to a saturating dose of DMMP. On TiO₂, H₂, and CH₄ have been detected using TPD, and PO_x and PCH_x decomposition products were observed by XPS.²¹ More extensive decomposition on CeO₂ films results in desorption of methanol, formaldehyde, water, H₂, and CO, and the accumulation of PO_x, PCH_x, and CeOCH₃.²¹ Coverage estimates in these studies are not given but dosing was performed using an inlet directly in front of the sample with a pressure in the chamber of 3 x 10⁻¹⁰ Torr for 3 min,^{21,21} though the local pressure at the surface was most likely higher. The stronger adsorption and decomposition seen on these surfaces maybe due to under-coordinated metal sites. MoO₃ (010) lacks these sites and is considered relatively chemically inert, but structural defects are proposed to be catalytic sites.³⁰ The Mo⁵⁺ sites

in the polycrystalline sample here may play a role here as evidenced by the shift in the Mo⁵⁺ component of the Mo 3d spectra when heating in under a pressure of DMMP.

Conclusions

The DRIFTS results presented in this study are consistent with our previous observations of intact adsorption of DMMP on MoO₃. The reversible binding of DMMP seen by TPD and XPS while heating under vacuum conditions complements the DRIFTS data by suggesting the interaction between DMMP and the MoO₃ surface is weak. Higher coverages of DMMP on MoO₃ result in more decomposition, both at 10 mTorr and at 10⁻⁵ Torr DMMP partial pressures. At the higher pressure condition, PO_x and PCH_x decomposition products accumulate on the surface due to constant adsorption and decomposition of DMMP from the gas phase.

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