Adsorption and Decomposition of Dimethyl Methylphosphonate on Metal Oxides

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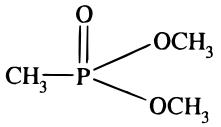
The adsorption and decomposition of dimethyl methylphosphonate (DMMP) have been examined on four different metal oxide surfaces: aluminum oxide, magnesium oxide, lanthanum oxide, and iron oxide. Aluminum, magnesium, and lanthanum oxides are observed to behave in much the same way, with initial binding of the P═O species to the surface at an acid site, followed by stepwise elimination of the methoxy groups, beginning at temperatures as low as 50 °C, which combine with surface hydrogens to yield methanol that evolves from the surface. The final product observed for these oxides is a surface-bound methylphosphonate, with the P−CH_3 bond intact, which is resistant to further oxidation even in the presence of 70 Torr of oxygen at 300−400 °C. Adsorption on iron oxide yields a different sequence of events, with the initial adsorption occurring again with the P═O moiety binding to an acid site, although there is some indication of the formation of a second type of surface complex. The primary interaction on iron oxide appears to be much stronger than with the other oxides, and probably involves the unidentate coordination of the DMMP to a Lewis acid site on the surface. Nonselective elimination of both the methoxy and the phosphorus-bound methyl groups begins only after heating above 200 °C, but occurs with total elimination of the methyl and methoxy groups observed after heating above 300 °C in vacuum. The ease with which iron oxide cleaves the P−CH_3 bond is attributed to the availability of multiple oxidation states to the iron atom. Participation of the Fe(III)/Fe(II) redox couple in the reaction provides a low-energy path for oxidative cleavage of the P−CH_3 bond. The other oxide surfaces cannot provide a similar path, and on these surfaces the P−CH_3 bond is resistant to cleavage. The use of infrared diffuse reflectance techniques, observing, in particular, the methyl stretch region of the infrared spectrum, has allowed the almost complete characterization of the decomposition processes which occur after DMMP adsorbs on aluminum oxide, magnesium oxide, lanthanum oxide, and iron oxide.

Introduction

Organophosphonate surface chemistry is an important but not a very well-characterized area of chemistry.[1] Within the last several years important studies of the fundamentals of the interactions between organophosphonate compounds and metal oxide surfaces have been carried out.[1−21] Dimethyl methylphosphonate (DMMP), **I**, is a widely used model compound



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for the simulation of the interactions of phosphonate esters with surfaces. Phosphonate esters occur widely in the spectrum of toxic man-made chemicals, being used as pesticides and chemical warfare agents. The interactions of phosphonate esters with metal oxide surfaces are important for the study of the fate and transport of pesticides in soils and in the development of catalytic agents for the destruction of chemical warfare agents and for protection of personnel.

The adsorption and reaction of DMMP on different substrates have been investigated by a number of groups. Tempelton and Weinberg[2,3] investigated the adsorption and decomposition of DMMP on alumina using inelastic electron tunneling spectroscopy. They found that at 200 K DMMP adsorbed molecularly, via hydrogen bonding of the phosphoryl oxygen to a surface OH site, whereas at higher temperatures between 295 and 473 K, they found that DMMP adsorbs dissociatively. The initial step involved the binding of the phosphoryl oxygen at a coordinately unsaturated aluminum atom and hydrogen bonding of one of the methoxy oxygens to a surface OH site. This was followed rapidly by nucleophilic substitution at phosphorus by a surface OH group, leading to loss of the hydrogen-bonded methoxy group as methanol, to give a bridging phosphonate species.

Templeton and Weinberg also observed that once the bridging phosphonate species was formed, it underwent nucleophilic substitution at the remaining methoxy carbon by a surface O atom, with simultaneous protonation at the methoxy oxygen by a surface hydroxy group to give surface-bound unsubstituted phosphonate and a surface methoxide. The unsubstituted phosphonate and methoxide rapidly eliminate to give gaseous methanol and a surface-bound methylphosphonate. The surface-bound hydroxy methylphosphonate was observed as an intermediate when DMMP was adsorbed at 373 K and heated to 573 K, but not when DMMP was adsorbed at 573 K. The final form of the adsorbed phosphonate in each case was methylphosphonate.[2,3]

Li, Schlup, and Klabunde,[4] and Lin and Klabunde[5] have investigated the interaction of DMMP with magnesium oxide surfaces using infrared photoacoustic techniques. They found that initial chemisorption involved Lewis acid Mg surface sites binding to the phosphoryl oxygen, similar to observations by Templeton and Weinberg with alumina. They observed that surface OH groups were generated by DMMP decomposition. They determined that only surface area is important, not some particular defect site. They found characteristic absorption bands for physisorbed DMMP (1238 cm^{-1} for the P═O stretch)

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and for the chemisorbed DMMP (1184 cm^{-1} for the P═O stretch). They observed a carbonyl band at 1745 cm^{-1}, presumably due to formic acid or formaldehyde from oxidized methanol. They observed intact $P-CH_3$ and $P-OCH_3$ groups on the surface even after heating to 500 °C.

Klabunde et al.[6−8] continued their investigations of DMMP adsorption on MgO using ultrahigh surface area (nanoscale particle) materials. The authors found that the volatile decomposition product is formic acid with smaller amounts of methanol formed depending on the reaction conditions. DMMP apparently reacts initially with the surface to form adsorbed methyl methylphosphonate and an adsorbed methoxy group. They proposed that the methoxy group is then oxidized by another DMMP molecule to yield the volatile formic acid product. They found that the presence of water in the reactant stream did not change the temperature of decomposition, but did change the product distribution. Methanol was formed in significant amounts when water was present. They found that the reaction between MgO and DMMP is a stoichiometric adsorption/decomposition reaction and not a catalytic one. After the loss of the first methoxy group, the residual adsorbed methyl methylphosphonate species is bound to two surface sites.

Henderson, Jin, and White[9] observed no significant decomposition when DMMP was adsorbed on silica using temperature-programmed desorption (TPD) and Auger electron spectroscopy (AES). However, on iron oxide, decomposition of DMMP was observed for monolayer coverages, even when adsorption was carried out at 170 K followed by heating to 250 K.

Aurian-Blajeni and Boucher[10] investigated the adsorption of DMMP on a number of metal oxides, including TiO_2, ZnO, Al_2O_3, MgO, and WO_3. In all cases they observed a decrease in the P═O stretching vibrational frequency, but were unable to correlate the magnitude of the shift with any property of the oxide substrate.

Kuiper et al.[11] were among the first to investigate the mechanism of adsorption and decomposition of an organophosphorus compound on a metal oxide. They showed that the nerve gas Sarin, closely related to DMMP, undergoes initial molecular adsorption on aluminum oxide at coordinatively unsaturated Al sites followed by slow hydrolysis at room temperature.

Weller et al.[12−14] have investigated the decomposition of DMMP and related nerve gas agents on Pt/alumina catalysts. They found very long protection times (50−135 h), time before breakthrough of DMMP, even for catalysts with Pt loadings as low as 0.5% and at temperatures as low as 250 °C. Prior to breakthrough, they observed almost stoichiometric amounts of CO_2 produced, indicating complete oxidation of the DMMP. Methanol was found in the outlet stream simultaneously with the breakthrough of DMMP itself. They recovered a trap condensate of the effluent from a badly deactivated catalyst, which was found to contain dimethyl phosphate, monomethyl phosphate, monomethyl methylphosphonate, dimethyl methylphosphonate, methyl phosphonic acid, and phosphoric acid. They did not report any volatile phosphorus-containing products from catalysts before breakthrough of DMMP itself. They concluded that the majority of the phosphorus which was sequestered on the support was present as $AlPO_4$.

Yates et al. have investigated the catalytic decomposition of DMMP on Mo(110),[15] and on Pd(111) and Ni(111).[16] They observed sustained catalytic oxidation of DMMP on the Mo(110) and the Pd(111) surfaces, without the production of a surface phosphate, at temperatures of 898 K for Mo(110) and 1075 K for Pd(111). CO and a phosphorus oxide gas-phase species were the products formed.

Two groups at the University of Pittsburgh have sought to minimize the deactivation caused by phosphate formation which results from the oxidation of DMMP on metal oxides by using hydroxyapatite, which is a naturally occurring calcium phosphate mineral having the formula $Ca_{10}(PO_4)_6(OH)_2$. Lee et al.[17] examined the catalytic oxidation of DMMP over hydroxyapatite and a copper-substituted hydroxyapatite. They found that the copper-substituted hydroxyapatite corresponding to the formula $Cu_2Ca_8(PO_4)_6(OH)_2$ had the highest activity. The materials appeared to deactivate through the formation of a methylphosphonate species which blocked the catalytic sites on the surface. These sites could be at least partially regenerated by heating the solid in oxygen to 500 °C, presumably by forming a surface phosphate which migrated to the support and away from the active site. Paluka et al.[18] studied the catalytic oxidation of DMMP on hydroxyapatite and its partially fluorinated analogue, fluorhydroxyapatite, with and without platinum. High surface area fluorhydroxyapatite samples showed an increase in protection time with increasing fluorine content. Platinum acted to oxidize a fraction of the methanol and dimethyl ether, the primary products observed in the absence of platinum, to carbon dioxide. None of these materials showed the long-lived protection periods observed for Pt/alumina by Weller et al.

Other investigators have studied the interaction of DMMP with clays, in the hope of gaining insight into the adsorption of pesticides in soils.[22−44] Bowen and co-workers[22,23] used infrared diffuse reflectance spectroscopy and infrared photoacoustic methods to study the adsorption and decomposition of DMMP on montmorillonite and calcium montmorillonite clay. They observed a small shift to lower frequency (−6 cm^{-1}) of the P═O stretching vibration when the DMMP was adsorbed on montmorillonite and a larger downward shift (−21 cm^{-1}) when DMMP was adsorbed on calcium montmorillonite. They interpreted these results to indicate that when DMMP adsorbed on calcium montmorillonite, it was binding directly to the cationic sites in the clay, and not through an intermediate water of hydration, giving rise to the relatively large shift for the P═O stretch.

The goal of this project has been to evaluate the adsorption and reaction behavior of DMMP on Al_2O_3, MgO, La_2O_3, and Fe_2O_3 in order to evaluate the activity of these different materials for the decomposition of organophosphonate compounds.

Experimental Section

Dimethyl methylphosphonate was obtained from Aldrich and used as received. The lanthanum oxide, magnesium oxide, and iron oxide were obtained from Fisher Scientific. The surface areas of these oxides were measured to be 24.6 m^2/g for MgO, 8.4 m^2/g for La_2O_3, and 20.6 m^2/g for Fe_2O_3. The aluminum oxide is a very pure (99.995%) γ-alumina obtained from Goodfellow, with a surface area measured to be 148 m^2/g and a particle diameter < 0.1 μm. The oxides were pretreated by heating them in a controlled environment cell in approximately 70 Torr of oxygen to 300−400 °C for 1 h followed by cooling to room temperature, at which time DMMP vapor was allowed to adsorb onto the oxide. The KBr used was obtained from Spectra Tech as chunks of crystalline KBr, which were then ground with a Wig-L-Bug and sieved using standard testing sieves.

Infrared spectra were obtained using an upgraded Nicolet 5 DX-B, with a water-cooled, high-intensity source, an MCT/B detector, and an 18-bit A/D converter using a Nicolet 680 data station. After a new instrument became available, some of the spectra were repeated using a Nicolet Magna 750 with an MCT/A detector. A Harrick Scientific DRA-2 diffuse reflec-

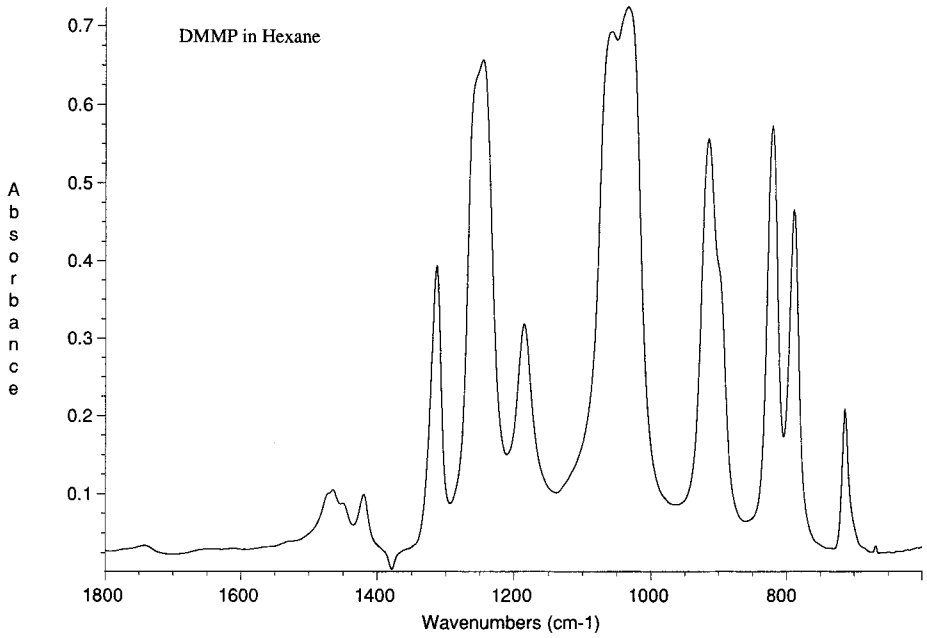


Figure 1. Infrared transmission spectrum of a thin film of DMMP in hexane, ratioed to pure hexane.

tance infrared Fourier transform spectroscopy (DRIFTS) optical accessory was used with an associated Harrick Scientific controlled environment cell, HVC-DR2.

Before adsorption of the DMMP vapor, a spectrum of the oxide being studied was obtained at each temperature. This spectrum was used as the background spectrum for the adsorption experiment, and each spectrum for DMMP adsorbed on that oxide was ratioed to the appropriate background spectrum. Adsorption of DMMP onto the metal oxide surfaces was carried out in a number of different ways, including batch impregnation of the oxide from hexane solution. Finally, two different vapor adsorption methods were used, depending on the sample. For the pure magnesia, lanthana, and iron oxide samples, DMMP vapor was collected in a gas vacuum manifold and delivered to the DRIFTS cell through a polyethylene tube connected to the manifold. The room temperature vapor pressure of DMMP ($\sim$ 1.0 Torr) was enough to accomplish adsorption of the vapor onto these oxides. Following adsorption of DMMP for approximately 1 h, the cell was evacuated, and infrared spectra were obtained at several different temperatures, typically 25, 50, 100, 150, 200, 250, and 300 °C, and then after oxidation for approximately 20 min at 300 °C in the presence of 70 Torr of oxygen. All spectra were collected with the sample under vacuum. The samples of DMMP on alumina and on iron oxide were examined at 400 °C before oxidation and at 400 °C after oxidation as carried out above. The samples were allowed to equilibrate under vacuum at each temperature for approximately 30 min before the spectra were collected.

For the aluminum oxide studies, it was necessary to dilute the aluminum oxide in KBr. With neat alumina samples, the strongly absorbing alumina framework vibrations prevented the observation of any adsorbate vibrational modes at frequencies less than 1150 cm^{-1}. In order to make reproducible measurements in this frequency region, the aluminum oxide was mixed 5 wt % with KBr for the preparation of the alumina samples. To avoid significant contributions from the adsorption of DMMP on KBr, the alumina was impregnated by exposing the calcined alumina (pretreated by heating to 500 °C in a muffle furnace in air) to DMMP vapor overnight at room temperature in a sealed glass container, and then the impregnated alumina was mixed with KBr and loaded into the DRIFTS controlled environment cell. A spectrum of the calcined alumina itself was subtracted from each spectrum of adsorbed DMMP at the different temperatures.

In order to evaluate differences in the two vapor adsorption methods, adsorption experiments using pure iron oxide were carried out using both vapor adsorption methods, the in situ adsorption in the DRIFTS cell and adsorption in the glass container. The spectra were identical except for some minor differences in relative intensities.

Results and Discussion

In the studies carried out here, it is assumed that the species which are observed correspond to a monolayer or less of DMMP on the surface of the oxides. Henderson et al.,[9] in their TPD study of DMMP on silica and iron oxide, observed molecular desorption from a multilayer state of DMMP on silica at 200−210 K and desorption corresponding to a monolayer state at 275 K. Molecular desorption from iron oxide, when it did occur, occurred in the same temperature region as that observed for silica, 200−210 K. In the current investigation, after exposure of the oxides to DMMP at room temperature, and, if necessary, placing the oxides in the infrared cell, the cell was evacuated and purged for a short time with nitrogen. Given that the multilayer desorption temperatures for DMMP on silica and on iron oxide are almost 100 K less than the lowest temperatures used in these experiments, it is reasonable to assume that only the monolayer state is being observed in the current investigation.

The interpretation of the spectral results has been significantly aided by the availability of carefully evaluated assignments of the infrared spectra of DMMP.[45,46] The two different groups of investigators who carried out the assignments used several different isotopic forms of DMMP to confirm their analysis. As a result, there is little doubt with regard to the assignments of the fundamental modes of DMMP which are referred to in the current investigation. Figure 1 is the spectrum of DMMP in hexane, and Table 1 lists the corresponding assignments.

The infrared diffuse reflectance spectra which are shown have been broken up into two different regions: the high-frequency region from approximately 3200−2600 cm^{-1}, which contains the methyl group stretching vibrations, and the region 1800−750 cm^{-1} which contains the C−O, C−P, and P═O stretching

TABLE 1: Vibrational Frequencies of DMMP in Hexane[a]

vibrational mode	freq (cm^{-1})	vibrational mode	freq (cm^{-1})
$\nu_a(CH_3P)$	2992[b]	ν(P═O)	1246
$\nu_a(CH_3O)$	2957[b]	$\rho(C_{H3}O)$	1185
$\nu_s(CH_3P)$	2926[b]	ν(CO)	1061
$\nu_s(CH_3O)$	2852[b]	ν(CO)	1033
$\delta_a(CH_3O)$	1467	$\rho(CH_3P)$	914
$\delta_s(CH_3O)$	1452	$\nu(PO_2)$	820
$\delta_a(CH_3P)$	1421	$\nu(PO_2)$	789
$\delta_s(CH_3P)$	1314	ν(PC)	711

[a] Due to the strong hexane absorptions in this region, these values are taken directly from ref 46. [b] a = antisymmetric. s = symmetric. wk = weak. sh = shoulder. br = broad. ν = stretch. δ = deformation. ρ = rock.

vibrations and the methyl deformation vibrations. These two regions provide distinct but complementary types of information and have been split for ease of comparison. Incident radiation at frequencies less than about 900 cm^{-1} is strongly absorbed by the metal oxides being studied, and no assignments were attempted for observed features below about 900 cm^{-1}. Some absorption features in this region which might be attributed to DMMP or its reaction products were observed, but strong absorption of the radiation by the substrates in this region makes identification of these bands, and the determination of the true absorption frequencies, subject to significant error.

The diffuse reflectance infrared spectra are presented with the intensity scale in Kubelka−Munk units, one of the standard formats for diffuse reflectance spectroscopy.[44−48] Kubelka−Munk units are similar to absorbance units used in transmission spectroscopy, in that the response is directly related to the concentration of the absorbing species. Studies in our laboratory have shown that diffuse reflectance measurements can yield quantitative results for species adsorbed on oxide surfaces.[49,50] When there is a chance that inhomogeneous processes are causing spectral broadening, as in the case of multiple adsorption sites for surface adsorbates, a linear response with concentration is obtained by integrating the absorption profile over the entire absorption band, rather than using peak intensities. This effectively adds together all the absorption intensities from the different sites for a particular vibrational motion. In some of the temperature sequences shown, it may not appear at first glance that, for example, the methoxy group absorptions have decreased in intensity by 50% on heating from one temperature to another. But the integrated intensity is strongly affected by the shape of the absorption profile. It is the integrated intensity of the absorption profile, not the peak intensity, which is the most reliable measure of the number of absorbing species.

Aluminum Oxide Adsorption. The high-frequency region of the absorption spectra from 4000 to 2600 cm^{-1} for aluminum oxide exposed to DMMP is shown in Figure 2. The spectra for DMMP on aluminum oxide are all presented using the same vertical scale, except as noted. Templeton and Weinberg[2,3] postulated two different modes of interaction for DMMP with alumina, one involving P═O interaction with coordinatively unsaturated aluminum (Lewis acid) sites, and one involving interaction of this same phosphoryl group with surface O−H (Bronsted acid) sites. Initial interaction of DMMP with the aluminum oxide surface apparently involves an interaction with O−H groups, since the spectra show a loss in concentration of O−H groups, relative to the oxide before DMMP adsorption (the inset shows this most clearly). The frequency of the O−H groups involved in the initial bonding indicates that they correspond to the most acidic protons which are not hydrogen bonded.[54] As the temperature is increased, increasing amounts of the hydrogen-bonded O−H groups are lost.

The methyl stretching modes provide clear evidence for the progress of the decomposition reaction as the temperature is increased (Figure 3). As the temperature increases from room temperature with the sample under vacuum, significant changes occur by 200 °C. A clear loss of intensity is observed for the bands which correspond to the methoxy methyl groups. The integrated intensities of the methoxy group methyl stretching vibrations, at 2956 and 2853 cm^{-1}, have decreased by approximately 50% by 200 °C, while the intensities of the methyl modes associated with the phosphorus-bound methyl group, at 2996 and 2930 cm^{-1}, remain constant. This is consistent with the loss of one methoxy group from the DMMP molecule and the formation of a surface-bound methyl methylphosphonate. The methoxy methyl group vibrations continue to lose intensity relative to those of the phosphorus-bound methyl group as the temperature is increased, and at 400 °C no methoxy groups remain. Table 2 lists the observed frequencies of the methyl vibrational modes, including the lower-frequency deformational modes, for DMMP on alumina as a function of temperature. Since the methyl groups are not directly involved in the bonding of DMMP, or its decomposition products, to the surface, the assignment of the corresponding vibrational modes is straightforward and based directly on the assignments of the parent compound.[45,46]

The lower-frequency spectral region for DMMP adsorbed on aluminum oxide is shown in Figure 4a. The P═O stretching vibration, which occurs at 1246 cm^{-1} for DMMP in hexane, is shifted to 1216 cm^{-1} upon adsorption at room temperature. Upon subsequent heating, this band shifts to 1202 cm^{-1} at 100 °C and then to 1185 cm^{-1} at 200 °C. The 1312 cm^{-1} band, which is one of the phosphorus-bound methyl group deformation modes, is consistently observed and undergoes very little change. The 1420 cm^{-1} band, which is the other CH_3(P) deformation mode, is also observed at all temperatures, although it is a weak absorption. The 1466 and 1450 cm^{-1} absorptions due to the methoxy methyl deformation modes, which have an intensity similar to the 1420 cm^{-1} $\delta_a(CH_3P)$ mode, exhibit the same temperature dependence as the stretching modes, which is to be expected (see Figure 4b).

The shift to lower frequency of the P═O absorption is consistent with a mechanism involving an interaction between the phosphoryl oxygen and the Lewis acid aluminum sites on the surface. As the temperature is increased and an Al−O bond is formed by 200 °C, with the P═O bond taking on more single-bond character, the frequency of the P−O stretch absorption decreases by approximately 60 cm^{-1}, and the 1185 cm^{-1} absorption can be associated with a surface-bound methyl methylphosphonate (MMP).

As mentioned above, it is the evolution of the methyl stretching modes which provides the clearest evidence regarding the nature of the absorbed DMMP species. The methoxy methyl group vibrations at 2956 and 2853 cm^{-1} are distinct form the stretching modes of the phosphorus-bound methyl group at 2996 and 2929 cm^{-1}. In addition, the integrated intensities of the methoxy methyl group modes scale reliably, depending on whether one or two methoxy groups are present. Thus, the structures of the species on the oxide surfaces are assigned primarily on the basis of the observed changes in the methyl stretching modes and to a lesser extent the deformation mode absorptions, particularly the strong 1315 cm^{-1} $\delta_s(CH_3P)$ mode. The strength of initial modes of interaction can be estimated in relative terms by examining the frequency of the P═O vibration. But once decomposition begins, the P═O bond no longer exists as a double bond, and the vibrations involving the P−O, C−O, and C−P bonds are all strongly coupled. The assignments in

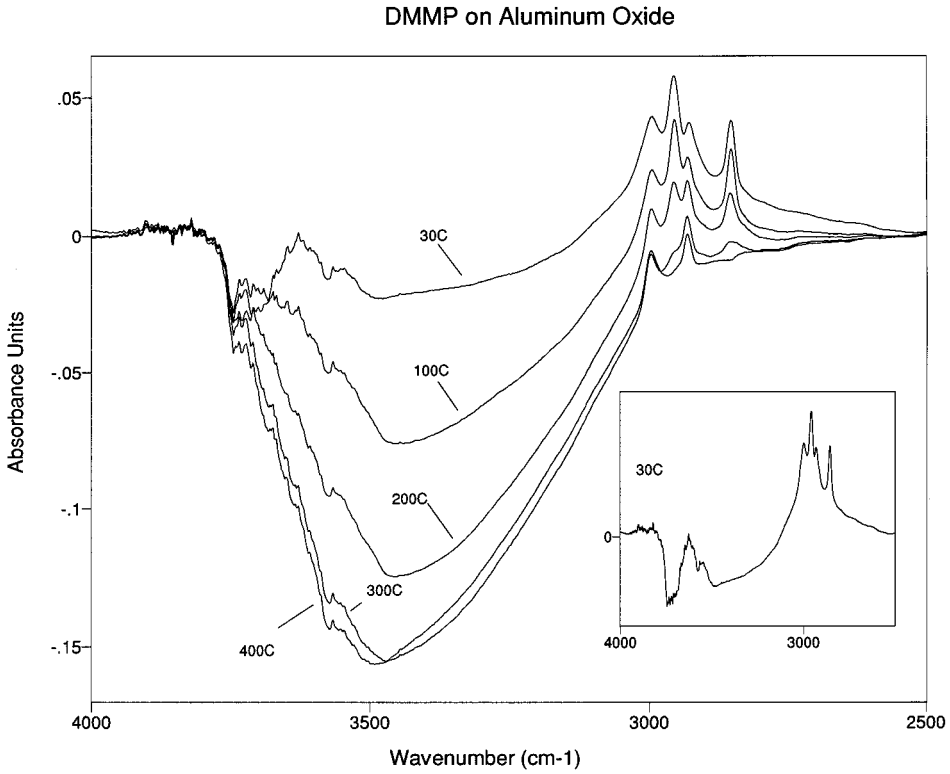


Figure 2. DRIFTS spectrum of DMMP on alumina at different temperatures. The loss of hydrogen-bonded O−H groups is indicated by the increasingly strong loss feature with a peak at approximately 3500 cm^{-1}.

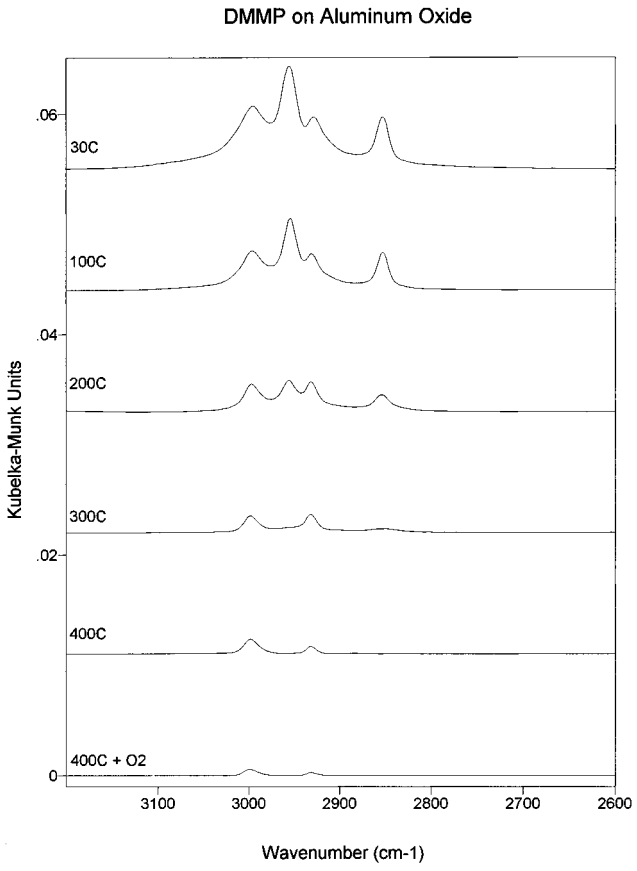


Figure 3. Methyl stretch region after adsorption of DMMP onto Al_2O_3. Spectra are measured under vacuum at different temperatures as noted.

Table 3 of the different sets of bands observed at a particular temperature to a distinct surface structure such as DMMP, MMP, or methylphosphonate (MP), are based on the methyl group vibrational absorptions. The assignments of the absorptions to particular vibrations in Table 3 are inferred from the most likely motions of the surface fragment and their probable frequencies, based on the frequencies of similar motions of the parent compound.

TABLE 2: Frequencies of Methyl Stretching and Deformation Modes for DMMP on Alumina

T (°C)	ν_a (CH_3P)	ν_a (CH_3O)	ν_s (CH_3P)	ν_s (CH_3O)	δ_a (CH_3O)	δ_s (CH_3O)	δ_a (CH_3P)	δ_s (CH_3P)
RT	2996	2956	2929	2853	1465	1450	1423	1314
100	2996	2954	2931	2852	1465	1450	1423	1312
200	2996	2956	2932	2932	1465 wk		1424	1312
300	2997		2932				1423	1315
400	2997		2932				1423	1317
400 + O_2	2997		2932				1424	1317

The ∼1060 cm^{-1} absorption is assigned as a C−O vibration of DMMP in hexane. And while a band at this approximate frequency is one of the more consistent features found in the spectra, the nature of the corresponding vibration is clearly changing since the C−O groups are eliminated from the surface by 300 °C. The absorptions in this region strongly overlap, and it is difficult to resolve the contributions of different vibrational modes. Between room temperature and 200 °C, the peak observed at approximately 1060 cm^{-1} decreases in intensity, corresponding with the loss of the first methoxy group. At 300 °C and higher temperatures, the absorption band is much broader, and must be due to one of the phosphonate stretching modes of the $CH_3-PO_3^{2-}$ species on the surface, since no methoxy groups remain.

No evidence is observed in any of the spectra for the formation of a surface-bound methoxy group on alumina. Experiments were carried out to examine the infrared spectra of adsorbed methanol, and the resultant spectra were clearly different from those observed here, particularly in the methyl stretch region, where adsorbed methanol yielded absorptions where none were observed for adsorbed DMMP. Additionally,

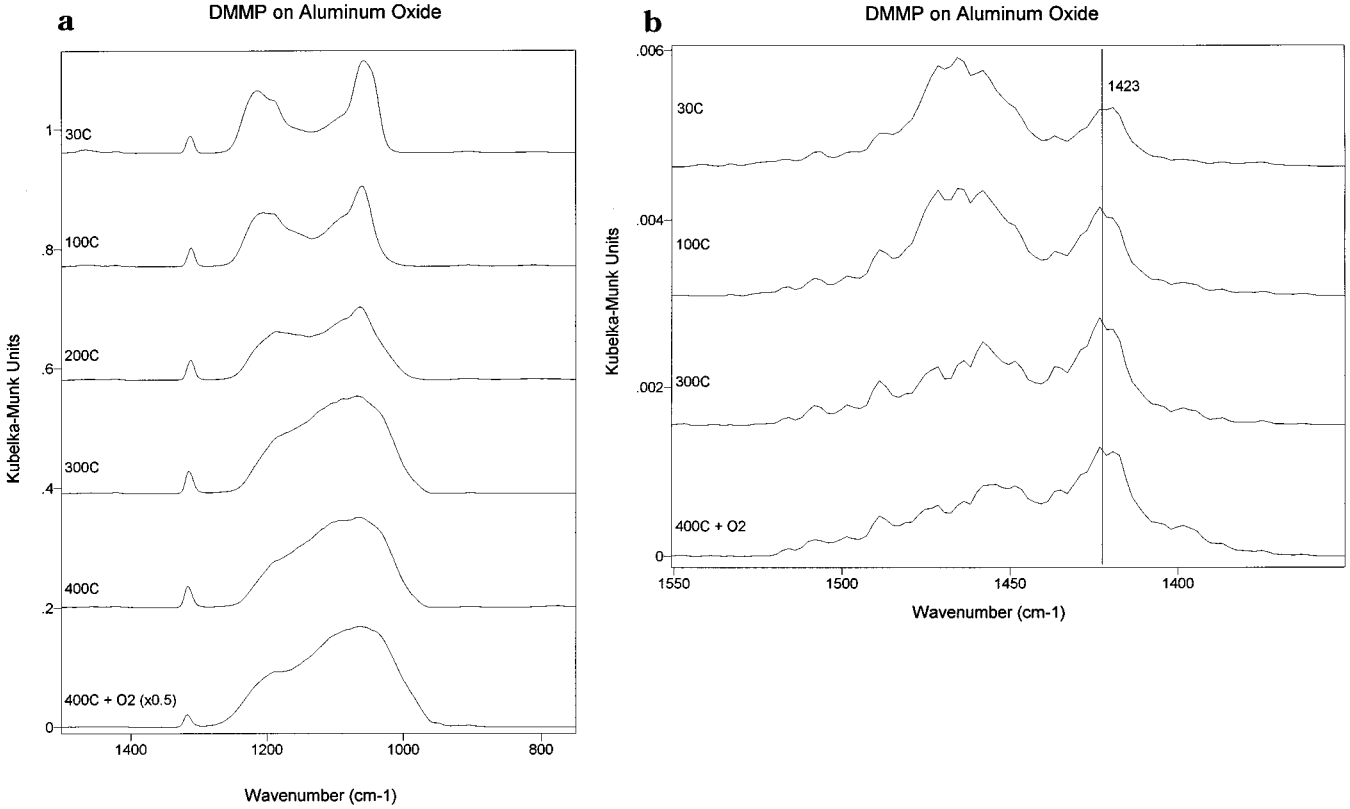


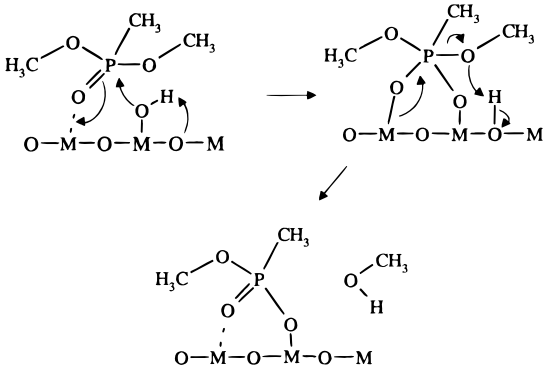
Figure 4. Lower-frequency region after adsorption of DMMP onto Al_2O_3. Spectra are measured under vacuum at different temperatures as noted.

TABLE 3: Phosphorus−Oxygen, Phosphorus−Carbon, and Carbon−Oxygen Modes for DMMP on Alumina

30 °C (DMMP)	ν(P═O)	$\rho(CH_3O)$	ν(CO)	$\rho(CH_3P)$
	1216	1190 sh	1058	904[a]
200 °C (MMP)	$\nu(PO_2)$/ $\rho(CH_3O)$		ν(CO)/ $\nu(PO_2)$	$\rho(CH_3P)$
	1188		1064	904[a]
400 °C + O_2 (MP)	$\nu(PO_3)$		$\nu(PO_3)$	$\rho(CH_3P)$
	1190		1065	902[a]

[a] This band is very weak due to the strong alumina absorption in this region, and the assignment is tentative but is expected.

SCHEME 1: Electrophilic Attack of the Surface on DMMP



no absorptions were observed which might correspond to adsorbed formate.

The observed combination of data leads to a relatively straightforward conclusion regarding the adsorption and reaction of DMMP on the alumina surface (see Scheme 1). The initial step involves the formation of a physisorbed species, bound to the surface through either the phosphoryl oxygen to surface Lewis acid sites or to surface hydroxyls. The progression to further products must involve the conversion of hydroxyl-bound DMMP to aluminum-bound DMMP. The next step in the reaction involves the loss of one methoxy group, and the formation of a bridging phosphonate species, MMP. This step is complete by 200 °C. The next step is the loss of the second methoxy group, and the formation of surface-bound MP, a step which goes to completion rapidly at a temperature somewhat greater than 300 °C. The methoxy groups which are lost from DMMP presumably abstract a hydrogen from the surface hydroxyls and evolve from the surface as methanol. This is consistent with the loss of O−H absorption intensity observed in Figure 2. The methyl phosphorus bond remains intact, even after exposure to 70 Torr of oxygen at 400 °C.

Templeton and Weinberg[2,3] suggested from their observations that DMMP undergoes dissociative adsorption on alumina at room temperature, i.e., that the first methoxy group is lost at room temperature, while in the current study, loss of the first methoxy group is not observed to be complete until 200 °C. Their experiments were carried out on an alumina that was created by oxidizing a thin layer of aluminum on a glass substrate in an oxygen−water plasma discharge in an ultrahigh vacuum chamber. Following exposure to between 100 and 2000 Langmuir of the vapor of DMMP, the samples were cooled to room temperature and coated with 2000 Å of lead in a cross strip pattern to form the tunnel junction. It is possible that the surface prepared by these methods is more active at low temperatures for dissociation of the DMMP than is the γ-alumina used in these studies, although the authors do indicate that X-ray measurements show a similarity between the oxide formed in this fashion and γ-alumina. The study by Templeton and Weinberg and the current one do agree that the loss of the second methoxy group is observed at temperatures between 300 and 400 °C.

Magnesium Oxide Adsorption. The methyl stretching region for DMMP adsorbed on magnesium oxide is shown in Figure 5. The spectra in the magnesium oxide stacked plots have been scaled individually to show the frequency shifts more clearly. The methyl modes are again clear indicators of the

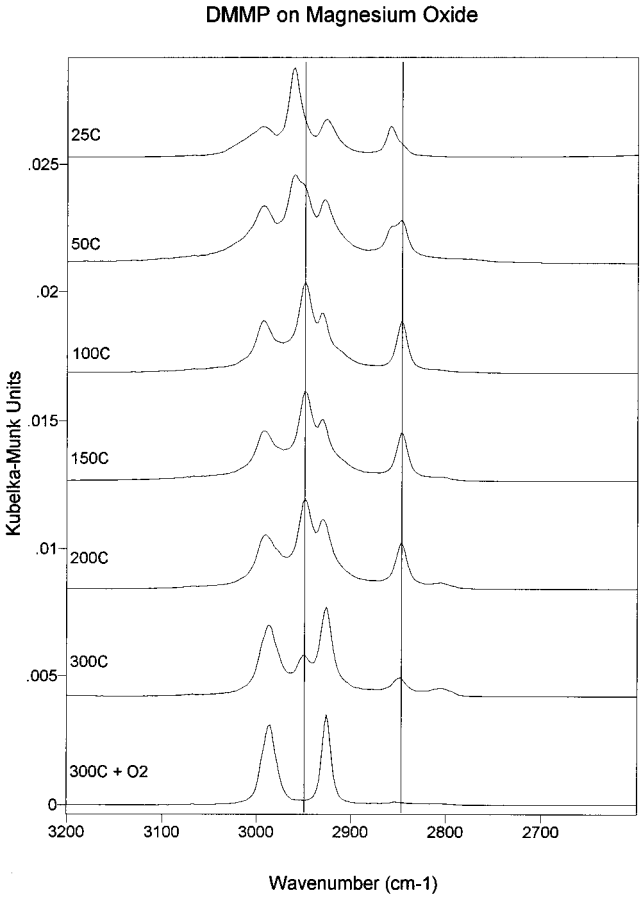


Figure 5. Methyl stretch region after adsorption of DMMP onto MgO. Spectra are measured under vacuum at different temperatures as noted.

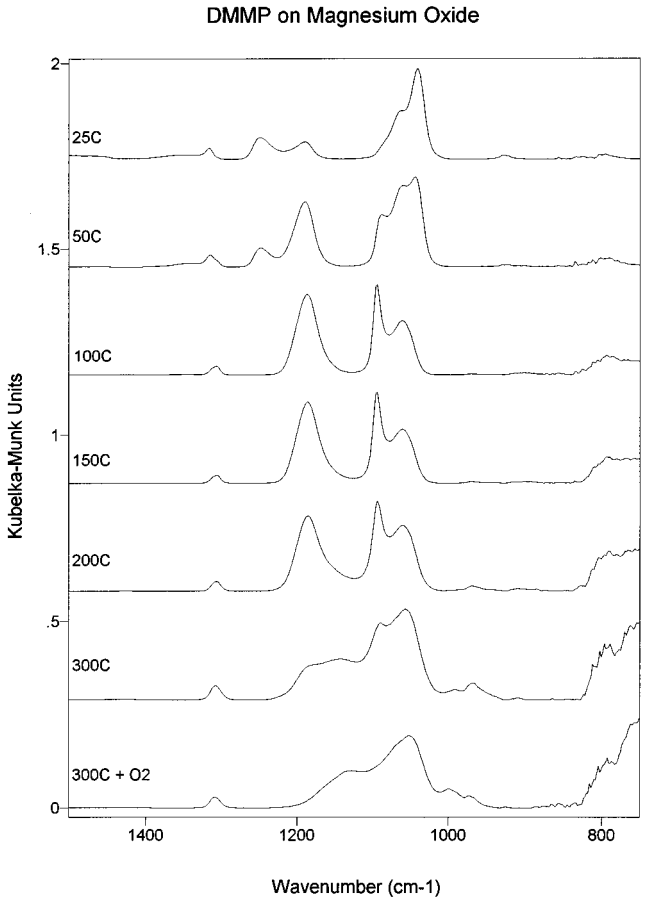


Figure 6. Lower-frequency region after adsorption of DMMP onto MgO. Spectra are measured under vacuum at different temperatures as noted.

evolution of DMMP on this surface. DMMP adsorbs initially on the magnesia surface with little change in the methyl stretching vibrations, but by 50 °C, clear shifts are observed in the 2962 and 2858 cm^{-1} absorptions, and at 100 °C, the 2962 absorption has shifted to 2949 cm^{-1} and the 2858 absorption has shifted to 2847 cm^{-1}. The bands which are shifting are associated with the methoxy methyl groups. It can also be seen that the relative intensities have changed. The intensities of two methoxy methyl stretching absorptions relative to the intensities of the other two methyl stretching modes, those associated with the phosphorus-bound methyl group, decrease as the temperature is increased from 25 to 100 °C. By 100 °C, the relative intensities of the now shifted methoxy methyl group vibrations have decreased by approximately 50% (calculated from the integrated Kubelka−Munk intensities) relative to the phosphorus-bound methyl group absorptions. These shifted methoxy group absorptions are assigned to the surface-bound methyl methylphosphonate species. The shifted methoxy absorptions continue to decrease in intensity with increasing temperature, most dramatically between 200 and 300 °C. After addition of oxygen at 300 °C, none of the methoxy groups remain. The absorptions of the methyl group attached to the phosphorus, however, have undergone virtually no decrease in intensity. On the basis of this loss in relative intensity, the vibrations observed after oxidation at 300 °C are assigned to a surface-bound methylphosphonate. Table 4 lists the frequencies observed for the methyl group vibrations as a function of temperature.

Spectral changes are also observed in the lower-frequency region, Figure 6. Upon adsorption, bands at 1249 and 1190 cm^{-1} are observed, along with the C−O−P vibrations at 1041 and 1061 cm^{-1}. The phosphorus-bound methyl group symmetric deformation mode is observed as it was for DMMP on alumina. The 1190 cm^{-1} absorption is almost certainly due to the P═O vibration, shifted due to a strong interaction with a surface acid site. A similar shift was observed by Klabunde et al.[4,5] in their work with DMMP on magnesia. The 1249 cm^{-1} band is no doubt also a P═O vibration due to its proximity to the absorption frequency of that mode observed for DMMP in hexane and is probably due to DMMP adsorbed at a second type of adsorption site. This site does not play an important role, however, since the absorption disappears upon heating.

TABLE 4: Frequencies of Methyl Stretching and Deformation Modes for DMMP on Magnesia

T (°C)	ν_a (CH_3P)	ν_a (CH_3O)	ν_s (CH_3P)	ν_s (CH_3O)	surf-OCH_3	δ_a (CH_3O)	δ_a (CH_3P)	δ_s (CH_3P)
25	2994	2962	2927	2858		1465	1425	1317
50	2994	2960/51	2930	2856/48		1465	1425	1316
100	2994	2949	2931	2847	2805	1461	1426	1307
150	2992	2949	2930	2846	2805	1461	1426	1307
200	2991	2949	2930	2846	2805	1449	1426	1307
300	2987	2950	2927	2848	2805		1425	1308
300 + O2	2987		2926				1425	1309

At 100 °C, the 1249 cm^{-1} band is completely gone, and the intense 1187 cm^{-1} is assigned to a $\nu(PO_2)$ stretch vibration. While the 1187 cm^{-1} frequency is similar to that assigned to the $\rho(CH_3O)$ mode of DMMP, this absorption is relatively weak compared to the P═O absorption, as seen in Figure 1 for DMMP in hexane. Given the dominant nature of the absorption at 1190 cm^{-1} for DMMP on MgO, it is believed that most of the intensity of this band must come from a shifted PO_2 vibrational absorption. The growth of the new strong, narrow band at 1095 cm^{-1} is observed at this temperature. This group of bands is

TABLE 5: Phosphorus−Oxygen, Phosphorus−Carbon, and Carbon−Oxygen Modes for DMMP on Magnesia

25 °C	ν(P═O)	$\rho(CH_3O)$		ν(CO)	ν(CO)
(DMMP)	1249	1190		1061 sh	1041
100 °C	$\nu(PO_2)/\rho(CH_3O)$		$\nu(PO_2)$	$\nu(CO)/\nu(PO_2)$	
(MMP)	1187		1095	1060	
300 °C+ O_2	$\nu(PO_3)$			$\nu(PO_3)$	
(MP)	1132			1051	

stable until 200 °C and, with the loss of one methoxy group observed in the high-frequency region, is assigned to a surface-bound MMP. The 1095 cm^{-1} absorption is the most notable difference observed for this species on magnesia and the corresponding species on alumina. This difference in the spectra for what is nominally the same species on two different surfaces is probably due to different modes of coordination of the MMP species on the particular oxide surface.

Between 200 and 300 °C, the bands at 1089 and 1186 cm^{-1} decrease in intensity, until at 300 °C the 1089 cm^{-1} band has become just a shoulder on the strong 1056 cm^{-1} absorption and the 1186 cm^{-1} absorption has almost disappeared as a distinct peak. The 1308 cm^{-1} peak, characteristic of the phosphorus-bound methyl group, is still present. After the addition of oxygen, the spectral changes which were seen in the 300 °C spectrum are completed, and, with the data from the methyl vibrational modes, the spectrum of the adsorbed species is assigned to MP.

The overall shape of the absorption bands in the lower-frequency region of the methylphosphonate spectrum on magnesia is similar to that observed for methylphosphonate on alumina. Both of these spectra show a strong, broad absorption in the neighborhood of 1050 cm^{-1}, with a shoulder at higher frequency and a band due to the $\delta_s(CH_3P)$ vibration occurring at about 1309 cm^{-1}. The strong peak observed for magnesia occurs at 1051 cm^{-1} while that observed for alumina occurs at 1065 cm^{-1}. The shoulder is observed at approximately 1132 cm^{-1} in the case of magnesia, while the corresponding shoulder is observed at approximately 1190 cm^{-1} for alumina. This difference may well be due to differences in coordination. Table 5 lists the absorptions of the different surface species in the lower-frequency region, along with tentative assignments.

Li et al.[4] used photoacoustic spectroscopy to examine the same system and came to similar conclusions regarding the loss of the first methoxy group, i.e., that this group appears to be lost at approximately 200 °C. However, they proposed from their observations that one of the methoxy groups was still part of the fragment at 500 °C. A band assigned as the P−O−C stretching mode appears to be a consistent feature in the spectra, even after, as we have observed, complete elimination of the methoxy groups has occurred. Li et al. used this band as an indicator of the presence of a P−O−C group. However, as was discussed above, the P−C, P−O, and C−O vibrations of the fragments are strongly mixed; it is just coincidence that the methylphosphonate species has an absorption at a similar frequency. Li et al. did not examine the methyl stretching region and did not observe the clear indications for structural changes provided by these vibrational modes.

As in the alumina study above, an attempt was made to determine whether there is any evidence for adsorbed methanol. An experiment was carried out exposing pure MgO to methanol and evacuating. A band was observed in the methyl stretching region at 2808 cm^{-1} which is within the experimental resolution of the band observed in these experiments for DMMP on MgO at 2805 cm^{-1}. We assign this band to adsorbed methanol. Unfortunately, all of the other bands observed for MeOH on MgO overlap the much stronger bands due to DMMP or its fragments on MgO, so the assignment is somewhat tentative.

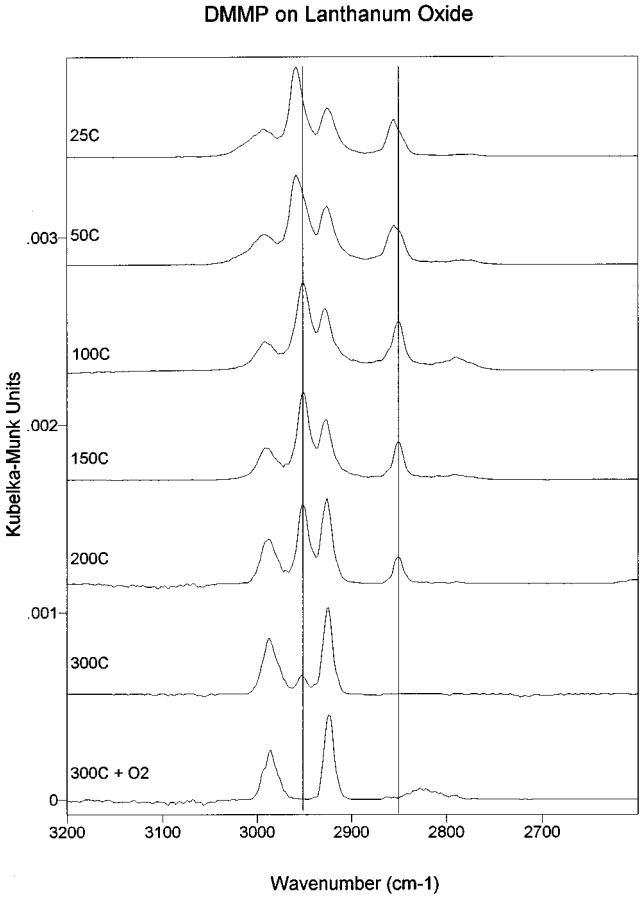


Figure 7. Methyl stretch region after adsorption of DMMP onto La_2O_3. Spectra are measured under vacuum at different temperatures as noted.

The other possible surface product from adsorbed methanol, an adsorbed formate species, would have a relatively strong band near 1600 cm^{-1} due to the antisymmetric COO mode, but such a feature is not seen in these spectra.

Lanthanum Oxide Adsorption. The changes which were observed for adsorption of DMMP on lanthanum oxide are very similar to those observed on magnesium oxide. The frequencies are slightly shifted for the lanthana-adsorbed species. The methyl stretch region is shown in Figure 7. The spectra in the lanthanum oxide stacked plots have been scaled individually to show the frequency shifts more clearly. It is clear that many of the same changes are observed for DMMP on lanthanum oxide as were observed on magnesia, at similar temperatures. The same type of shift in the methyl stretch region as the first methoxy group is lost is observed and is complete at the same temperature as was observed for MgO, and surface MMP is the stable form at 100 °C. After heating to 300 °C in vacuum almost all the methoxy groups are lost, a process which is completed by adding oxygen to the 300 °C sample. The phosphorus-bound methyl group remains attached to the DMMP fragment on the surface as in the results from alumina and magnesia above, indicated by the methyl stretching modes and the deformation mode at 1307 cm^{-1}. This evidence taken together indicates the formation of the surface-bound MP. A band is observed at 2780−2790 cm^{-1}, and, given the similarity in frequency to the feature seen on MgO, is assigned as a band due to a surface-bound methoxy group. Table 6 lists the methyl group absorptions of DMMP and its fragments on lanthanum oxide as a function of temperature.

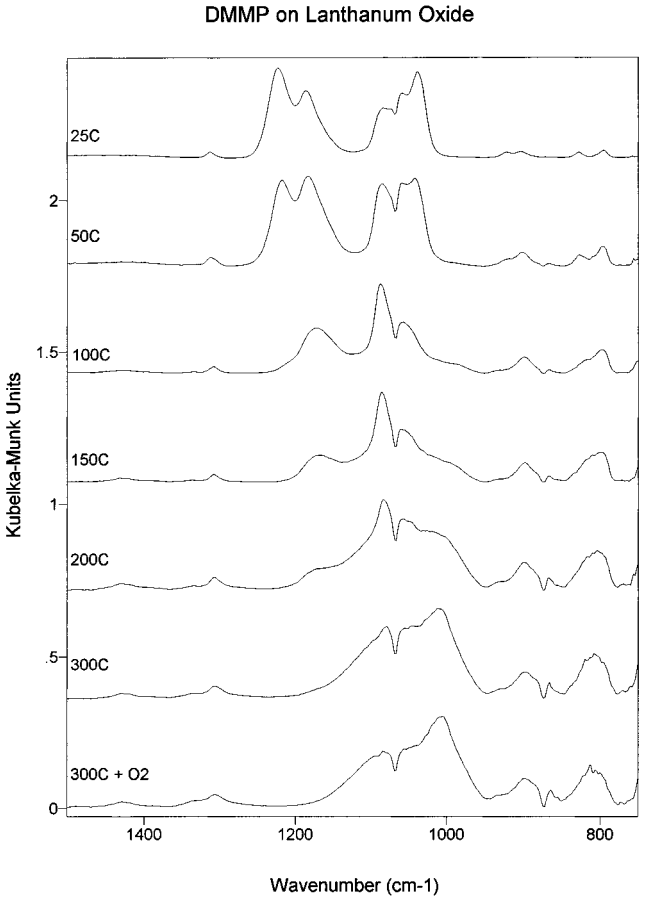


Figure 8. Lower-frequency region after adsorption of DMMP onto La_2O_3. Spectra are measured under vacuum at different temperatures as noted.

TABLE 6: Frequencies of Methyl Stretching and Deformation Modes for DMMP on Lanthana

T (°C)	$\nu_a(CH_3P)$	$\nu_a(CH_3O)$	$\nu_s(CH_3P)$	$\nu_s(CH_3O)$	surf-OCH_3	$\delta_s(CH_3P)$
25	2993	2959	2926	2856	2780 wk	1314
50	2992	2959	2927	2855	2783	1313
100	2991	2952	2928	2850	2790	1309
150	2990	2951	2927	2850	2790	1308
200	2987	2951	2926	2850	2789 wk	1307
250	2988	2952	2926	2850	2790 wk	1307
300	2988	2953	2925	2850		1307
300 + O_2	2987		2924			1307

The spectra for the lower-frequency region are shown in Figure 8. Two negative features in the spectra are sharp spectral features seen in the spectrum of lanthanum oxide itself. As the temperature increases, these features undergo intensity changes which are temperature-dependent, and the result is that these sharp features contribute negative features to the observed spectra.

It appears that there may also be two different adsorption sites on lanthanum oxide as was observed for magnesium oxide, since at room temperature, two different strong absorptions are seen for adsorbed DMMP. The difference in the interaction with the surface is probably due to a difference in the degree with which the phosphoryl oxygen interacts with acid sites on the surface. It is possible, though it cannot be proven, that the species responsible for the P═O absorption at 1224 cm^{-1} may be those interacting with O−H sites on the surface, while those with P═O absorptions at 1186 cm^{-1} may be those adsorbed at Lewis acid sites.

Overall, however, this region of the DMMP on lanthana spectra appear remarkably similar to those observed for DMMP on magnesia. The strong narrow feature observed at 1088 cm^{-1} in the spectra at 100−250 °C is similar to the absorption observed for DMMP on magnesia at 1095 cm^{-1}, and is apparently indicative of the methyl methylphosphonate surface structure, since it coincides with the loss of one methyl group. Table 7 lists the frequencies observed in the lower-frequency region for DMMP and the stable fragments of DMMP on lanthanum oxide with tentative assignments. Lanthanum oxide itself has a strong absorption band which spans the region 1300−1700 cm^{-1}. This strong absorption limits our ability to observe weak absorptions in this region, and thus the weak methyl deformation modes in this region are not noted in Table 7.

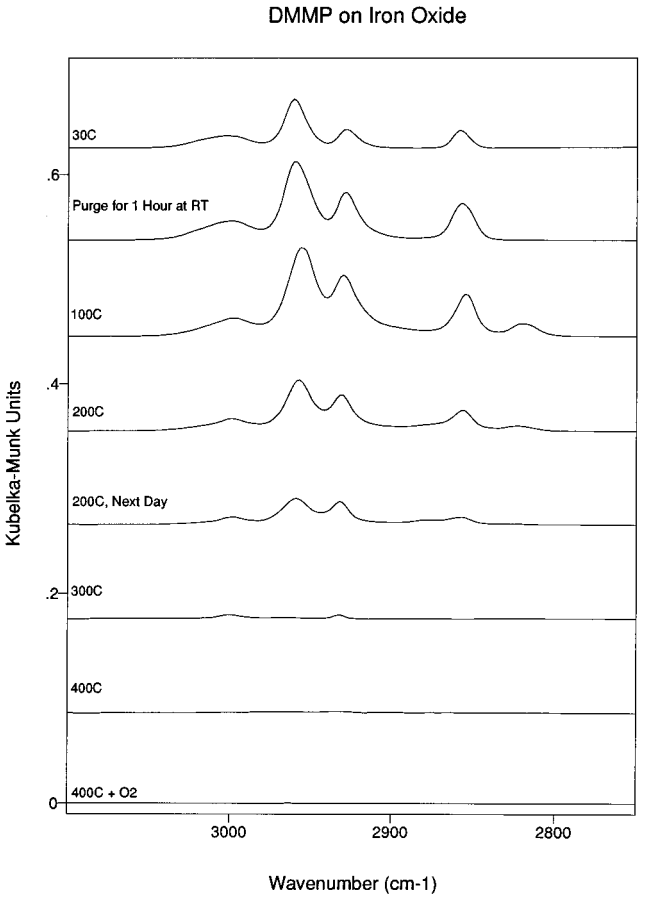


Figure 9. Methyl stretch region after adsorption of DMMP onto Fe_2O_3. Spectra are measured under vacuum at different temperatures as noted.

TABLE 7: Phosphorus−Oxygen and Phosphorus−Carbon Modes for DMMP on Lanthana

25 °C	ν(P═O)	$\rho(CH_3O)$		ν(CO)	ν(CO)	$\rho(CH_3P)$
(DMMP)	1224	1186		1058	1038	904
100 °C	$\nu(PO_2)/\rho(CH_3O)$		$\nu(PO_2)$	ν(CO)		$\rho(CH_3P)$
(MMP)	1174		1088	1061		899
300 °C + O_2	$\nu(PO_3)$				$\nu(PO_3)$	$\rho(CH_3P)$
(MP)	1099				1005	899

Iron Oxide Adsorption. The results from the iron oxide adsorption are different from those observed for the other systems. The methyl stretching region is shown in Figure 9, and what is observed is that the relative intensity of the bands remains approximately constant, and between 200 and 300 °C, virtually all the methyl groups are lost. At 300 °C, some very small fraction of the surface species still contain the phosphorus-bound methyl group as indicated by the bands at 3000 and 2932 cm^{-1}.

A band at 2820 cm^{-1} was also clearly observed at 100 °C. Experiments were carried out to determine whether this band could be due to the methyl stretching vibration of a surface-

TABLE 8: Frequencies of Methyl Stretching and Deformation Modes for DMMP on Iron Oxide

T (°C)	surf-O_2CH	$\nu_a(CH_3P)$	$\nu_a(CH_3O)$	$\nu_s(CH_3P)$	$\nu_s(CH_3O)$	surf-OCH_3	$\delta_a(CH_3O)$	$\delta_a(CH_3P)$	$\delta_s(CH_3P)$
30		3002	2960	2928	2858	2820 wk	1465	1419	1316
30 (1 h)	3071	3000	2960	2929	2857	2821 wk	1464	1418	1314
100	3072	2997	2955	2930	2854	2819	1455	1419	1311?
200	3073	2998	2957	2931	2857	2822		1418	1313?
300	3073	3000		2932		2820 br			
400									
400 + O_2									

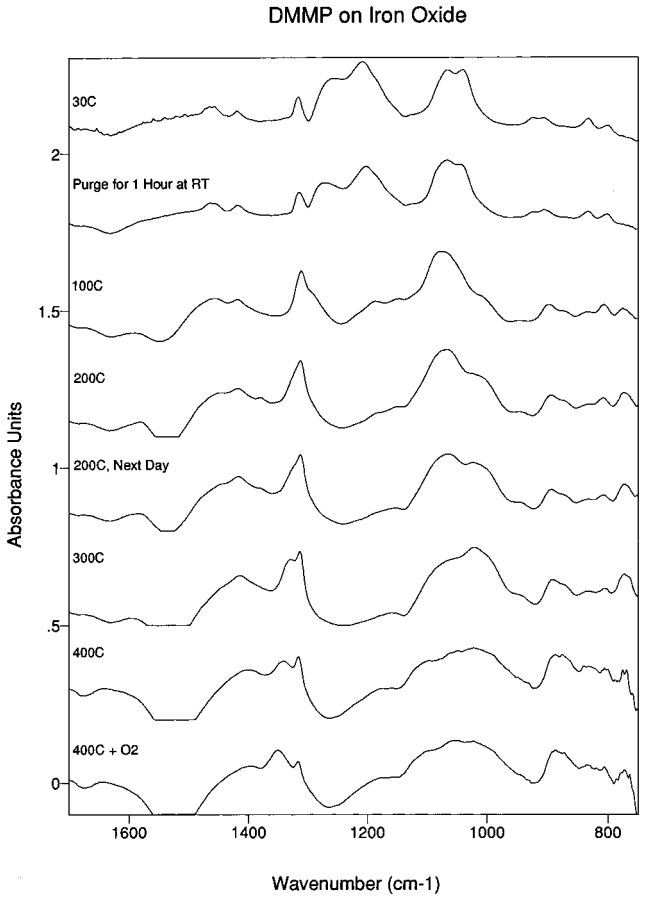


Figure 10. Lower-frequency region after adsorption of DMMP onto Fe_2O_3. Spectra are measured under vacuum at different temperatures as noted.

bound methoxy group. It was found that the most intense band of methanol adsorbed on iron oxide was the symmetric methyl stretch mode at 2820 cm^{-1}. As in the case of methanol on magnesia, all the other bands for adsorbed methanol overlap strong absorptions of DMMP or its products on iron oxide. And while the identification of an intermediate based on one absorption must be tentative, such an assignment is in agreement with other studies as described below. The intensity of this 2820 cm^{-1} surface-bound methoxy absorption reaches a maximum at 100 °C, and decreases with increasing temperature. One other band is observed in this region, at 3072 cm^{-1}. We speculate that this band is due to an adsorbed formate species, formed from the oxidation of the adsorbed methanol. Table 8 lists the methyl group frequencies observed for DMMP and its decomposition products on iron oxide as a function of temperature.

In the lower-frequency region, Figure 10, dramatic changes are also observed. Immediately after adsorption, the "normal" DMMP bands are observed. Purging for 1 h with N_2 does not change the spectrum significantly. As the sample is heated from room temperature, the spectrum evolves as can be seen in Figure 10. A strong negative feature is observed in the spectra at about

TABLE 9: Phosphorus−Oxygen and Phosphorus−Carbon Modes for DMMP on Iron Oxide

T (°C)	2nd site?	ν(P═O)	ν(CO)	ν(CO)	$\nu(PO_2)$	$\rho(CH_3P)/\nu(PO_2)$
30	1255	1208	1065	1041		906
30 (1 h)	1271	1202	1066	1044		906
100	1294	1186	1077			898
200	1326	1150 sh	1067		1018	895
300	1343	1158	1060 sh		1021	893
400	1352	1170			1020	881
400 + O_2		1164 sh			1038 br	885

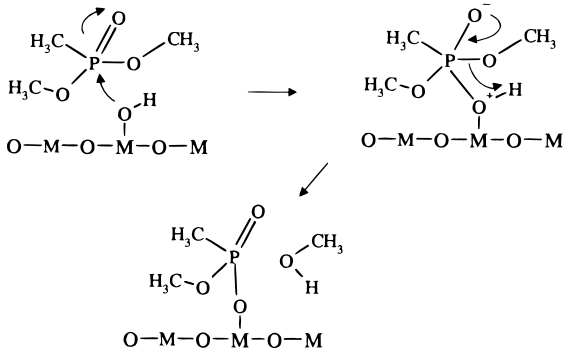
1525 cm^{-1}. This corresponds to an absorption feature of pure iron oxide which is observed in the absence of DMMP at this frequency and which undergoes changes in intensity as the temperature changes. We speculate that this negative feature may be due to the loss of surface Fe−O−Fe or Fe−OH species brought about by the adsorption of DMMP. The evolution of the bands between 1300 and 1000 cm^{-1} is due to the evolution of the surface phosphonate. Table 9 lists the frequencies of the observed absorptions in the lower-frequency region.

On iron oxide, the 1316 cm^{-1} band is a poor indicator of the presence of the phosphorus-bound methyl group. In the spectra of DMMP on the other oxides, the presence of an absorption at this frequency was a clear indicator of the presence of the CH_3−P bond, since the $\delta_s(CH_3P)$ vibration occurs at this frequency. However, at temperatures above room temperature, it is not clear how much this vibration is contributing to the absorption intensity at this frequency. It clearly cannot be responsible for all of the intensity at this frequency, since the intensity increases very dramatically at 100 °C, yet it does contribute some, presumably, since the integrity of the P−CH_3 bond is indicated by the observed stretching modes. However, above 300 °C an absorption is observed at this frequency which cannot be due to the $\delta_s(CH_3P)$ mode since all the CH_3 groups have been eliminated from the surface, as indicated by the lack of absorption in the methyl stretch region.

One of the difficulties associated with the spectra of DMMP on iron oxide is reconciling the large differences observed in the 1600−800 cm^{-1} region as the temperature is changed from room temperature to 100 °C, with the apparent lack of significant change in the methyl stretching region during that same temperature change. The evolution of DMMP on iron oxide apparently involves a much different intermediate than that observed in the case of the other oxides. As the temperature increases from 100 to 200 °C, approximately half of the intensity of *all* the methyl stretching vibrations is lost. After cooling to room temperature overnight in vacuum and reheating to 200 °C the next day, some additional intensity is lost in the methyl stretch region. And virtually all of the rest of the methyl groups are lost by 300 °C. What is interesting is that intensity is lost in the methyl stretching region with little or no apparent specificity for the phosphorus-bound methyl group or, especially, for the methoxy groups, as was seen for the other oxides.

In light of the observed spectra, it is likely that the strong absorption at 1077 cm^{-1} observed at 100 °C is due to a strongly shifted P═O vibration, the result of the P═O group interacting

SCHEME 2: Nucleophilic Attack of the Surface on DMMP



strongly with a Lewis acid site on the surface. At least initially, this interaction apparently does not involve any methyl groups, since most of the intensity in the methyl stretch region remains at frequencies near those of uncomplexed DMMP. One interpretation of these results is that the complex involves the unidentate coordination of the DMMP to the surface through the P═O bond.

There also appears to be a contribution from a second type of interaction mechanism. This is indicated by an absorption at 1255 cm^{-1} in the spectra of initially adsorbed DMMP, which is no doubt due to a shifted P═O vibration due to its proximity to the P═O stretch in neat DMMP or DMMP in hexane. This absorption appears to shift to 1277 cm^{-1} after 1 h in flowing nitrogen and may even account for the strong feature at approximately 1326 cm^{-1} (and higher frequencies as the temperature increases) that overlaps the 1313 cm^{-1} $\delta_s(CH_3P)$ mode at 200 °C. Insight into the nature of the interaction of the second adsorption site with DMMP is provided by the direction of the shift of the P═O vibration. The observed shift is to higher frequency, and one likely adsorption interaction which would lead to an increase in the P═O frequency as opposed to a decrease is adsorption that involves nucleophilic attack of surface OH groups at the phosphorus atom of the DMMP. This type of interaction can then proceed to the formation of a stable surface intermediate as shown in Scheme 2. The importance of the formation of two different types of adsorbed surface species and the different roles that they play in the decomposition is not clear from the current study and is the subject of further investigation.

After adsorption of DMMP on the surface, subsequent steps in the decomposition of DMMP on the surface, which occur between 100 and 200 °C, involve the loss of the methyl groups, with no apparent selectivity for either the methoxy methyl groups or the phosphorus-bound methyl group. From the spectra reported here, it is not possible to determine whether the P−O or the O−C bond of the methoxy methyl groups is cleaved.

Henderson et al.[9] examined the interaction of DMMP with iron oxide using temperature-programmed desorption and Auger electron spectroscopy (TPD/AES). They observed that DMMP adsorbs strongly at 170 K (−103 °C), with molecular desorption occurring only after very high doses of DMMP were applied, and that one of the first bonds cleaved is the P−CH_3 bond, occurring at temperatures as low as 247 K (−26 °C). They also suggest that one of the P−OCH_3 bonds is broken upon adsorption as well. Decomposition products were observed on heating the iron oxide to approximately 300 °C. No decomposition products were observed to evolve from the surface before this temperature, which meant that those fragments that did form remained on the surface. Their interpretation of their results is that when DMMP adsorbs on iron oxide, a surface phosphonate and 1−2 surface methoxy groups are formed. Further decomposition occurs on heating to temperatures in excess of 300 °C, leading to the formation of bulk phosphate, and no remaining carbon-containing species on the surface. No phosphorus-containing fragments were observed to evolve from the surface at any temperature.

The results of Henderson et al. agree with the current study with regard to the formation of surface-bound products. In the current study, however, some loss of the surface-bound methoxide is seen below 200 °C, due to the decrease in the intensity of the surface methoxide C−H stretching mode at 2820 cm^{-1}. A model which is consistent with both sets of results is the oxidation of the surface methoxide species to form a surface formate species at temperatures less than 300 °C. Above 300 °C, the surface methoxide and surface formate species then evolve from the surface, presumably as methanol and formic acid.

One of the most interesting observations regarding the interaction of DMMP on iron oxide is the fact that this surface oxidizes the P−CH_3 bond between 200 and 300 °C under vacuum, whereas the other three oxides studied could not accomplish this oxidation even upon heating to higher temperatures or adding oxygen.

The observations of the current study regarding the mode of decomposition of DMMP on Al_2O_3, MgO, and La_2O_3 are consistent with a nucleophilic displacement reaction, with surface hydroxyl or oxide groups acting as the nucleophile, displacing the H_3CO^- groups. The initial step in the reaction corresponds to the initial step in the electrophilic catalysis of nucleophilic displacement reactions, with the surface metal atom acting as a Lewis acid that coordinates with the phosphoryl oxygen.[55] Overall, though, the surface is not acting as a true catalyst since the nucleophile replacing the methoxide group is attached to the surface and reaction products block surface adsorption sites. In homogeneous systems, this mechanism would easily account for the fact that the loss of the methoxy groups occurs much more easily than does the loss of the methyl group: the H_3CO^- group is a much better leaving group than is the H_3C^- group. A similar argument no doubt holds for these heterogeneous systems.

The nucleophilic displacement path is also available on the Fe_2O_3 surface, but this surface can participate in another mode of decomposition. Because of the availability of multiple oxidation states for the iron atom, Fe(II) and Fe(III), the iron oxide surface can act as an oxidation catalyst via the Mars and Van Krevelen mechanism.[56]

$$Fe_2O_3 + 2e^- \rightarrow 2FeO + O^{2-}$$

$$(H_3CO)_2P(O)-CH_3 + O^{2-} \rightarrow (H_3CO)_2P(O)^-_{ads} + H_3CO^-_{ads}$$

$$2FeO + {}^1/_2O_2 \rightarrow Fe_2O_3$$

Lattice oxygen from the surface oxidizes the adsorbed DMMP to form the products. Gas-phase oxygen is reduced at the surface and replaces the lattice oxygen as a final step in the sequence. In this way, the iron oxide surface provides a low-energy pathway for the oxidative cleavage of the P−CH_3 bond, a path which is not available on the Al_2O_3, MgO, and La_2O_3 surfaces.

One way of comparing the abilities of the different oxides for participation in this latter process is by examining their corresponding half-reactions. The reduction potential for $Fe^{3+} + e^- \rightarrow Fe^{2+}$ is 0.77V, relative to the standard hydrogen

electrode, making the Fe(III)/Fe(II) couple a good candidate for oxidizing an adsorbate. The corresponding half-reactions on the other three oxides all involve multielectron transfers and are $E°(Al(III)/Al) = -1.66$ V, $E°(Mg(II)/Mg) = -2.36$ V, $E°(La(III)/La) = -2.52$ V. These values indicate that aluminum, lanthanum, and magnesium oxides are much less likely than iron oxide to oxidize an adsorbate via a mechanism which involves a change in the oxidation state of the metal because the energy barriers are much higher.

Conclusion

The decomposition behavior of DMMP on metal oxides can be most easily examined with infrared spectroscopy by studying the methyl stretching modes. The decomposition proceeds on alumina, magnesia, and lanthana via very similar paths. The first step is coordination on the surface through the P═O bond to acidic surface sites. Subsequently, stepwise loss of the two methoxy groups is observed, with the presumed evolution of methanol from the surface. In the case of magnesia, evidence is seen for the formation of a surface methoxy group which is lost when oxygen is added at 300 °C. Evidence is found for the formation of surface methoxy groups on both magnesia and lanthana. The integrity of the $P-CH_3$ bond is not compromised even on heating to 300−400 °C in oxygen.

On iron oxide, the interaction of the surface with DMMP appears to proceed in a different fashion. The complex formed between the surface and the P═O bond is much stronger, since the P═O vibration appears to shift to 1077 cm^{-1} at 100 °C, compared to a shift to 1172 at 100 °C on lanthana. Additionally, there is indication of the formation of a second type of complex, one involving the nucleophilic attack of a surface OH group at the phosphorus atom of DMMP. However, even at 100 °C, no elimination of a significant fraction of the methyl groups is indicated by a loss of intensity, unlike on magnesia or lanthana surfaces, where by 100 °C, one methoxy group had already been eliminated. Decomposition takes place on the iron oxide surface at 100 °C and even more strongly by 200 °C, as indicated by the loss of intensity in the methyl stretching region and the formation of the surface methoxy groups; however, there is no apparent selectivity for either the methoxy groups or the phosphorus-bound methyl group. On iron oxide, all the carbon-containing species appear to be eliminated from the surface by 300 °C. We believe that the oxidation of the $P-CH_3$ bond of DMMP on iron oxide is made possible by the participation of the Fe(III)/Fe(II) couple.

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