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An Infrared Study of Adsorbed Organophosphonates on Silica: A Prefiltering Strategy for the Detection of Nerve Agents on Metal Oxide Sensors

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The gas-phase adsorption of the nerve gas simulant dimethyl methylphosphonate (DMMP) along with trimethyl phosphate (TMP), methyl dichlorophosphate (MDCP), and trichlorophosphate (TCP) on silica have been studied using infrared spectroscopy. Each phosphonate compound adsorbs through a different number of H-bonds of the methoxy and P=O moieties with the surface hydroxyl groups on silica. The strength of the adsorption depends on the number and type of the H-bonds and follows the order TCP < MDCP < DMMP < TMP. TCP is completely removed from silica by evacuation at room temperature, adsorbed MDCP is removed by evacuation at 150 °C, DMMP requires an evacuation temperature of 300 °C, and TMP is eliminated at 400 °C. All phosphonate compounds molecularly desorb, and the silica returns to its original state. The differences in the reactivity of phosphonate compounds on silica from other oxides demonstrate the potential use of silica in prefiltering/preconcentrating strategies for semiconductive metal oxide based sensing devices. Specifically, it is shown that silica can be used to selectively adsorb DMMP from a gas stream containing methanol/DMMP mixtures.

1. Introduction

Dimethyl methyl phosphonate (DMMP) is the most commonly used simulant molecule for toxic nerve agents such as sarin in the development and testing of semiconducting metal oxide (SMO) based sensors. Owing to its importance to sensor development, there have been several studies aimed at obtaining a basic understanding of the underlying chemical reactions occurring between adsorbed organophosphonate compounds and metal oxide surfaces.^{1–11} While SMO based sensors have demonstrated high sensitivity in detecting low levels of gaseous phosphonate compounds, the main technical hurdle continues to be a lack of selectivity in the detection of a specific target molecule among an array of interferent molecules. Detection selectivity in SMO based sensors would clearly benefit from the use of prefiltering or preconcentration strategies that lead to a reduction in the number of possible interferent molecules in a gas stream.

The necessity for the prefiltering strategy to improve the sensor selectivity has prompted us to investigate the reaction of DMMP and other phosphonate compounds on silica. Our interest in silica as a material for prefiltering is based on the observation that it is the only known oxide in which DMMP molecularly desorbs without decomposition at elevated temperatures.¹¹ It is noted that silica is not a semiconductive metal oxide and therefore would solely be used in a filtering capacity. The gas stream would pass through the silica before coming in contact with a SMO based sensor element.

Little is known about the molecular interactions of DMMP with the silica surface. To the best of our knowledge there is a single Auger electron spectroscopy (AES) and thermal programmed desorption (TPD) study in which it was shown that DMMP completely desorbs from silica at 300 °C.¹¹ This contrasts to the behavior observed for adsorbed DMMP on MgO,^{1,12,13} ZnO,¹³ Al₂O₃,^{1,13,14} TiO₂,^{13–15} and La₂O₃.¹ On these oxides, the adsorption of DMMP at room temperature proceeds through a surface bond with the P=O group. Evacuation at elevated temperature gives rise to the sequential elimination of the methoxy groups, leaving a stable methyl phosphate attached to the surface. On iron oxide surfaces,^{1,11,16,17} the DMMP also adsorbs through the P=O bond at room temperature, but in this case, there is elimination of both the methoxy and methyl groups attached to the phosphorus atom with evacuation at 300 °C.¹ A phosphate species remains attached to the surface instead of the methyl phosphate obtained on oxides such as Al₂O₃, TiO₂, and MgO. Both the phosphate on iron oxide and the methyl phosphate on other oxides remain intact on the oxide surface with calcination at 400 °C.^{1,13,14}

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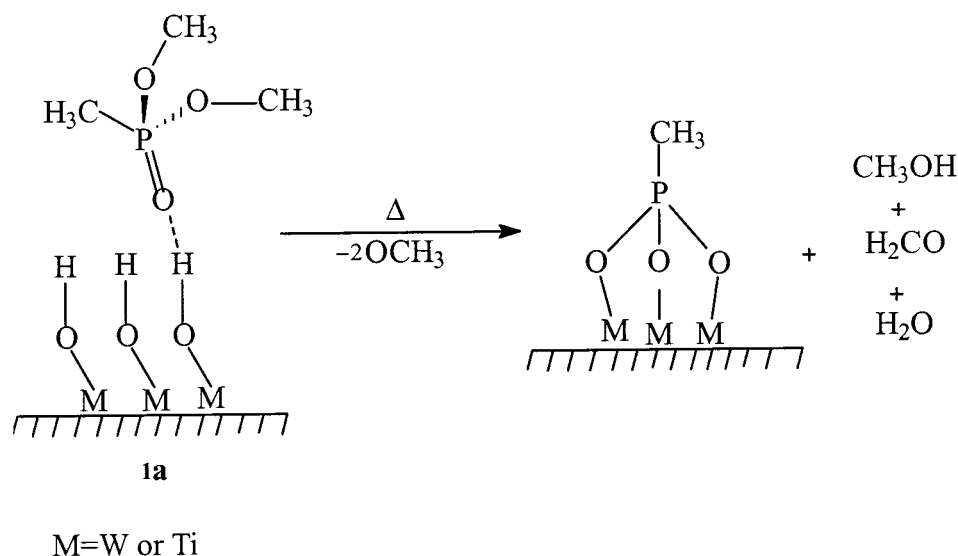
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Scheme 1



An understanding of the adsorption behavior of DMMP on WO_3 has garnered recent attention because of the importance of this oxide in chemiresistive based sensors.^{13,15,18} In a recent infrared study, it was shown that the adsorption/desorption characteristics of DMMP on WO_3 (depicted in Scheme 1) are similar to that obtained for Al_2O_3 and TiO_2 .¹⁵

In brief, DMMP adsorbs through a H-bond between the surface hydroxyl groups and the P=O functionality (see structure 1a), and evacuation at elevated temperature leads to sequential elimination of the methoxy groups, leaving behind a stable methyl phosphate attached to the surface. In related work¹⁸ it has been shown that the WO_3 sensor response to the initial adsorption of DMMP is small compared to the redox reaction with the surface that occurs with methoxy elimination or with methanol formed as a product of DMMP decomposition at elevated temperatures. This study also highlighted the selectivity issue as it was shown that the sensor response for methanol is difficult to discern from that of DMMP. Therefore, the detection selectivity of methoxylated organophosphorus compounds on WO_3 based sensors would benefit from a method that separates or distinguishes these compounds from potential interferences such as methanol.

In this paper, we use infrared spectroscopy to study the adsorption of DMMP and DMMP/methanol mixtures on silica with the aim of better understanding the adsorption behavior related to filtering capabilities. The adsorption of three DMMP analogues, trimethyl phosphate (TMP), methyl dichlorophosphate (MDCP), and trichlorophosphate (TCP), is included for comparative purposes. The three phosphonate compounds vary in the number of methoxy groups attached to the central phosphorus atom and are used to aid in deciphering the adsorption behavior of DMMP on silica. Specifically, we use a thin film infrared technique that enables detection of bands due to adsorbed species below 1300 cm^{-1} where the strong Si–O bulk modes reside. Access to the region below 1300 cm^{-1} is important because this region contains the characteristic P=O and Si–O–C methoxy modes. The latter bands have been the key in determining the adsorption behavior of methoxysilanes on silica,¹⁹ and it is anticipated that these bands will be equally important in determining the adsorption mechanism of DMMP on silica.

2. Experimental Section

The fumed silica Aerosil A380 with a surface area of $380\text{ m}^2\text{ g}^{-1}$ was obtained from DeGussa AG. Details of this thin film technique are described elsewhere.²⁰ The silica was evacuated at 400°C for 30 min followed by cooling to room temperature. Evacuation at 400°C results in the removal of the H-bonded hydroxyl groups from the surface, leaving surface containing isolated hydroxyl groups. The isolated hydroxyl groups give rise to a sharp band at 3747 cm^{-1} . Deuterated silica was prepared by repeated exposure of the silica film to D_2O vapor at $400\text{--}430^\circ\text{C}$.

Infrared spectra were collected at 4 cm^{-1} resolution on a Bomem Michelson 102 FTIR equipped with a CsI beam splitter and a DTGS detector. A total of 100 scans were coadded for each spectrum, and each scan required 6 s. Difference spectra are plotted where the reference spectrum is recorded using the thin film silica evacuated at 400°C and cooled to room temperature. Therefore, positive bands are due to bonds that formed on the surface, and negative bands represent bond removal from the surface. All spectra were recorded at ambient temperature.

DMMP, TMP, TCP, MDCP, D_2O , and hexamethyldisilazane were purchased from Aldrich Chemical Co. All reagents were used as received and were transferred to evacuable glass bulbs using standard freeze–thaw cycles.

3. Results and Discussion

The gas-phase spectrum of DMMP and other phosphonate derivatives, namely, trimethyl phosphate (TMP), trichlorophosphate (TCP), and methyl dichlorophosphate (MDCP), are shown in Figures 1a to 4a, respectively. The assignments of the various bands are given in Table 1, and the structures of these compounds are shown in Chart 1.

Adsorption of DMMP on Silica. The infrared spectra of DMMP vapor and DMMP adsorbed on silica are shown in parts a and b of Figure 1, respectively. DMMP adsorbs through hydrogen bonds (H-bonds) with the surface hydroxyl groups as evidenced by the downward shift of the SiO–H stretching mode (negative bands at 3747 cm^{-1}) to a broad feature centered at 3223 cm^{-1} .¹⁹ This is accompanied by an upward shift of the SiO–H bending modes (negative bands at $863/768\text{ cm}^{-1}$) to a broad band in the $1050\text{--}900\text{ cm}^{-1}$ region.

A stronger H-bond will result in a greater frequency shift in the stretching and bending SiOH modes.^{19,21,22} For example, adsorption of methoxysilanes shift the SiOH

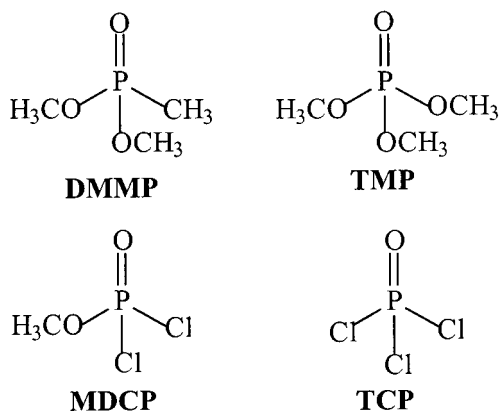
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Table 1. Assignment of the Infrared Bands (in cm^{-1}) for Gaseous DMMP, TMP, MDCP, and TCP

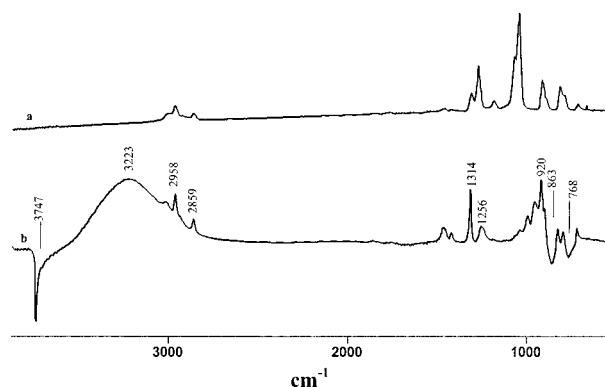
DMMP	TMP	MDCP	TCP	assignment
3006	3006	2999		$\nu_a(\text{CH}_3)$, $\nu(\text{CH}_3\text{O})$
2958	2963	2968		$\nu_a(\text{CH}_3\text{O})$
2917	2920			$\nu_a(\text{CH}_3)$, $\nu(\text{CH}_3\text{O})$
2859	2863	2866		$\nu_s(\text{CH}_3)$
1471				$\delta_a(\text{P}-\text{CH}_3)$
1459	1457	1460		$\delta_s(\text{O}-\text{CH}_3)$
1420				$\delta_s(\text{P}-\text{CH}_3)$
1319				$\delta_a(\text{P}-\text{CH}_3)$
1275	1290	1316	1321	$\nu(\text{P}=\text{O})$
1190	1195	1192		$\rho(\text{O}-\text{CH}_3)$
1075/1049	1061	1078/1046		$\nu(\text{O}-\text{CH}_3)$
914	914			$\rho(\text{P}-\text{CH}_3)$
816	858	811		$\nu(\text{P}-\text{O}-\text{C})$
		617	593	$\nu_s(\text{P}-\text{Cl})$
		593	480	$\nu_a(\text{P}-\text{Cl})$

Chart 1

stretching and bending modes to 3350 and 935 cm^{-1} , respectively, whereas a more strongly H-bonded triethylamine gives rise to corresponding broad bands located at 2677 and 953 cm^{-1} . Given that the shifted OH stretching band arising from adsorbed DMMP appears at 3223 cm^{-1} , it is concluded that the individual H-bond of adsorbed DMMP is slightly stronger than that observed for adsorbed methoxysilanes but weaker than that of adsorbed amines. Furthermore, it is noted that DMMP adsorption on silica only occurs with the surface hydroxyl groups. In a separate experiment, a thin film of silica was first reacted with hexamethyldisilazane (HMDS) to convert all the isolated SiOH groups to $\text{SiOSi}(\text{CH}_3)_3$ species.^{23,24} The infrared spectrum recorded after exposure of excess DMMP vapor at room temperature to the HMDS treated silica showed no evidence of adsorbed DMMP.

In principle, DMMP has three different functionalities (PCH_3 , $\text{P}=\text{O}$, POCH_3) that could be responsible for the H-bonding with the surface hydroxyl groups. Clearly, adsorption through the PCH_3 group of the DMMP would not produce a large shift in the SiOH bands due to a weak van der Waals interaction. Furthermore, the spectra in Figure 1 show that the PCH_3 modes at 2998, 2917, 2850, 1420, 1319, and 916 cm^{-1} for the gaseous molecule do not shift or change upon adsorption.

In contrast, a shift in frequency in the $\text{P}=\text{O}$ gaseous DMMP at 1275 cm^{-1} to 1256 cm^{-1} and a disappearance of the $\text{O}-\text{CH}_3$ stretching modes at 1075 and 1049 cm^{-1} occur when DMMP is adsorbed on silica (Figure 1b). Furthermore, the disappearance of the $\text{O}-\text{CH}_3$ stretching

**Figure 1.** Infrared spectra of DMMP (a) gas phase and (b) after addition of excess DMMP vapor to thin film silica for 10 s followed by evacuation for 2 min at room temperature.

modes is not accompanied by any change in the $\text{OC}-\text{H}_3$ stretching modes at 2958 and 2859 cm^{-1} . This shows that the absence of the lower frequency $\text{O}-\text{CH}_3$ modes is not due to a reaction involving elimination of the methoxy moieties. It is also noted that the behavior of the methoxy modes differs from the spectra obtained for DMMP adsorbed on TiO_2 and WO_3 .¹⁵

Adsorption of DMMP on TiO_2 and WO_3 gives rise to spectra containing all four methoxy modes at 2958 and 2954 cm^{-1} and the strong $\text{O}-\text{CH}_3$ stretching modes at 1061 and 1037 cm^{-1} .¹⁵ On TiO_2 or WO_3 , the intensity of the four methoxy modes decreases only when the methoxy groups are eliminated via evacuation at elevated temperature. Furthermore, the shift of the $\text{P}=\text{O}$ stretching mode on silica (1256 cm^{-1}) is much less than observed on WO_3 (1223 cm^{-1}) or TiO_2 (1237 cm^{-1}). From this spectral data, it was concluded that DMMP adsorbs solely through an interaction of the $\text{P}=\text{O}$ group and surface sites on WO_3 and TiO_2 (structure 1a). Given the vast differences in the spectral data observed with DMMP adsorbed on silica compared to WO_3 and TiO_2 , the adsorbed species on silica is clearly different from that depicted in structure 1a.

The adsorption of methoxysilanes on silica provides a clue to the role of the DMMP methoxy groups in the adsorption process. The adsorption of $(\text{CH}_3\text{O})_x\text{Si}(\text{CH}_3)_{4-x}$ on silica (where $x = 1, 2, 3$) produces identical spectral behavior for the methoxy modes found for DMMP on silica.^{19,25} For all three methoxymethylsilanes, the isolated SiOH stretching mode at 3747 cm^{-1} is shifted to 3350 cm^{-1} due to a H-bonding interaction of the methoxy groups with the surface SiOH groups. More important, as with DMMP adsorption, the $\text{OC}-\text{H}$ modes in the $3000\text{--}2800\text{ cm}^{-1}$ region remained unchanged whereas the strong $\text{O}-\text{CH}$ modes near 1100 cm^{-1} completely disappear. It was reported that the $\text{C}-\text{H}$ stretching modes of the methoxy groups in the $3000\text{--}2800\text{ cm}^{-1}$ region are not structure sensitive whereas, the low-frequency $\text{H}_3\text{C}-\text{O}$ modes are directly involved with H-bond formation, and these bands become broad and weak in intensity.¹⁹ Thus, the infrared data showed that all methoxy groups of the mono-, di-, or trimethoxysilanes form H-bonds with the surface hydroxyl groups. For example, each adsorbed $(\text{CH}_3\text{O})_3\text{SiCH}_3$ molecule formed three H-bonds with three surface SiOH groups. Given the similarity of the behavior for the methoxy modes obtained for adsorption of DMMP on silica, we conclude that H-bonds occur with both methoxy groups of the DMMP molecule.

Two possible structures (structures 1b and 1c), one with and one without a third bond between the $\text{P}=\text{O}$ and surface

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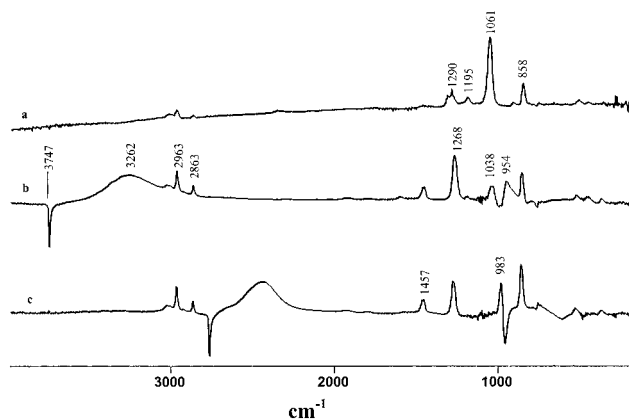
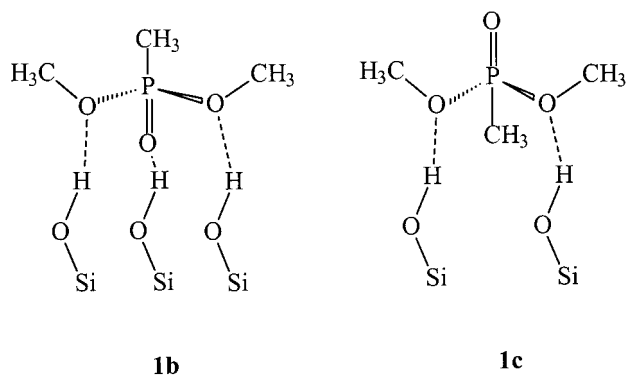


Figure 2. Infrared spectra of (a) gas-phase TMP. After addition of excess TMP vapor to (b) thin film silica and (c) deuterated silica for 10 s followed by evacuation for 2 min at room temperature.

SiOH groups, can be envisaged. To better understand the role of the P=O and methoxy groups in the adsorption of DMMP, we turn to the data obtained for TMP, TCP, and MDCP adsorption on silica at room temperature and with subsequent desorption at elevated temperatures. The four phosphonate compounds vary in the number of methoxy groups attached to the central phosphorus atom, and the desorption behavior for each molecule will depend on both the strength and number of individual H-bonds formed with P=O and the methoxy groups with the surface SiOH.



Adsorption of TMP, TCP, and MDCP on Silica.

Parts a and b of Figure 2 show the infrared spectra of TMP in the gas phase and after adsorption on silica, respectively. In Figure 2b, the SiO–H stretching band at 3747 cm^{-1} (sharp negative band) is downward shifted to a broad feature located at 3262 cm^{-1} . The absence of the strong methoxy modes at 1061 and 1195 cm^{-1} shows that the adsorption of TMP on silica occurs through H-bonding between the three methoxy groups and the isolated SiOH groups. There is a positive weak band near 1038 cm^{-1} that is too low in frequency to be attributed to a small number of unperturbed methoxy groups. Furthermore, this band shifts when TMP adsorbs on deuterated silica (see Figure 2c). Therefore, we assign this band to a surface mode and not to any mode associated with the methoxy groups. The band at 1038 cm^{-1} is the high-frequency side of the broad SiOH bending modes that shift upward with hydrogen bonding. Superimposed on this broad band is a negative band at 973 cm^{-1} due to the Si–O stretching mode of the surface SiOH groups, and this gives the false appearance of two bands at 1038 and 954 cm^{-1} .

The TCP molecule has no methoxy groups to form a strong H-bond with the surface. The infrared spectra of the TCP gas phase and TCP adsorbed on silica are shown

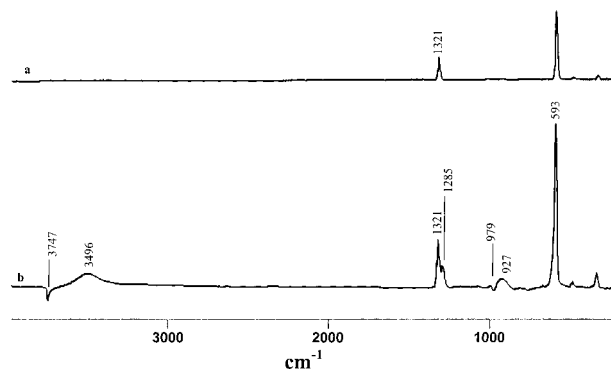
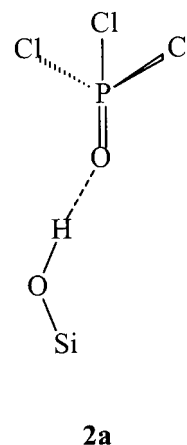


Figure 3. Infrared spectra of TCP (a) gas phase and (b) after addition of excess TCP vapor to thin film silica for 2 min.

in Figure 3, a and b, respectively. Figure 3b is recorded in the presence of TCP vapor because it is completely removed with evacuation at room temperature. Nevertheless, the P=O band is shifted from 1321 cm^{-1} in the gas phase to 1285 cm^{-1} upon adsorption on silica, and there is no observable frequency shift in the P–Cl modes. Thus, adsorption of TCP on silica occurs through a weak H-bond between the P=O and the free silanol (see structure 2a).



Parts a and b of Figure 4 show the infrared spectra of MDCP in the gas phase and after adsorption on silica, respectively. While the P–Cl stretching modes at the low-frequency region (at 620–400 cm^{-1}) do not change upon adsorption, the P=O band shifts from 1316 to 1291 cm^{-1} . Furthermore, the OCH₃ rocking and O–CH₃ stretching modes in the gas phase at 1192 and 1046 cm^{-1} disappear, showing that MDCP adsorbs on silica through at least a H-bond between the methoxy moiety and surface SiOH groups.

Desorption at Elevated Temperatures. The infrared spectra of the adsorbed DMMP on silica evacuated as a function of temperature are shown in Figure 5. All bands due to adsorbed DMMP decrease in unison and are completely eliminated at 300 °C. At 300 °C the difference spectrum (curve 3d) is featureless, showing that there are no decomposition products remaining on the surface and that the silica has returned to its original state with the same concentration of surface hydroxyl groups. This is in agreement with the TPD and AES study by White et al.¹¹ that showed that the molecular desorption of DMMP on silica occurred without decomposition products such as CH₃OH, CO₂, CO, H₂O, or phosphorus-containing molecules.

In the interest of brevity, we do not show the spectra obtained for the desorption of TMP, TCP, and MDCP but

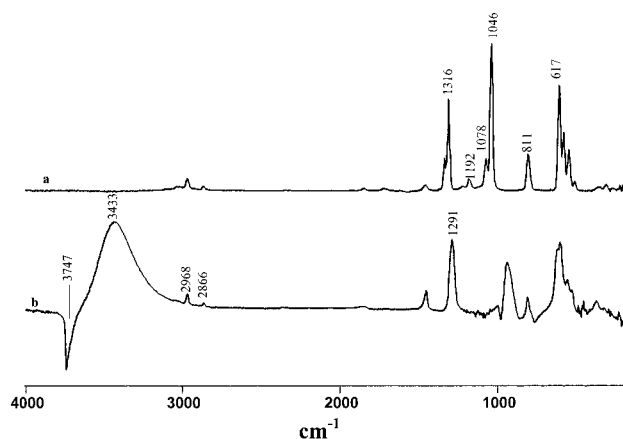


Figure 4. Infrared spectra of MDCP (a) gas phase and (b) after addition of excess MDCP vapor to thin film silica for 10 s followed by evacuation for 2 min at room temperature.

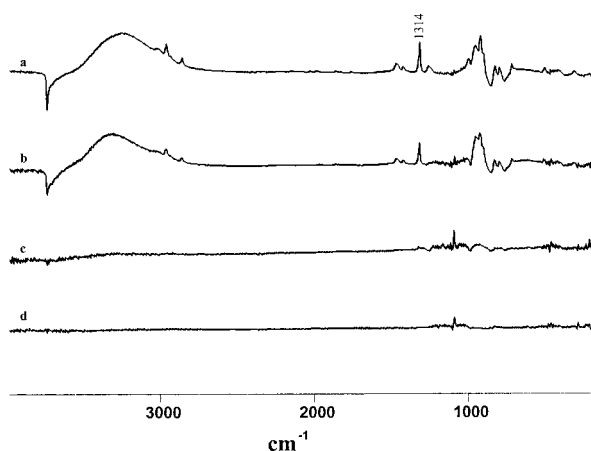


Figure 5. Infrared spectra of adsorbed DMMP on silica, evacuated at (a) 24 °C, then (b) 100 °C, then (c) 200 °C, and then (d) 300 °C.

note that similar spectra are obtained for DMMP and these three compounds. That is, for TMP, TCP, and MDCP, the bands due to adsorbed compounds decrease in unison and are completely removed (albeit at different evacuation temperatures), and the silica is returned to its original state. Thus, all four compounds are found to molecularly desorb from the silica surface. We recall that the desorption temperature of the H-bonded DMMP, TMP, MDCP, and TCP depends on the individual strength and number of H-bonds to the surface SiOH groups. Figure 6 is a plot of the relative amount of adsorbed phosphonate compound remaining on the silica surface as a function of evacuation temperature. This was obtained from a measurement of the change in integrated intensity of absorption bands at 1314, 1457, and 1451 cm^{-1} for DMMP, TMP, and MDCP, respectively. The data show that TCP is removed by evacuation at room temperature, MDCP requires evacuation at 150 °C, whereas DMMP and TMP require higher temperatures of 300 and 400 °C, respectively.

We recall that the shift in the SiOH band at 3747 cm^{-1} follows the order TCP (3488 cm^{-1}), MDCP (3425 cm^{-1}), TMP (3262 cm^{-1}), and DMMP (3223 cm^{-1}) and that all four compounds show a shift in the P=O stretching mode. TCP is removed by evacuation at room temperature because of a single weak H-bond between the P=O and surface SiOH group (structure **2a**). MDCP has a slightly stronger H-bond with the surface, but it is expected to desorb at room temperature if it is singly bonded as TCP through the P=O group or through a single H-bond with

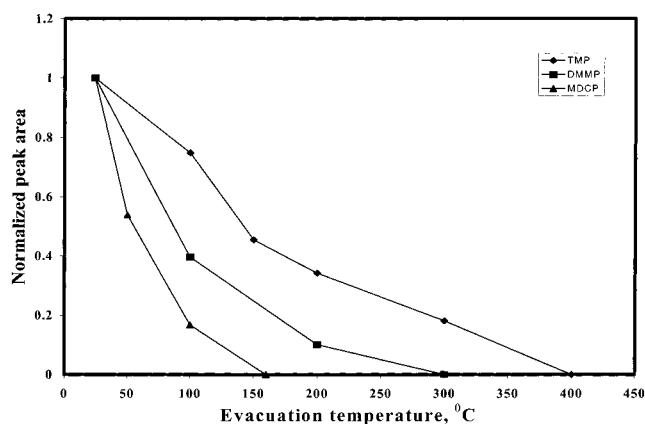
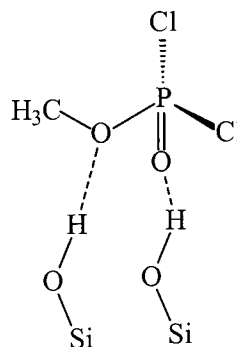


Figure 6. Desorption of DMMP, TMP, and MDCP as a function of evacuated temperatures. The amount of adsorbed DMMP, TMP, and MDCP was determined from the integrated band areas at 1314, 1457, and 1451 cm^{-1} , respectively.

the methoxy group. In the latter case, comparison is made to the adsorption of $\text{CH}_3\text{OSi}(\text{CH}_3)_3$ and $(\text{CH}_3\text{O})_2\text{Si}(\text{CH}_3)_2$, which both show a broad band at 3350 cm^{-1} with adsorption on silica.¹⁹ However, $\text{CH}_3\text{OSi}(\text{CH}_3)_3$ is removed by evacuation at room temperature whereas $(\text{CH}_3\text{O})_2\text{Si}(\text{CH}_3)_2$ requires an evacuation temperature of about 100 °C.^{19,26} A higher temperature is required for the dimethoxy-methylsilane because there are two H-bonds per molecule. Given that the shifted SiOH band for adsorbed MDCP is at a higher frequency than for the methoxysilanes, we conclude that it must adsorb by both the P=O and methoxy functionality (structure **2b**).



2b

On the other hand, TMP desorbs from silica at a higher temperature than DMMP despite having a shifted SiOH band appearing at a slightly higher frequency (3262 cm^{-1}) than that obtained with adsorbed DMMP (3223 cm^{-1}). One explanation is that TMP forms three H-bonds and DMMP forms two H-bonds between the methoxy groups and the free silanols (structures **2c** and **1c**, respectively). If DMMP is trifunctionally adsorbed through two methoxy groups and a more weakly bound P=O group, then we would expect to see two shifted SiOH bands: one at 3223 cm^{-1} for the two H-bonded methoxy groups and a band at a higher frequency above 3400 cm^{-1} as obtained for adsorbed TCP and MDCP. Because there is a single broad peak at 3223 cm^{-1} , we conclude that the differences between desorption temperature for TMP and DMMP is the result of DMMP adsorbed only through the two

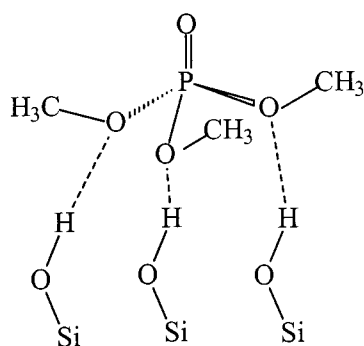
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Table 2. Observed Shift for the P=O Stretching Mode of the Adsorbed DMMP at Various Surfaces

surface	$\nu(\text{P=O})$, cm^{-1}	ref	surface	$\nu(\text{P=O})$, cm^{-1}	ref
SiO ₂	1256		Al ₂ O ₃	1190	13
WO ₃	1223	15		1216	1
TiO ₂	1237	15	MgO	1190	1
TiO ₂ /Nb	1210	13	La ₂ O ₃	1224	1
Au/ \sim SCH ₂ R ^a	1212	5	Fe ₂ O ₃	1077	1
Pt(111)	1215	3			

^a ω -Substituted alkanethiolates on gold.

methoxy groups (structure **1c**). An adsorbed DMMP molecule on silica that does not have a H-bond between the P=O groups and the surface silanols is consistent with the observed small shift in the P=O stretching mode. From Table 2, we see that a shift of 19 cm^{-1} is much lower than the range of values (52–200 cm^{-1}) obtained for DMMP adsorbed on other oxides.

**2c**

For steric reasons, a TMP adsorbed through H-bonds with the three methoxy groups (see structure **2c**) cannot form a bond between the P=O functionality and the surface hydroxyl groups. Despite this fact, there is an observed shift of the P=O stretching mode of TMP from 1290 cm^{-1} in the gas phase (Figure 2a) to 1268 cm^{-1} upon adsorption on silica (Figure 2b) or deuterated silica (Figure 2c). Since both TMP and DMMP do not adsorb via a H-bond with the P=O group, there remains to explain the shift in the P=O stretching mode when these two compounds adsorb on silica. One possible explanation is that the formation of three H-bonds between the three methoxy groups for TMP and two methoxy groups for DMMP reduces the electron-donating strength from the methoxy groups to the phosphorus atom and a resultant decrease of the P=O frequency. In support of this conclusion, it is noted that the position of the P=O stretching frequency in known phosphonate compounds is highly sensitive to the type of functionalities attached to the central P atom.²⁷ This sensitivity to frequency is evident by the position of the

P=O stretching frequency in the four phosphonate compounds given in Table 1.

Adsorption of DMMP/Methanol Mixtures. Methanol has been identified as a major interferent to the selective detection of DMMP on WO₃ based sensors.¹⁸ Methanol forms a weaker H-bond with the surface hydroxyl groups on silica (the SiOH band at 3747 cm^{-1} shifts to about 3400 cm^{-1}) than the H-bond formed with DMMP, and is removed with evacuation at room temperature.¹⁹ In separate experiments, our infrared data showed that adsorbed DMMP is not displaced by exposure to methanol vapor, and in the reverse order, adsorbed methanol is easily displaced by DMMP. Furthermore, and perhaps more important, when mixtures of methanol/DMMP vapor (two concentrations were tested, about 1:1 and 100:1 ratios) are passed over silica, there is evidence of only DMMP adsorbed on the surface. This selectivity is because each DMMP molecule is H-bonded to two surface hydroxyl groups, whereas there is a corresponding 1:1 interaction with the alcohol. Given that DMMP molecularly desorbs from silica at 300 °C, this oxide could provide a means for filtering and concentrating DMMP from a gas stream containing methanol for later release by the application of a thermal pulse.

4. Conclusion

In this study, we found that the adsorption of DMMP on SiO₂ is markedly different from the adsorption of DMMP on WO₃, TiO₂, and Al₂O₃. The decomposition of DMMP occurs at elevated temperatures with the loss of methoxy groups on WO₃, TiO₂, and Al₂O₃ whereas molecular desorption occurs on high surface area SiO₂ powders. The organophosphonates adsorb through H-bonds of the P=O and methoxy groups with the surface SiOH groups. The strength of the adsorption depends on the number and type of H-bonds and follows the order TCP < MDCP < DMMP < TMP. TCP is adsorbed through a weak H-bond with the P=O groups and is completely removed by evacuation at room temperature. MDCP forms two H-bonds with the P=O and methoxy groups and is eliminated with evacuation at 150 °C. DMMP adsorbs through two H-bonds with the methoxy groups and is removed by evacuation at 300 °C. TMP is most strongly adsorbed because it adsorbs through three H-bonds and is removed at 400 °C. All four compounds molecularly desorb from the silica, and the silica returns to its original state.

The adsorption behavior of DMMP/methanol on silica suggests a possible route to a prefiltering/preconcentrating strategy. The DMMP would be selectively extracted from the gas stream and concentrated on the silica surface, whereas methanol would pass through the filter. Subsequent removal of the concentrated DMMP can be accomplished with a thermal pulse.

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