

where the matrix elements  $M_{ij}$  are very complicated functions of  $\beta$ ,  $\gamma$ ,  $\eta$ ,  $\sin 2\theta$ , and  $\cos 2\theta$ . The light intensity at the detector is

$$I_d(0) = \frac{1}{2}e^{-2A}[(P_x^2 + P_y^2)[M_{00} + M_{02} \sin(\delta + \alpha) - M_{03} \cos(\delta + \alpha)] + (P_x^2 - P_y^2)[\sin 2a[M_{10} + M_{12} \sin(\delta + \alpha) - M_{13} \cos(\delta + \alpha)] + \cos 2a[M_{30} + M_{32} \sin(\delta + \alpha) - M_{33} \cos(\delta + \alpha)]] \quad (68)$$

The  $W_m$  and dc components of the electric signal are

$$V_{ac}(0^\circ, W_m) = (4K/\pi)[(P_x^2 + P_y^2)M_{02} + (P_x^2 - P_y^2)[M_{12} \sin 2a + M_{32} \cos 2a] \cdot [J_1 \delta_m^\circ \sin W_m t \cos \alpha + J_2 \delta_m^\circ R(2W_m) \sin \alpha] - [(P_x^2 + P_y^2)M_{03} + (P_x^2 - P_y^2)(M_{13} \sin 2a + M_{33} \cos 2a)][J_2 \delta_m^\circ R(2W_m) \cos \alpha - J_1 \delta_m^\circ \sin W_m t \sin \alpha] \quad (69)$$

$$V_{dc}(0) = (P_x^2 + P_y^2)[M_{00} + M_{02}J_0 \delta_m^\circ \sin \alpha - M_{03}J_0 \delta_m^\circ \cos \alpha] + (P_x^2 - P_y^2)[[M_{10} + M_{12}J_0 \delta_m^\circ \sin \alpha - M_{13}J_0 \delta_m^\circ \cos \alpha] \times \sin 2a + [M_{30} + M_{32}J_0 \delta_m^\circ \sin \alpha - M_{33}J_0 \delta_m^\circ \cos \alpha] \cos 2a] \quad (70)$$

The output to the recorder,  $CD_r = V_{ac}(W_m)/V_{dc}$ , is not equal to zero. Thus, there is the apparent CD spectra having no relation to the CD in any aspects. The rotation of the helical pile around the light beam induces no "CD" sign change in the apparent CD spectra because of its helical structure. Thus, we can never conclude from the apparent CD spectra that the optically inactive

molecules become chiral when dissolved in cholesteric liquid crystals.

### Conclusion

The above considered cases show clearly that there may be several obscure points in LCICD data reported so far in the literature. We cannot deny completely the possibility that achiral molecules become optically active in cholesteric liquid crystals. But the apparent CD spectra observed in cholesteric liquid crystals with commercially available CD spectrophotometers can generally not provide us with the proof that the optical activity is induced in achiral molecules. Other methods besides CD spectroscopy are therefore necessary to confirm experimentally the presence of the induced optical activity in optically inactive molecules.

Finally, let us give a bit of advice to persons who intend to study induced CD in possibly anisotropic systems. Read the book on polarized light,<sup>8</sup> a paper on the Mueller matrix approach to the polarization-modulation spectroscopy,<sup>4,17</sup> and a number of papers on problems of CD spectropolarimeters<sup>2,3,6,7,9,10</sup> before starting work. We believe it is essential to fully understand the real meanings of the signal which will be observed.

We are going to comment on fluorescence detected circular dichroism in the next paper.

**Acknowledgment.** This work was supported, in part, by research grants (56540254) to Fukui University from the Ministry of Education and Culture. We are grateful to K. Mizuno for her helpful advice and assistance.

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## Adsorption and Decomposition of Dimethyl Methylphosphonate on an Aluminum Oxide Surface

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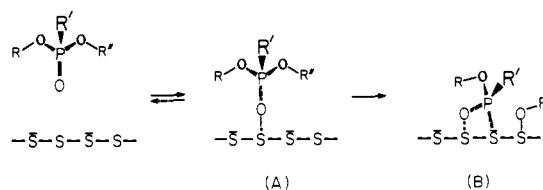
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**Abstract:** The adsorption of gaseous dimethyl methylphosphonate (DMMP) on aluminum oxide film surfaces has been investigated with inelastic electron tunneling spectroscopy. Surface temperatures ranged between 200 and 673 K, and exposures ranged between  $3 \times 10^{-4}$  and 10 torr-s. Tunneling spectra of deuterium-labeled DMMP, methyl alcohol- $d_4$ , methyl methylphosphonate, methylphosphonic acid, and trimethylphosphine oxide, all adsorbed on aluminum oxide surfaces, were used to clarify the structures of the species resulting from the adsorption and decomposition of DMMP. At 200 K, DMMP is adsorbed molecularly with high surface coverages. At surface temperatures above 295 K, DMMP is adsorbed dissociatively in low coverages. Surface temperatures above 473 K lead to the dealkylation of the adspecies, resulting in the formation of adsorbed methylphosphonate.

### I. Introduction

The interaction between phosphonate esters and aluminum oxide surfaces is important in two contexts. Not only does it elucidate the surface chemistry of phosphorus/metal oxide systems but it also serves to clarify the chemical nature of the aluminum oxide surface. Perhaps the foremost method for probing surface properties of oxides is through the use of adsorbates. The adsorptions of Lewis and Brønsted bases, such as pyridine and ammonia, were among the first methods used to probe the acid/base properties of aluminum oxide.<sup>1</sup> However, adsorption studies are by no means limited to examining acid/base properties. For example, the adsorption of alcohols, aldehydes, and ketones has been used to demonstrate the nucleophilic character of oxygen atoms on aluminum oxide.<sup>2-4</sup> The adsorption of phosphonate

### Scheme I



esters can potentially add to the overall understanding of surface chemical properties and their interrelation, since these esters can serve as Lewis bases, modifiers of surface acidity, and/or centers for nucleophilic substitution. For example, the phosphonate ester

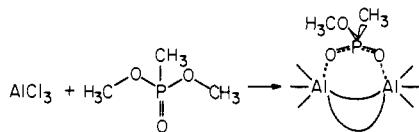
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Scheme II



might react with the aluminum oxide in at least three ways: (1) the electron-rich phosphoryl oxygen could simply form an adduct with a Lewis acid surface site; (2) the adsorbed phosphonate ester might modify the surface acidity, as is observed with other phosphorous compounds;<sup>5</sup> and/or (3) the phosphorus center of the phosphonate ester might be subject to nucleophilic attack by the surface oxygens. Although this is an incomplete list, it serves to show that by determining the type of interactions and when they occur, important information concerning the dominant chemical processes on the aluminum oxide surface will be learned.

Previous infrared spectroscopic studies of the adsorption of phosphonate esters suggest two forms of adsorption, molecular and dissociative.<sup>6,7</sup> These are shown respectively in Scheme I, A and B. Here, the simplified surface is shown consisting of two types of sites, S and  $\bar{S}$ . In addition, note that the dissociative adsorption reaction (Scheme IB) is presumed to occur through cleavage of the phosphorus–oxygen bond, but this will depend in general on the specific nature of the surface. In the infrared studies, the structural determination is usually made on the basis of the observed vibrational frequencies for the phosphoryl stretching mode and/or the phosphorus oxygen stretching vibrations, since these shift characteristically upon complex formation.<sup>8–10</sup> The adsorption of diisopropyl methylphosphonate,  $[(CH_3)_2CHO]_2(CH_3)P(O)$ , and dimethyl methylphosphonate,  $(CH_3O)_2(CH_3)P(O)$ , onto powdered  $FeCl_3$  at 295 K was found to produce only a molecularly adsorbed species as in Scheme IA.<sup>6</sup> Similarly, adsorption of diisopropyl methylphosphonate (DIMP) onto undehydroxylated alumina powders at 295 K was found to produce a molecularly adsorbed species.<sup>7</sup> However, in addition, a low concentration of the dissociatively adsorbed species was also present on this surface (Scheme IB).

Homogenous analogues to the molecularly and dissociatively adsorbed species have been isolated.<sup>8–10</sup> Here, since we are specifically interested in aluminum oxide surfaces and dimethyl methylphosphonate (DMMP), two of these homogeneous analogies are worth mentioning. In the  $[Al^{3+}(DMMP)_6](ClO_4^-)_3$  complex,<sup>8</sup> the phosphonate ester molecule is weakly bound to the aluminum cation via a Lewis acid/Lewis base bond between the metal cation and the phosphoryl oxygen (the oxygen of the  $O=P$  bond). Thus, this complex embodies the type of coordination analogous to Scheme IA that might be observed on the aluminum oxide surface.

On the other hand, when DMMP is added to anhydrous  $AlCl_3$ , a violent reaction ensues, which produces polymeric  $Al(CH_3O)(CH_3)PO_2$  and liberates gaseous  $ClCH_3$ , as indicated in Scheme II.<sup>9,10</sup> The bonding in this complex exhibits the type of coordination analogous to Scheme IB that might be observed on the aluminum oxide surface.

## II. Experimental Procedures

**1. Adsorbates.** Dimethyl methylphosphonate  $[(CH_3O)_2(CH_3)P(O)]$  (97+%) and methanol- $d_4$  ( $CD_3OD$ ) (99+%) were obtained from Aldrich Chemical Co. Methylphosphonic acid  $[CH_3P(O)(OH)_2]$  (98%) was obtained from Alfa Products. Trimethylphosphine oxide  $[(CH_3)_3P(O)]$  was obtained from Strem Chemicals. Except for the dimethyl methylphosphonate, to which a minute amount of sodium carbonate was added to remove any traces of formic acid, all were used without further purification.

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Deuterated dimethyl methylphosphonate  $[(CD_3O)_2(CH_3)P(O)]$  was synthesized by a standard procedure from  $CD_3OD$  and methylphosphonic dichloride  $[CH_3P(O)Cl_2]$ .<sup>11,12</sup> The methylphosphonic dichloride was obtained from Alfa Products and used without further purification. The synthesis was initiated by dissolving the  $CH_3P(O)Cl_2$  in anhydrous diethyl ether. Two equivalents of dry distilled pyridine were added, and the  $CD_3OD$  was added dropwise while the reaction mixture was stirred and maintained at room temperature. After 24 h, the liquid was decanted and the ether flash-evaporated to give the crude  $(CD_3O)_2(CH_3)P(O)$ , which was then purified further by distillation under an aspirator-produced vacuum. The purity of the final product was confirmed with  $^1H$  NMR. Depolarized Raman spectra were taken of labeled and unlabeled neat samples of the dimethyl methylphosphonate esters in order to characterize the vibrational modes of the molecular species.

Methyl methylphosphonate,  $(CH_3O)(CH_3)P(O)(OH)$ , was synthesized by partial hydrolysis of dimethyl methylphosphonate in an aqueous sodium hydroxide solution.<sup>12,13</sup> The preparation method was a modified version of previously published procedures for monoester synthesis and methyl methylphosphonate synthesis. To 150 mL of a 10% base solution (0.375 mol of NaOH), 0.140 mol of dimethyl methylphosphonate was added. The mixture was refluxed gently for 5 h. The cooled solution was acidified to pH  $\approx$  2 and vacuum distilled until NaCl precipitated strongly. This mixture was then heavily acidified with concentrated HCl (total HCl added to this point 0.375 mol). The concentrated acid/salt solution was then extracted several times with reagent grade acetone, the salt was filtered out, and the extract was dried several hours over anhydrous  $CaSO_4$ . The acetone extract was then flash-evaporated, and the concentrated product was distilled under vacuum at 143 °C to give the purified product. Yields of this procedure were approximately 20%, and  $^1H$  NMR<sup>12</sup> and IR indicated the purity to be greater than 95%. The methyl methylphosphonate was stored in a freezer until needed.

**2. Tunnel Junction Fabrication Procedures.** Typically, tunnel junction fabrication was begun by the evaporation of an 800 Å thick aluminum film from a tungsten coil onto a Corning 7059 borosilicate glass substrate. The base pressure prior to evaporation was below  $10^{-8}$  torr, and the film thickness was monitored by a quartz crystal microbalance. Deposition rates were approximately 10 Å/s. A cohesive oxide barrier was then grown on the aluminum film by an oxygen–water plasma discharge ( $O_2:H_2O \sim 100:1$ ) with pressures during the discharge of approximately 200  $\mu$ m. The oxygen plasma was formed by an ionizing field of 100 kV/m, and the oxidation time was on the order of 350 s. Tunneling barriers with acceptable current–voltage characteristics could not be grown in the UHV environment without the presence of small concentrations of water in the oxygen plasma atmosphere. Pumpdown was followed by exposure to the vapor phase of the adsorbate. During this step, the technique developed by Bowser and Weinberg<sup>14</sup> for simultaneous heating and temperature measurement was used to heat the aluminum film and thus also the thin aluminum oxide film. Briefly, this method of temperature control employs the temperature dependence of the resistance of the aluminum film to provide the temperature measurement. In order to obtain reproducible results, it was necessary first to anneal the aluminum film at moderate temperatures ( $\sim$ 500 K), and this was done prior to growth of the oxide barrier. Typical exposures for both heated and room-temperature work ranged from  $1 \times 10^{-4}$  torr for 1000 s to  $1 \times 10^{-3}$  torr for 1000 s.

In most cases, the adsorbate vapor was exposed to the aluminum oxide after the latter had attained the desired temperature. However, some experiments were carried out by dosing the surface at room temperature and subsequently heating the surface in a vacuum of approximately  $5 \times 10^{-6}$  torr. Junctions prepared by different methods were qualitatively similar, although apparent differences are discussed below.

Following exposure to the adsorbate the substrates were cooled to 295 K, and 2000 Å of lead were evaporated at a pressure below  $1 \times 10^{-6}$  torr in a cross strip pattern to form the completed junction. In order to measure their current–voltage characteristics, junctions were removed from the vacuum system and mounted for immersion in liquid helium. All measurements were carried out in liquid helium at 4.2 K with PDP 11/10 digitally controlled electronics.<sup>15</sup> The spectra were accumulated through multiple scan averaging, typically on the order of several hundred separate scans. The data were then processed as follows: (1) the spectra

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were first smoothed by a cubic convolute;<sup>16</sup> (2) an attempt was made at background removal (only linear functions of voltage were used to fit the background); (3) the peaks were located by a least-squares fit of the first derivative, followed by an interpolated location of the first derivative zero crossings; and (4) peak energies were corrected for the lead superconducting band gap and for modulation effects on the band gap width.<sup>17</sup>

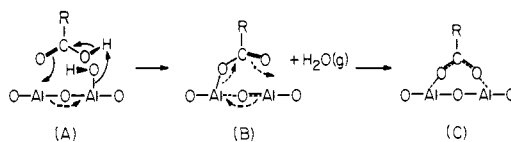
In some instances, adsorption was carried out on substrates at temperatures of approximately 200 K. These temperatures were attained by using liquid nitrogen to cool the cold fingers to which the substrate holders were attached. Special precautions were taken to ensure that the cooled aluminum oxide surfaces were not exposed to other readily condensable gases, and typical base pressures before dosing the surface were below  $2 \times 10^{-8}$  torr. Exposures to the vapor of the adsorbate ranged between 100 and 2000 L for the phosphorus compounds to 20000 L for perdeuteriomethanol [1 Langmuir (L) =  $1 \times 10^{-6}$  torr-s]. In most of the low-temperature adsorption experiments, the lead counterelectrode was evaporated while the substrates were still at low temperature. The junctions were then allowed to warm to room temperature prior to removal from the vacuum chamber. Subsequent mounting and measurement of these junctions were identical with that described above.

The methyl methylphosphonate and methylphosphonic acid possessed such low vapor pressures that they were unsuitable for vapor-phase dosing. Consequently, it was necessary to contact the aluminum oxide with a solution of the adsorbate dissolved in an appropriate solvent. To accommodate this, the fabrication procedure outlined above was modified in the following way. After the aluminum oxide barrier was formed, the vacuum chamber was vented to atmospheric pressure with high-purity nitrogen and a small drop of the adsorbate solution was placed on the aluminum oxide surface. Then, the vacuum chamber was sealed and evacuated with cryosorption pumps, followed by a liquid nitrogen trapped diffusion pump.<sup>18</sup> The remaining steps of the fabrication procedure were carried out normally. The modified adsorption procedure kept contamination to a minimum since the vacuum chamber remained open to atmosphere for only 5 to 7 min. During this time, the solvent would evaporate either completely or partially. A slightly more controlled version of this procedure has been used routinely in several laboratories for studying adsorption on aluminum oxide surfaces.<sup>19</sup> Furthermore, studies have indicated that several common solvents can be used that will insignificantly perturb the tunneling spectrum of the chemisorbed species as compared to the spectrum obtained by vapor exposure.<sup>20</sup> For studying methylphosphonic acid adsorption, a dilute solution was prepared with distilled water. For methyl methylphosphonate, spectroscopic grade hexane was the preferred solvent. Clean junctions dosed with either solvent showed negligible amounts of contamination.

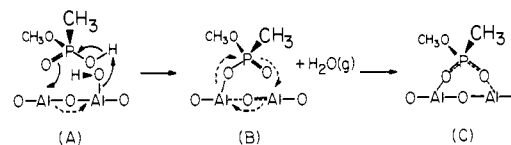
### III. Results and Discussion

**1. Identification of the Adsorbed Species.** This section deals with the identification of the surface species resulting from the adsorption of DMMP. Section III.1.a examines the adsorption of methyl methylphosphonate (MMP) since the adsorbed form of this compound is identical with that which is produced by the dissociative adsorption of DMMP. Consequently, the tunneling spectrum of adsorbed MMP will give the spectral signatures to identify the dissociatively adsorbed form of DMMP. In section III.1.b the tunneling spectrum of adsorbed MMP is compared with the tunneling spectrum of DMMP adsorbed at 200 K. Although the comparison suggests that DMMP is molecularly adsorbed at 200 K, due to the weak electron-vibration coupling constant of the phosphorus-oxygen bond, further work was needed. Therefore, as will be discussed in section III.1.c, isotopically labeled DMMP is used in further adsorption experiments. These experiments lead to the definitive conclusion that DMMP adsorbs molecularly at 200 K, probably by formation of an acid-base adduct with a surface hydroxyl. On the other hand, as discussed in section III.1.d, it is also evident that between 295 and 473 K the adsorption of DMMP is dissociative. Adsorption experiments with trimethylphosphine oxide (TMPO) are useful in this determination, as is discussed also in section III.1.d. The identification of other fragments of dissociative adsorption (primarily a surface meth-

#### Scheme III



#### Scheme IV



oxide) is undertaken in section III.1.e. In section III.2, the discussion concerns the temperature- and exposure-dependent interrelations among these surface species.

**a. A Model for the Dissociatively Adsorbed Species: Adsorbed Methyl Methylphosphonate.** In order to determine whether DMMP adsorbs dissociatively on the aluminum oxide, it is essential to know the spectral signatures of the dissociative adspecies. Although good estimates of these can be obtained, for example, from the infrared spectrum of the analogous homogeneous organometallic complexes, it is far better to take a "model" compound that is known to adsorb as the species in question and to prepare a tunneling spectrum of this adsorbed model compound. Methyl methylphosphonate is such a model compound, as may be determined most simply by analogy with the adsorption chemistry of carboxylic acids on aluminum oxide.

The chemisorption of carboxylic acids on aluminum oxide has been studied extensively both with infrared spectroscopy<sup>21</sup> and with tunneling spectroscopy.<sup>22-24</sup> Chemisorption proceeds dissociatively at 295 K, and the resulting adspecies has been identified as the symmetrical, bidentate bridging carboxylate anion of the corresponding carboxylic acid.<sup>24</sup> The chemisorption reaction is thought to proceed via Scheme III. There are two parameters of obvious importance in Scheme III first, the geometrical match between the oxygen-to-oxygen distance of the carboxylate group and the oxygen-to-oxygen distance of the aluminum oxide lattice, and second, the dissociation constant of the acid. Since the dissociation constant for methyl methylphosphonate [ $pK_a \approx 2.37^{12}$ ] exceeds the dissociation constant for carboxylic acids [ $pK_a \approx 4.5^{25}$ ] and the oxygen-to-oxygen distance of the phosphonate anion [ $2.44 \text{ \AA}^{26}$ ] is comparable to the oxygen-to-oxygen distance of the carboxylate anion [ $2.20 \text{ \AA}^{27}$ ], it is entirely plausible that the chemisorption of MMP proceeds in a fashion analogous to the chemisorption of carboxylic acids as illustrated in Scheme IV. Accordingly, MMP adsorbs dissociatively on aluminum oxide with the loss of a proton and the formation of the symmetrical, bidentate bridging methyl methylphosphonate adspecies [Scheme IV C]. The dissociated proton either combines with a surface hydroxyl to form water (as shown in Scheme IV) or attaches to an oxygen anion to form a surface hydroxyl.

Spectroscopic evidence supports a reaction such as Scheme IV, where adsorbed methyl methylphosphonate is the predominant surface species. From the tunneling spectrum of MMP adsorbed on aluminum oxide (see Figure 1a and Table I), it is apparent that both the  $(\text{CH}_3)\text{-P}$  and the  $(\text{CH}_3)\text{-O-P}$  linkages of the adsorbate remain intact following adsorption. At the same time, the near negligible intensity of the  $(\text{P})\text{-O-H}$  stretching mode near

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Table I<sup>a</sup>

DMMP(l) Raman	DMMP/Al <sub>2</sub> O <sub>3</sub> 200 K; IETS	assignments DMMP/DDMMP	DDMMP/Al <sub>2</sub> O <sub>3</sub> 200 K; IETS	DDMMP(l) Raman	MMPA/Al <sub>2</sub> O <sub>3</sub> 295 K; IETS
3022		$\nu_a[(O)CH_3]$			
2999	2981	$\nu_a[(P)CH_3]$	2980	2997	2983
2957P		$\nu_s[(O)CH_3]$			
2928P	2912	$\nu_s[(P)CH_3]$	2912	2928P	2917
2852P	2843	$\nu_s[(O)CH_3]$			2840
			2252	2821 w	
			2195	2265	
			2137	2211P	
			2074	2133P	
				2082P	
1466/1454	1452	$\delta_a[(O)CH_3]$			1453
1421		$\delta_s[(O)CH_3]$			
	1409	$\delta_a[(P)CH_3]$	1408	1421	1409
1313	1308	$\delta_s[(P)CH_3]$	1310	1318 vw	1307
1240P		$\nu[P-O]$	1217	1248P	
1186P	1177	$\rho[(O)CH_3]$			1182 sh
1170	1166				1162
				1098	
				1067	
1058	1048	$\nu[C-O(P)]$	1059	1050	1048
1032					
			929	930P	
896P	900	$\rho[(P)CH_3]$	899	898P	901
820	830	$\nu[(C)O-P]$	820	807	822
788	820 sh			756	
714P	736 sh	$\nu[P-C]$	720 sh	689P	749
705P	721	$\nu[P-C]$	695	682P	
	630 vw	$\nu[Al-O(P)]$			
502P	501		492	492P	488 vbr
467P	469		455	456P	
414	413		404	408	
306P	310		302	299	312
	257				269 sh

<sup>a</sup>DMMP = dimethyl methylphosphonate, (CH<sub>3</sub>O)<sub>2</sub>(CH<sub>3</sub>)P(O). DDMMP = deuterated dimethyl methylphosphonate, (CD<sub>3</sub>O)<sub>2</sub>(CH<sub>3</sub>)P(O). MMP = methyl methylphosphonate, (CH<sub>3</sub>O)(CH<sub>3</sub>)P(O)(OH).

2450 cm<sup>-1</sup> is indicative of a broken (P)O-H bond in the adsorbate. The incomplete disappearance of the (P)O-H mode is not surprising in view of the high adsorbate coverage and indicates the presence of a small amount of molecularly adsorbed MMP. Unfortunately, the expected appearance of the PO<sub>2</sub><sup>-</sup> group is impossible to confirm spectroscopically from Figure 1a. Although the  $\nu_s(O-P-O)$  and  $\nu_a(O-P-O)$  of this group are expected near 1058 and 1185 cm<sup>-1</sup>, respectively [these estimates are based on the observed positions of these modes in polymeric Al(MMP)<sub>3</sub><sup>9</sup>], unlike their carbon counterparts, phosphorus-oxygen vibrations have weak electron-vibration coupling constants. (This will be discussed in more detail in section III.1.c.) Consequently, these modes are eclipsed by other intense modes falling in the same spectral region. However, when the isopropyl analogue of MMP, isopropyl methylphosphonate, [(CH<sub>3</sub>)<sub>2</sub>CHO](CH<sub>3</sub>)P(O)(OH), is adsorbed on untreated alumina powder, modes at 1090 and 1180 cm<sup>-1</sup> are observed with infrared spectroscopy.<sup>7</sup> No modes attributable to a downshifted phosphoryl mode are observed. Thus, dissociative adsorption for the isopropoxy analogue of MMP is conclusive, and this suggests that MMP adsorbs dissociatively also.

Kinetic parameters confirm the mechanistic similarity between carboxylic acid chemisorption and MMP chemisorption, i.e., adsorption probabilities for carboxylic acids and for MMP are similar. The tunneling spectrum of Figure 1a was prepared by contacting a 0.005 M solution of MMP with the aluminum oxide surface. Contacting a carboxylic acid solution of similar concentration with aluminum oxide gives a tunneling spectrum showing similar surface coverage.<sup>20</sup> In contrast, more than a 250-fold increase in concentration is necessary before solutions of DMMP produce surface coverages similar to those in Figure 1a.

In summary, spectroscopic and kinetic data point to the similarity between carboxylic acid and MMP chemisorption. Consequently, the spectrum of aluminum oxide exposed to MMP (Figure 1a) reflects the spectral signature of the methyl methylphosphonate adspecies.

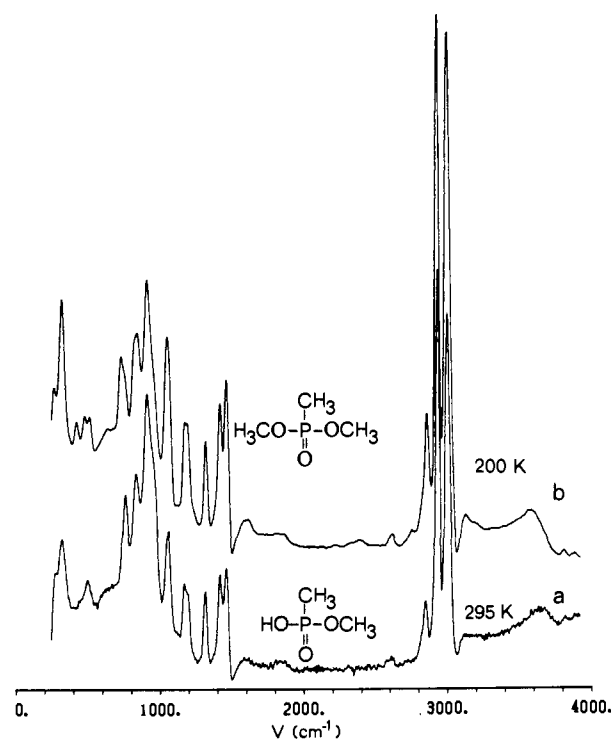
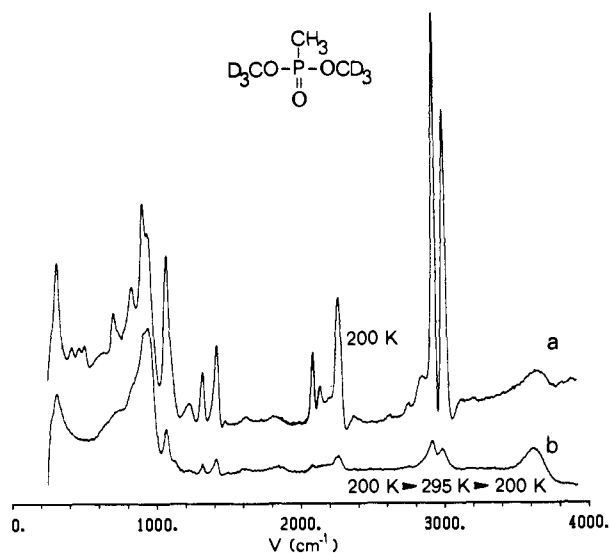


Figure 1. (a) Inelastic electron tunneling spectrum of aluminum oxide exposed at 295 K to a 0.005 M solution of methyl methylphosphonate in hexane. (b) Inelastic electron tunneling spectrum of aluminum oxide after a saturation exposure of DDMMP at 200 K. The lead counterelectrode was evaporated onto this surface at 200 K.

**b. Comparison between Adsorbed DDMMP and Adsorbed Methyl Methylphosphonate.** Figure 1b shows the spectrum of DDMMP



**Figure 2.** Inelastic electron tunneling spectra of aluminum oxide exposed to 2100 L of DDMMP at 200 K. (a) Immediately following the exposure, the lead counterelectrode was evaporated onto the cold surface. (b) Following the exposure the surface was warmed to 295 K and then cooled to 200 K before the lead counterelectrode was evaporated.

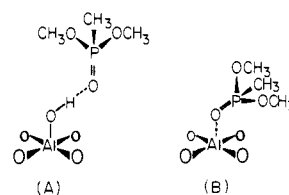
adsorbed on aluminum oxide at 200 K. Table I compares the vibrational frequencies between this spectrum (Figure 1b) and the spectrum of adsorbed MMP (Figure 1a). Several small discrepancies between these two spectra are observed. Among these are the following (see Table I). The C–P stretching mode and the (C)O–P stretching mode appear as doublets in the spectrum of adsorbed DMMP but only as singlets in the spectrum of adsorbed MMP. The C–P mode is downshifted approximately 30  $\text{cm}^{-1}$  in the spectrum of adsorbed DMMP from where it appears in the spectrum of adsorbed MMP. The region between 550 and 400  $\text{cm}^{-1}$  appears as three distinct modes in the spectrum of adsorbed DMMP while it appears as only a single very broad mode in the spectrum of adsorbed MMP. These differences are unlikely to be manifestations of the difference in surface coverages between part a and b of Figure 1.

The reason that a definitive assessment cannot be made is due apparently to the insensitivity of the tunneling spectrum for discriminating between the molecularly adsorbed species and the dissociatively adsorbed species. This is expected for the following two reasons. First, the P–O vibrations, which allow one to discern between molecular adsorption and dissociative adsorption, have weak electron-vibration coupling constants and are therefore eclipsed by other intense modes. Second, aside from the P–O vibrations, the remaining vibrational modes of the molecularly adsorbed DMMP are very similar to the vibrational modes of the dissociatively adsorbed DMMP. This conclusion is demonstrated also in Table I: neglecting P–O modes, the Raman spectrum of liquid DMMP agrees quite well with the tunneling spectrum of adsorbed MMP.

**c. Molecular Chemisorption: The Adsorption of Deuterium-Labeled DMMP at 200 K.** When deuterium-labeled DMMP  $[(\text{CD}_3\text{O})_2(\text{CH}_3)\text{P}(\text{O})]$  is used as the adsorbate, the strong modes occluding the phosphoryl region are isotopically shifted. This is shown in Figure 2a, which is the tunneling spectrum of aluminum oxide exposed to 2100 L of deuterium-labeled dimethyl methylphosphonate (DDMMP) at 200 K. (Note that saturation coverage is reached with exposures of less than 300 L at this temperature.)

The important feature in the spectrum of adsorbed DDMMP (Figure 2a) is the mode at 1217  $\text{cm}^{-1}$ . This mode is now clearly visible because the intense methoxy rocking modes  $\rho[(\text{O})\text{CH}_3]$  appearing at 1166 and 1177  $\text{cm}^{-1}$  in the spectrum of adsorbed, unlabeled DMMP are isotopically shifted clear of the phosphoryl stretching region in the spectrum of adsorbed DDMMP (see Table I). The phosphoryl stretching mode appears in the spectrum of  $[\text{Al}^{3+}(\text{DMMP})_6](\text{ClO}_4^-)_3$  at 1212  $\text{cm}^{-1}$ <sup>8</sup> and in the spectrum of

**Scheme V**



DDMMP adsorbed on  $\text{Al}_2\text{O}_3$  at 1220  $\text{cm}^{-1}$ .<sup>7</sup> Furthermore, although the phosphoryl mode at 1217 extends below 1160  $\text{cm}^{-1}$ , the contribution from the region near 1185  $\text{cm}^{-1}$ , which would characterize the  $\nu_2(\text{O}-\text{P}-\text{O})$  vibrational mode of the dissociatively adsorbed DDMMP, is small in comparison to the entire phosphoryl mode. Thus, most of the DDMMP is chemisorbed molecularly at 200 K.

It is important to distinguish between two possible adsorption sites: surface hydroxyls or coordinatively unsaturated aluminum atoms. A and B in Scheme V depict DMMP that is adsorbed molecularly to these respective sites. The nonlinear Lewis acid  $\text{O}=\text{P}$  bond is suggested by an X-ray crystallographic study of a similar Lewis acid/Lewis base adduct,  $(\text{CH}_3)_3\text{PO}\cdot\text{SbCl}_5$ , where the P–O–Sb bond angle is 139 °C.<sup>28</sup>

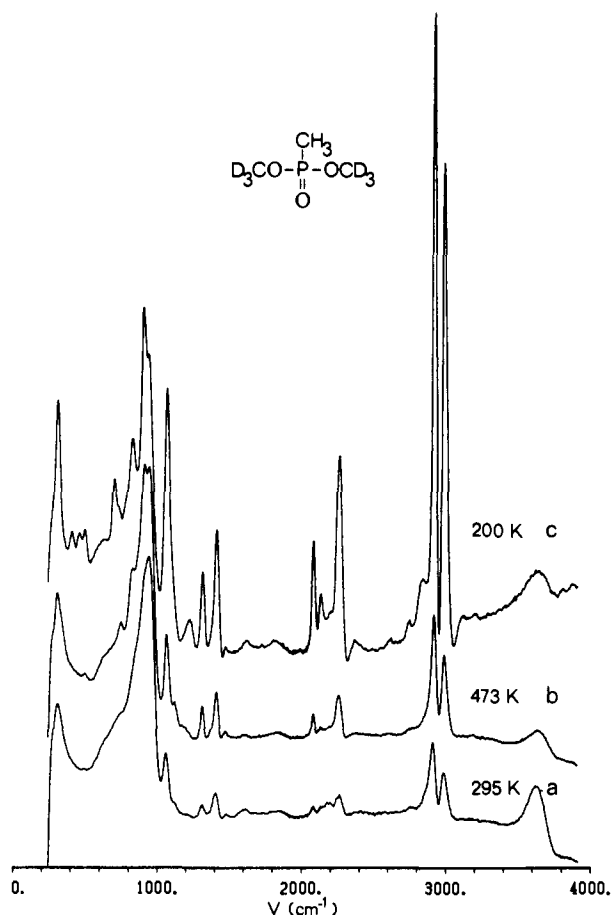
An important distinction between the adsorption sites of A and B in Scheme V can be made in terms of the binding energy or heat of adsorption which should be considerably lower for the surface hydroxyl site than for the coordinately unsaturated aluminum site. This is suggested by calorimetric determinations of the heat of formation of Lewis acid/Lewis base complexes similar to A and B in Scheme V: an adduct similar to site A, Scheme V,  $(\text{C}_6\text{H}_5)_3\text{PO}\cdot\text{HOC}_6\text{H}_5$ , has a heat of formation of 7.0 kcal/mol<sup>29</sup> while the corresponding adduct similar to site B, Scheme V,  $(\text{C}_6\text{H}_5)_3\text{PO}\cdot\text{Al}(\text{CH}_3)_3$ , has a heat of formation of 28.6 kcal/mol.<sup>30</sup> Unfortunately, it is impossible to determine the difference between these sites based on the stretching frequency of the phosphoryl bond, since the adducts similar to sites A and B in Scheme V have phosphoryl stretching frequencies of 1164 and 1167  $\text{cm}^{-1}$ , respectively—a difference of only three wavenumbers<sup>29, 30</sup>—whereas the phosphoryl mode in Figure 2a has a full-width at half-maximum of 70  $\text{cm}^{-1}$ . However, the adduct formed with the hydroxyl site will downshift the OH stretching mode by approximately 430  $\text{cm}^{-1}$ .<sup>30</sup> Although a small mode at 415  $\text{cm}^{-1}$  below the normal hydroxyl stretching mode appears in the spectrum of adsorbed DDMMP in Figure 2a, it is due to a combination band rather than a downshifted hydroxyl.

To distinguish between these two structures, the following experiment was carried out. The aluminum oxide surface was cooled to 200 K and exposed to DDMMP. However, rather than evaporating the lead counterelectrode at this point as in Figure 2a, the aluminum oxide was warmed to 295 K and then cooled to 200 K before the lead counterelectrode was evaporated. The purpose of the intermediate warming to 295 K was to allow any weakly chemisorbed molecules to desorb. On the other hand, temperatures of approximately 400 K are necessary for the desorption of molecules bound by approximately 25 kcal/mol (assuming a preexponential of 500  $\text{cm}^{-1}$ ). The resulting spectrum is shown in Figure 2b. *From a comparison between a and b in Figure 2, it is apparent that virtually all the DDMMP exists in a weakly chemisorbed state on the aluminum oxide surface at 200 K.* Thus, the adsorbate is probably chemisorbed through the hydroxyl as indicated in Scheme VA, in accordance with the much lower binding energy expected for this type of site. Since the surfaces of undehydroxylated alumina powders are terminated with a monolayer of surface hydroxyls, this is exactly what would be expected.<sup>31</sup>

(28) C. Bränden and Lindqvist, *Acta Chem. Scand.*, **15**, 167 (1961).

(29) E. I. Matrosov and I. Kabachnik, *Dokl. Akad. Nauk SSSR*, **232**, 89 (1977).

(30) K. M. Nykerk and D. P. Eyman, *Inorg. Nucl. Chem. Lett.*, **4**, 253 (1968).



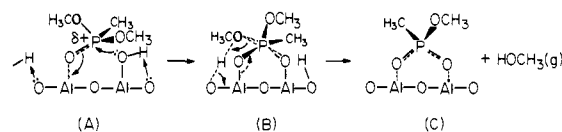
**Figure 3.** Inelastic electron tunneling spectra of aluminum oxide exposed to 1.0 torr-s of DDMMP at various temperatures: (a) 295 K, (b) 473 K, (c) same as Figure 2a.

**d. Dissociative Chemisorption: The Adsorption of Deuterium-Labeled DMMP at 295 K and Above.** It should be noted that a small but significant amount of adsorbed DDMMP remains on the aluminum oxide surface after warming to 295 K (Figure 2b). This could be due either to the existence of some strongly chemisorbed molecular DDMMP (as in Scheme VB) or the existence of a small amount of dissociatively chemisorbed DDMMP. For an investigation of these possibilities, DDMMP was exposed [1.0 torr-s] to the aluminum oxide surface at 295 and 473 K. The resulting tunneling spectra are displayed in Figure 3, a and b, respectively. The tunneling spectrum of DDMMP adsorbed at 200 K is displayed in Figure 3c for comparison.

There are two small but important distinctions to be made between the spectra of DMMP adsorbed at and above 295 K (Figure 3, a and b) and the spectrum of DDMMP adsorbed at 200 K (Figure 3c). First, the C-P stretching vibration that occurs at  $695\text{ cm}^{-1}$  in DDMMP adsorbed at 200 K (Figure 3c) is upshifted substantially to  $740\text{ cm}^{-1}$  in DDMMP adsorbed above 295 K (Figure 3, a and b). This upshifted position corresponds closely to the position of the C-P stretching vibration that is observed in adsorbed MMP, namely  $750\text{ cm}^{-1}$  (the  $10\text{-cm}^{-1}$  discrepancy is attributed to an isotopic shift). Presumably, this upshift represents a strengthening of the C-P bond due to a negative charge gain at the phosphorus caused by dissociative adsorption, i.e., the molecularly adsorbed DMMP is similar to a neutral species, whereas the dissociatively adsorbed species is more similar to the methyl methylphosphonate anion. The second important difference between the spectrum of DDMMP adsorbed at 200 K (Figure 3c) and the spectra of DDMMP adsorbed above 295 K (Figure 3, a and b) is in the position of the P-O stretching vibration: from a position of  $1217\text{ cm}^{-1}$  in the former, it is downshifted to  $1190\text{ cm}^{-1}$  in the latter. This new position corresponds

(31) H. Knözinger and P. Ratnasamy, *Catal. Rev. Sci. Eng.*, **17**, 31 (1978).

**Scheme VI**



closely with the position of the asymmetric O-P-O stretching vibration observed in  $\text{Al}(\text{MMP})_3$  at  $1185\text{ cm}^{-1}$ ,<sup>9</sup> and with the position of the corresponding mode observed in isopropyl methylphosphonate  $[(\text{CH}_3)_2\text{CHO}(\text{CH}_3)\text{P}(\text{O})\text{OH}]$  adsorbed on alumina at  $1180\text{ cm}^{-1}$ .<sup>7</sup> These observations suggest strongly that DDMMP adsorbs dissociatively on aluminum oxide above 295 K.

In order to rule out the possibility that these observations could rather be due to a difference in charge transfer between DDMMP molecularly adsorbed as in Scheme VA and DMMP molecularly adsorbed as in Scheme VB, adsorption experiments were performed with trimethylphosphine oxide  $[(\text{CH}_3)_3\text{PO}]$ . Trimethylphosphine oxide (TMPO) differs from DMMP in that the former has methyl groups in place of the methoxy groups found in the latter. Although C-P bonds are thermodynamically weaker than P-O bonds, they are not so easily subject to heterolytic cleavage as are the latter. Consequently, TMPO can only chemisorb molecularly on the aluminum oxide surface through its phosphoryl oxygen. For example, TMPO forms Lewis base/Lewis acid adducts with phenol,  $(\text{CH}_3)_3\text{PO} \rightarrow \text{HOC}_6\text{H}_5$ .<sup>30</sup> In addition, TMPO forms molecular Lewis base/Lewis acid adducts with  $\text{Al}(\text{CH}_3)_3$ ,  $(\text{CH}_3)_3\text{PO} \rightarrow \text{Al}(\text{CH}_3)_3$ ,<sup>30</sup> and also with  $\{\text{Al}[\text{OSi}(\text{CH}_3)_3]_2\}_2$ ,  $2\{(\text{CH}_3)_3\text{PO} \rightarrow \text{Al}[\text{OSi}(\text{CH}_3)_3]_2\}$ .<sup>32</sup> These two classes of adducts are excellent analogues for the two types of molecular adsorption depicted in Scheme V, A and B, respectively. As discussed previously, a large difference is expected in the heats of adsorption between A and B in Scheme V: the heat of formation of the TMPO-phenol adduct is estimated at  $8.0\text{ kcal/mol}$ , while the heat of formation of the TMPO- $\text{Al}(\text{CH}_3)_3$  adduct is measured calorimetrically to be  $32.0\text{ kcal/mol}$ .<sup>30</sup>

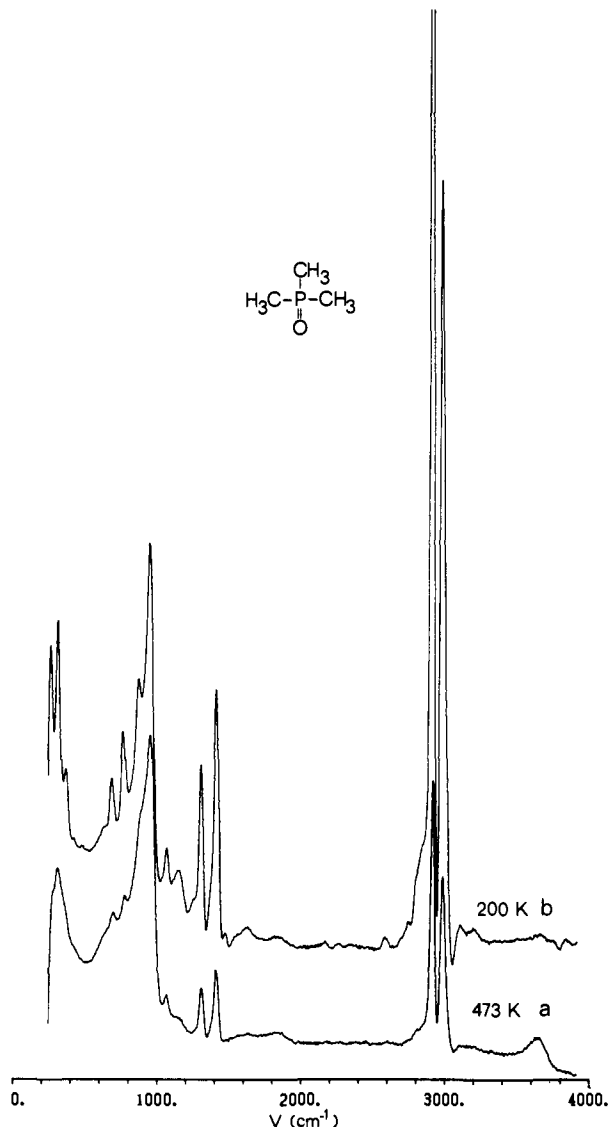
The tunneling spectra of TMPO adsorbed on the aluminum oxide at 473 and 200 K are shown in Figure 4, a and b, respectively. The extreme temperature dependence of the surface coverage that is observed is suggestive of the two different adsorption sites depicted in Scheme VA, B. Again, this behavior is quite similar to what was observed for DDMMP in Figure 3, with one extremely important exception: C-P and P-O stretching vibrations in the spectra of adsorbed TMPO remain unchanged in going from adsorption at 473 K (Figure 4a) to adsorption at 200 K (Figure 4b). This suggests that the shifts experienced by these modes in the spectra of adsorbed DDMMP for adsorption above 295 K (Figure 3, a and b) and adsorption at 200 K (Figure 3c) are not produced by a change in adsorption site of a molecularly adsorbed species. Therefore, this supports the earlier conclusion that DDMMP is adsorbed dissociatively on aluminum oxide above 295 K, giving rise to the methyl methylphosphonate adspecies.

This is not to say that only one type of site participates in the adsorption of DDMMP. Rather, two types of sites participate. However, the hydroxyl site is capable only of molecular adsorption (as in Scheme VA), while the coordinately unsaturated site adsorbs DDMMP dissociatively. This is due probably to the destabilizing amount of electron transfer experienced by the DDMMP following coordination as in Scheme VB. Thus the sequence of events for the dissociative adsorption might be depicted as in Scheme VI. Note that adsorption may proceed via the well-known penta-coordinate transition state of phosphorus<sup>33</sup> as in Scheme VIB.

Other spectroscopic assignments make us confident of the dissociative nature of the adsorption above 295 K. While modes associated with a surface methoxide (these will be identified in the next section) appear and disappear between 295 and 473 K,

(32) F. Schindler and H. Schmidbaur, *Chem. Ber.*, **101**, 1656 (1968).

(33) J. Emsley and D. Hall, "The Chemistry of Phosphorus", Harper and Row Ltd., London, 1976, p 319.

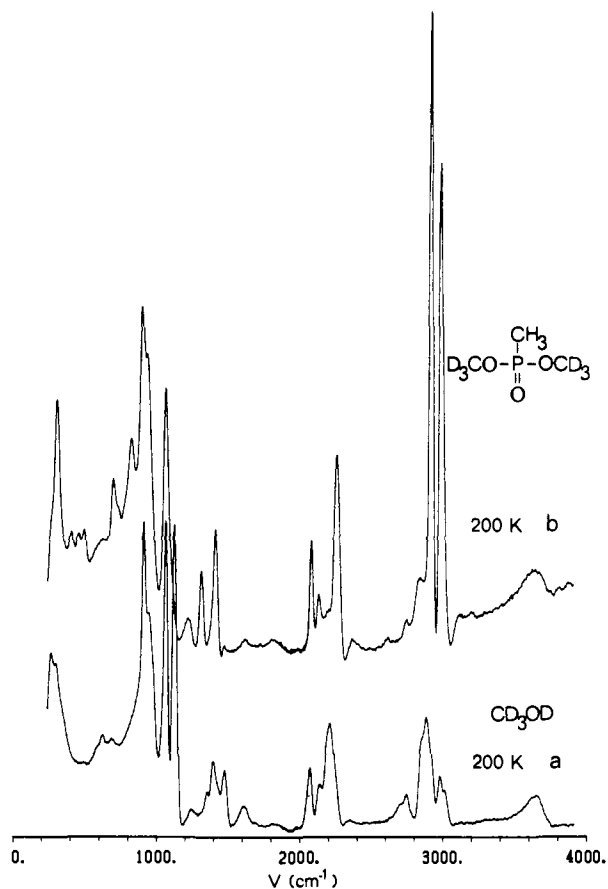


**Figure 4.** Inelastic electron tunneling spectra of aluminum oxide exposed to trimethylphosphine oxide at various temperatures: (a) 0.061 torr-s at 473 K, (b) 1000 L at 200 K. For spectrum b, the lead counterelectrode was evaporated onto the cold surface.

the relative intensities of the MMP modes are completely invariant. This indicates strongly that some process other than the decomposition of the MMP adspecies gives rise to a surface methoxide. Presumably, this process is the dissociative adsorption of DDMMP where both the MMP and the methoxy fragments are chemisorbed.

Related chemistry also suggests the dissociative adsorption of DDMMP at 295 K. The reaction between unsolvated  $\text{AlCl}_3$  and DMMP is instantaneous and violent at 295 K producing polymeric  $\text{Al}(\text{MMP})_3$ , and  $\text{AlCl}_3$  is expected to have properties similar to those of the coordinately unsaturated aluminum site. In addition, carboxylic acid esters have been shown recently to adsorb dissociatively at 295 K on aluminum oxide.<sup>34</sup>

**e. Other Fragments of Dissociative Adsorption: The Surface Methoxides.** Dissociative adsorption produces two molecular fragments. Thus far, attention has been focused on the identification of the fragment that forms the MMP adspecies. Scheme VI tentatively indicates that the other fragment, the methoxy moiety, combines with a surface proton and is subsequently desorbed as methyl alcohol. However, some spectroscopic evidence for or against this would be desirable. Such evidence is virtually impossible to obtain when DMMP is used as the adsorbate since



**Figure 5.** (a) Inelastic electron tunneling spectrum of aluminum oxide exposed to 0.021 torr-s of  $\text{CD}_3\text{OD}$  at 200 K. The lead counterelectrode was evaporated onto the cold surface. (b) Same as Figure 2a.

the resolution of the tunneling spectrum is insufficient to distinguish among the several types of methyl groups that are present.





However, the reaction pathway of the methoxy group can be investigated if DDMMP is used as the adsorbate. In DDMMP  $[(\text{CD}_3\text{O})_2(\text{CH}_3)\text{P}(\text{O})]$ , the deuterium selectively labels the methoxy groups. This increases the splitting between the asymmetric and symmetric stretching vibrations of the methoxy group and also shifts them to a region of the spectrum that is free from otherwise interfering C-H stretching vibrations. The only difficulty then is in knowing the vibrational signatures of a surface methoxide in order to distinguish it from the methoxy that remains attached to the phosphorus in the MMP adspecies. For these signatures to be determined unequivocally, it is necessary to prepare the tunneling spectrum of adsorbed methyl alcohol- $d_4$  ( $\text{CD}_3\text{OD}$ ).

The chemisorption of methyl alcohol and methyl alcohol- $d_4$  on aluminum oxide has been studied extensively with infrared spectroscopy.<sup>2</sup> Chemisorption has been determined to occur dissociatively at 295 K on  $\gamma$ -alumina that was pretreated under vacuum at temperatures above 573 K.<sup>2</sup> This results in a surface methoxide that is bound through the oxygen to a surface aluminum ion. Consequently, a comparison between the tunneling spectrum of chemisorbed methyl alcohol- $d_4$  and the tunneling spectrum of molecularly adsorbed DDMMP will determine which bands can be used to identify a surface methoxide.

The tunneling spectrum of methyl alcohol- $d_4$  chemisorbed on the aluminum oxide is shown in Figure 5a. This spectrum was measured after exposing the aluminum oxide to 21 000 L of  $\text{CD}_3\text{OD}$  at 200 K, which is close to the saturation exposure under these conditions. For comparison, the spectrum of DDMMP adsorbed at 200 K is displayed in Figure 5b. A direct comparison between a and b in Figure 5 is impossible since there are a significant number of modes in the spectrum of chemisorbed  $\text{CD}_3\text{OD}$  (Figure 5a) that are not due to the labeled surface methoxide species.

(34) A. Bayman, P. K. Hansma, and L. H. Gale, *Surf. Sci.*, **125**, 613 (1983).

Table II

CD <sub>3</sub> OD/Al <sub>2</sub> O <sub>3</sub> 200 K; IETS		assignments				
rel intensity	freq, cm <sup>-1</sup>					misc.
10	3650					$\nu(\text{OH})$
11	3003 sh			$\nu(\text{CH})$		
17	2971	$\nu_a(\text{CH}_3)$		$A_1\nu(\text{CH})$		
37	2880	$\nu_s(\text{CH}_3)$		$\nu(\text{CH})$		
30	2860 sh					$\nu(\text{OD})$
11	2738					
8	2700					
2	2360					
36	2204					
28	2180 sh		$\nu_a(\text{CD}_3)$		$A_1\nu(\text{CD})$	
16	2131				$\nu(\text{CD})$	
21	2062		$\nu_s(\text{CD}_3)$			
8	1605					
20	1469	$\delta_a(\text{CH}_3)$		$B_2\nu_a(\text{OCO})$		
15	1406 sh	$\delta_s(\text{CH}_3)$		$A_1\nu_s(\text{OCO})$		
23	1389			$B_2\delta(\text{CH})$		
13	1355				$A_1\nu_s(\text{OCO})$	
7	1248					
100	1118	$\rho(\text{CH}_3)$				
95	1058	$\nu(\text{O-CH}_3)$	$\delta_a(\text{CD}_3)$	$B_1\delta(\text{CH})$		
74	941		$\delta_s(\text{CD}_3)$		$B_2\delta(\text{CD})$	
50	906				$B_1\delta(\text{CD})$	$\nu(\text{Al-O})$
3	682			$A_1\delta_s(\text{OCO})$		
3	619					
30	293					
30	261					

These additional adspecies result when surface reactions transform the chemisorbed methoxide into additional surface products. In particular, nucleophilic attack of the surface methoxide by lattice oxygen produces a surface formate, and hydrogen-deuterium exchange via the surface hydroxyls is responsible for the carbon-hydrogen stretching modes of the methoxide and the formate. Fortunately, there have been several studies of the adsorption of formic acid<sup>23,35-38</sup> and deuterium-labeled formic acid<sup>23</sup> on aluminum oxide with tunneling spectroscopy. With the aid of these, it is possible to make the proper peak assignments (see Table II). There are several unusual issues concerning the spectrum of adsorbed CD<sub>3</sub>OD (Figure 5a). First, previous infrared spectroscopic results indicate that the adsorbed methoxide is converted to a formate only at temperatures above 450 K.<sup>2</sup> Consequently, it is surprising that a surface formate is observed on this surface which was not heated above 295 K. Second, although it is not surprising that the proton of the surface formate can readily exchange with the protons from surface hydroxyls, it seems quite unusual to observe the exchange of the deuterium atoms in the methoxide with surface hydroxyls, since this reaction has not been heretofore reported. It is quite possible that the explanation for these observations lies in the sample preparation procedure.

Since the strongest C-D stretching mode of the surface methoxide occurs at 2204 cm<sup>-1</sup> (see Table II), and since the spectrum of DDMMP, molecularly adsorbed at 200 K, has its weakest C-D stretching mode here (~2195 cm<sup>-1</sup>) (see Table I), it follows that the concentration of surface methoxide in the spectrum of dissociatively adsorbed DDMMP (for example, Figure 3a) will be proportional to the intensity of the mode at 2204 cm<sup>-1</sup> (provided there is a sufficient surface methoxide concentration to allow the mode to rise above its nonzero base-line value). Unfortunately, because the electron-vibration coupling constants are poorly understood, it is futile to attempt to relate the surface

methoxide coverage to the dissociatively adsorbed DDMMP coverage. Nonetheless, having some independent indication of the surface methoxide coverage will be useful (e.g., section III.2).

**2. Adsorption of (CD<sub>3</sub>O)<sub>2</sub>(CH<sub>3</sub>)P(O) between 295 and 673 K.** Thus far, identification of the various surface species taking part in the adsorption of dimethyl methylphosphonate on aluminum oxide has been emphasized. Now that the spectral signatures for these species have been identified clearly, we have the ability to assess the ways in which temperature and exposure affect the interaction between the aluminum oxide surface and gaseous dimethyl methylphosphonate.

For adsorption between 295 and 473 K, there are only three surface species present: MMP, surface methoxides and surface hydroxyls. However, as the adsorption temperature is increased from 295 to 473 K, the relative surface coverages of these three adspecies change. These changes are discussed quantitatively in section III.2.a. Increasing the temperature of adsorption further to 573 K and above leads to the formation of a new surface species, a methyl phosphonate (MP). Therefore, section III.2.b discusses adsorption at these temperatures separately. Finally, in section III.2.c the exposure dependence and temperature dependence of the surface coverage of MMP are compared. This leads to conclusions concerning the nature of the adsorption sites and the mechanism for adsorption. In particular, the surface consists of a small number of sites that are highly active for the dissociative adsorption of DDMMP, and activated adsorption is responsible for the temperature dependence of the surface coverage of the MMP at constant exposure.

Displayed in Figure 6 are the tunneling spectra of aluminum oxide surfaces that were exposed to 1.0 torr-s of DDMMP at progressively higher temperatures: 295 K (Figure 6a), 373 K (Figure 6b), 473 K (Figure 6c), 573 K (Figure 6d), and 673 K (Figure 6e). In the following, we report changes in surface coverage based on comparisons among peak areas in the different spectra of Figure 6 and among other similarly scaled sets of spectra. It is important to emphasize the approximate nature of these comparisons. The uncertainty arises because each of these spectra is recorded from a different tunnel junction, and a reliable theory does not exist to relate absolute coverages measured on different tunnel junctions. The following steps are taken in an attempt to accomplish this empirically. The sloping background

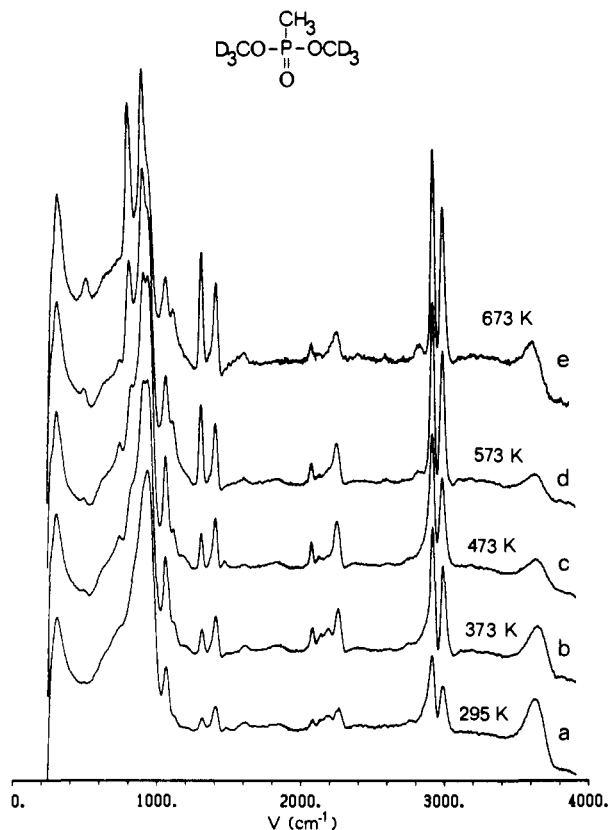
(35) S. De Cheveigne, S. Gauthier, J. Kline, A. Leger, C. Gurnet, M. Bellin, and D. Deforneau, *Surf. Sci.*, **105**, 377 (1981).

(36) B. F. Lewis, M. Mosesman, and W. H. Weinberg, *Surf. Sci.*, **41**, 142 (1974).

(37) O. I. Shklyarevskii, A. A. Lysykh, and I. K. Yanson, *Sov. J. Low Temp. Phys.*, **2**, 328 (1976).

(38) R. Magno and J. G. Adler, *J. Appl. Phys.*, **49**, 4465 (1978).





**Figure 6.** Inelastic electron tunneling spectra of aluminum oxide exposed to 1.0 torr-s of DDMMP at various temperatures: (a) 295 K, (b) 373 K, (c) 473 K, (d) 573 K, (e) 673 K.

of each spectrum is removed by subtracting a linear function of energy until a flat mid-region is obtained. The spectra are then scaled so that the magnitude of the Al–O bulk stretching mode at approximately  $940\text{ cm}^{-1}$  is uniform. The Al–O bulk stretching mode was chosen as the constant of scaling on the following basis. If the fractional adsorbate coverage is  $\theta$ , then the aluminum oxide surface coverage is  $1 - \theta$ . If the adsorbate coverage is small, then variations  $\delta$  in this coverage cause the adsorbate mode intensity to increase as  $\delta/\theta$  relative to its former intensity. On the other hand, the Al–O mode intensity decreases only as  $\delta + \delta\theta + \dots$  relative to its former intensity, and it is therefore less sensitive to variations in the adsorbate surface coverage. Thus when the surface coverage is small, for moderate variations in the surface coverage (on the order of the adsorbate coverage itself), the Al–O mode intensity represents a feature of approximately constant coverage. Obviously, this procedure is hardly rigorously correct. Nonetheless, judging from Figure 6, it seems to be efficacious; the nonlinear background has the same shape and magnitude in each spectrum in Figure 6, even though the resistances of the tunnel junctions vary substantially ( $50\text{--}300\ \Omega$ ). In general, a variation in resistance is attributable to any factor that changes the shape of the tunneling barrier, i.e., changes in the barrier height are equally important as changes in the barrier width. Changes in the barrier height are largely manifest by changes in the adsorbate surface coverage and the adsorbate species. For example, Coleman et al.<sup>39</sup> have examined the very substantial effects of the hydroxyl layer on the barrier shape.

**a. Adsorption between 295 and 473 K at Exposures of 1.0 torr-s.** The tunneling spectra of aluminum oxide exposed to 1.0 torr-s of DDMMP at 295, 373, and 473 K are shown respectively in Figure 6, a–c. Comparisons among a–c in Figure 6 are facilitated by recognizing the three distinct surface species that appear in these spectra. These are the surface hydroxyls, the surface methoxides, and the MMP adspecies, each of which has distinct

vibrational modes. The surface hydroxyls account for the very broad mode at approximately  $3630\text{ cm}^{-1}$ . Of the four distinct C–D stretching peaks observed, the surface methoxides best account for the central two modes at  $2200$  and  $2130\text{ cm}^{-1}$ . The MMP adspecies account for many distinct modes, and we will focus arbitrarily on the most intense C–D and C–H stretching modes at  $2250$  and  $2915\text{ cm}^{-1}$ , respectively. Thus, the relative surface coverage of each adspecies can be assessed independently by following the relative changes in the intensities of these three groups of modes.

**i. The Surface Hydroxyl.** The hydroxyl surface coverage decreases substantially as the temperature of adsorption is increased from 295 to 473 K. A comparison among the relative peak areas of the surface hydroxyl stretching mode at approximately  $3630\text{ cm}^{-1}$  quantifies this statement; the hydroxyl fractional surface coverage falls from unity at 295 K, to 0.73 at 373 K, to 0.46 at 473 K (to 0.42 at 573 K). In this estimate, the aluminum oxide surface is assumed to be terminated by a monolayer of hydroxyls at 295 K, and the intensity of the mode is assumed to be proportional to the surface coverage raised to the 1.4 power.<sup>40</sup> Normally, surfaces of bulk aluminas have physically adsorbed water in addition to a monolayer of surface hydroxyls. However, physically adsorbed water has seldom been observed on the low area aluminum oxide surfaces used in tunneling spectroscopy. Indeed, the agreement is surprisingly good between gravimetric studies of the dehydroxylation of bulk aluminas and the crude measurements for our low surface area alumina. On bulk aluminas, the fractional hydroxyl coverage decreases from 0.87 at 373 K to 0.61 at 473 K (to 0.50 at 573 K).<sup>31</sup>

**ii. The Surface Methyl Methylphosphonate.** The MMP adspecies is stable on the aluminum oxide to 473 K, based on the following experimental observations. Two aluminum oxide surfaces were exposed to 1.0 torr-s of DDMMP at 373 K (as in Figure 6b). One of these was subsequently heated in vacuo to 473 K. Since the intensities of the modes of the MMP adspecies between the resulting spectra were identical, the surface coverage of the MMP is unaffected by heating to 473 K, and thus the MMP does not decompose into other surface species or gaseous products below 473 K.

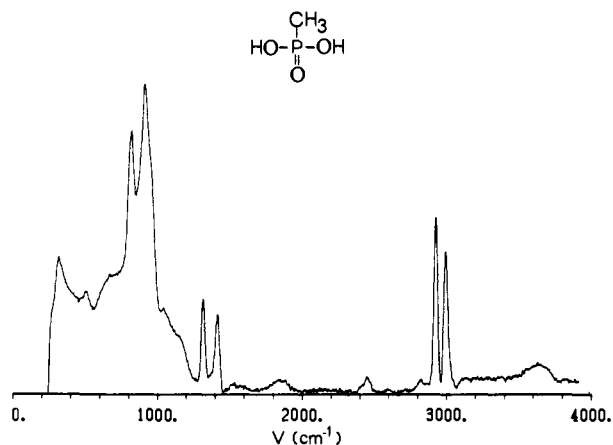
On the other hand, at a constant exposure, the surface coverage of the MMP increases markedly as the temperature of adsorption is increased from 295 to 473 K. A manifestation of this is the overall increase in intensity of the MMP modes in going from 295 to 473 K. On the basis of a comparison of the integrated intensity of the C–H stretching modes, the surface coverage of MMP increases by 16% at 373 K (Figure 6b) and by 22% at 473 K (Figure 6c). (Note that judgments based solely on peak amplitudes are misleading; the amplitude of the  $2915\text{-cm}^{-1}$  peak at 295 K increases by 68% at 373 K.)

The activated adsorption of DDMMP is responsible for the increase in MMP surface coverage with temperature. Dehydroxylation of the aluminum oxide surface at higher temperatures does not create additional adsorption sites. Experiments demonstrating this are discussed in section III.2.c.

**iii. The Surface Methoxide.** The number of surface methoxides formed per dissociatively adsorbed DDMMP decreases substantially as the adsorption temperature is increased from 295 to 473 K. This follows from the decrease in the intensity of the mode at  $2200\text{ cm}^{-1}$  relative to the mode at  $2250\text{ cm}^{-1}$  as the adsorption temperature is increased. The former is characteristic of the surface methoxide, while the latter is characteristic of the MMP adspecies [ $\nu_2(\text{CD}_3)$ ]. Two concerted effects are responsible for this; namely, any surface methoxide formed during the dissociative adsorption of DDMMP would be transformed to a surface formate above 450 K,<sup>2</sup> and the dissociative adsorption reaction appears to produce less surface methoxide at higher adsorption temperatures. Of these two effects, we feel the latter is most responsible

(39) R. A. Dragosset, E. S. Phillips, and R. V. Coleman, *Phys. Rev. B*, **26**, 5333 (1982).

(40) J. D. Langan and P. K. Hansma, *Surf. Sci.*, **52**, 211 (1975); A. A. Cederberg, *Surf. Sci.*, **103**, 148 (1981); S. L. Cunningham, W. H. Weinberg, and J. R. Hardy In "Inelastic Electron Tunneling Spectroscopy", T. Wolfram, Ed., Springer, Berlin, 1978, p 125.



**Figure 7.** Inelastic electron tunneling spectrum of aluminum oxide exposed at 295 K to a 0.0033 M solution of methylphosphonic acid in water.

for the decrease in the surface methoxide coverage.

The transformation of the surface methoxide into the surface formate above 450 K necessarily implies that formate bands should increase in intensity when the adsorption temperature is increased from 373 K (Figure 6b) to 473 K (Figure 6c). An examination of the appropriate spectra (Figure 6, b and c) indicates that this is not the case. Although modes of the surface methoxide decrease markedly in going from adsorption at 373 K (Figure 6b) to adsorption at 473 K (Figure 6c), a concomitant increase in formate modes fails to occur. Of course, interfering modes from the neighboring C-H stretching region might mask this small increase.

On the other hand, the methoxide conversion to formate cannot explain the substantial decrease in the ratio of surface methoxide to MMP in going from adsorption at 295 K (Figure 6a) to adsorption at 373 K (Figure 6b). Thus, it tentatively appears that a substantial decrease in the stability of the methoxide occurs as the adsorption temperature is increased.

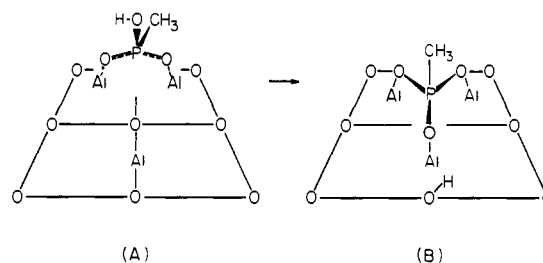
**b. Adsorption of  $(\text{CD}_3\text{O})_2(\text{CH}_3)\text{P}(\text{O})$  between 573 and 673 K.**

Adsorption of DDMMP on aluminum oxide at 573 K produces a new surface species. This is apparent from the subtle changes taking place in the tunneling spectra as the adsorption temperature is increased from 473 K (Figure 6c) to 573 K (Figure 6d). In particular, the mode at  $800\text{ cm}^{-1}$ , which occurs on the low-energy shoulder of the Al-O stretching mode, appears with much higher intensity at 573 K (Figure 6d). In addition, the relative intensity between the mode at  $1418\text{ cm}^{-1}$  [ $\delta_a\text{CH}_3(-\text{P})$ ] and the mode at  $1308\text{ cm}^{-1}$  [ $\delta_s\text{CH}_3(-\text{P})$ ] changes significantly; at 473 K (Figure 6c), the former is much stronger than the latter, while the reverse is true at 573 K (Figure 6d). Finally, the intensity of the  $\nu_a(\text{PO})\text{CD}_3$  mode declines relative to the intensity of the  $\nu_a(\text{P})\text{CH}_3$  mode, suggesting that a methoxy is being lost from the MMP.

The new surface species is adsorbed methyl phosphonate (MP). This identification is made by a comparison between the tunneling spectrum of DDMMP adsorbed at 573 K (Figure 6d) and the tunneling spectrum of methylphosphonic acid (MPA) adsorbed on aluminum oxide at 295 K (Figure 7). The spectrum of adsorbed methylphosphonic acid (Figure 7) reproduces nicely the new features that appear in the spectrum of adsorbed DDMMP when the adsorption temperature is increased to 573 K (Figure 6d).

Relative to the surface coverage of the MMP, the surface coverage of the MP increases as the adsorption temperature is increased from 573 to 673 K. This is apparent from the decrease in the ratio of the mode intensity at  $2250\text{ cm}^{-1}$  to the mode intensity at  $2915\text{ cm}^{-1}$  as the adsorption temperature is increased, since the former is proportional to the surface coverage of the MMP while the latter is proportional to the combined surface coverage of the MMP and MP. A properly scaled ratio of the intensities of these two modes will be proportional to  $\theta_{\text{MMP}}/(\theta_{\text{MMP}} + \theta_{\text{MP}})$ , assuming a weak dependence of mode intensity upon orientation. Such a ratio decreases from unity at 473 K, to 0.6 at 573 K, to 0.4 at 673 K. Note that the MMP still represents 40% of the total phosphorus containing surface population at the

**Scheme VII**



highest temperature examined (673 K). The MP is a product of the decomposition of the MMP. This is made clear from the following experiment. If DDMMP is adsorbed at 373 K and subsequently heated in vacuo to 573 K, then the MP adspecies again appears.

Before discussing the decomposition mechanisms giving rise to the MP adspecies, it is useful to discuss the structure of the adsorbed MP. To obtain the spectrum of adsorbed methylphosphonic acid (Figure 7), the aluminum oxide surface was contacted with a 0.0033 M solution of methylphosphonic acid (MPA) in water. By analogy to the adsorption mechanism for methyl methylphosphonate (see section III.1.a), the first step in the chemisorption of methylphosphonic acid is the transfer of one proton to the aluminum oxide surface and the formation of the bidentate hydroxy methylphosphonate adspecies, as shown in Scheme VIIA. In Scheme VII, the substrate depicted is one of the (100)  $\gamma$ -alumina planes. The (100) planes are low-energy cleavage planes and possibly represent the actual surface that is synthesized.<sup>31,41</sup> This surface contains aluminum in both octahedral and tetrahedral coordinations. Scheme VIIA depicts the MP adspecies anchored to the surface through two octahedral aluminum atoms. These sites were chosen because they bind the surface hydroxyls most weakly, and consequently, they are likely to be exposed for chemisorption most easily. In going from the bidentate species in Scheme VIIA to the tridentate species in Scheme VIIB, the hydroxy methylphosphonate has transferred another proton to the surface. Table III compares results from the tunneling spectrum of adsorbed MPA with results from the infrared spectrum of powdered  $\text{CH}_3\text{P}(\text{O})_2\text{Na}$ , the monobasic salt of MPA.<sup>42</sup> It is clear from the presence of the (P)O-H stretching mode in the tunneling spectrum that some of the bidentate species is stable on the surface. However, the  $\text{PO}_3$  stretching modes of metal complexes, analogous to the tridentate species, are characterized by a very broad absorption band between  $1200$  and  $1000\text{ cm}^{-1}$ , with its maximum located between  $1120$  and  $1030\text{ cm}^{-1}$ .<sup>10</sup> This information together with other spectra of the MP species showing negligible (P)OH modes leads us to conclude that the tridentate form represents the dominant form of the MP adspecies in Figure 7 in spite of the fortuitous match between the tunneling spectrum and the IR spectrum of the monobasic salt.

This interpretation can also explain the observed change in the relative intensity between the  $\delta_a(\text{P-})\text{CH}_3$  mode (at  $1408\text{ cm}^{-1}$ ) and the  $\delta_s(\text{P-})\text{CH}_3$  mode (at  $1308\text{ cm}^{-1}$ ) as the adsorption temperature is increased from 473 K (Figure 6c) to 573 K (Figure 6d). The dipole derivative of the  $\delta_s(\text{P-})\text{CH}_3$  mode changes from  $54.6^\circ$  off-normal with respect to the surface for the bidentate adspecies, which prevails in the spectrum of DDMMP adsorbed at 473 K (Figure 6c), to nearly normal in the tridentate adspecies, which prevails in the spectrum of DDMMP adsorbed at 573 K (Figure 6d). Since vibrational modes more normal to the surface are less attenuated by interaction with their image dipoles in the lead overlayer, the intensity of the  $\delta_s(\text{P-})\text{CH}_3$  mode increases in going from Figure 6c to Figure 6d. The opposite is true for the  $\delta_a(\text{P-})\text{CH}_3$  mode.

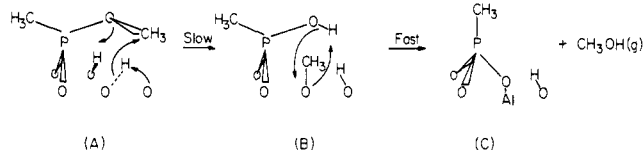
(41) B. C. Lippens and J. J. Steggerda In "Physical and Chemical Aspects of Adsorbents and Catalysts", Chapter 4, Academic Press, New York, 1970, p 171.

(42) B. Dupuy and C. Garrigou-Lagrange, *J. Chem. Phys.*, **65**, 632 (1968).

Table III

CH <sub>3</sub> PO <sub>3</sub> <sup>2-</sup> Na <sub>2</sub> <sup>2+</sup> IR aqueous soln <sup>9</sup>	CH <sub>3</sub> P(O)(OH) <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , 295 K, IETS		CH <sub>3</sub> P(O)(OH) <sub>2</sub> Na IR powder <sup>42</sup>	assignments	
	major species	minor species			
2985 vw	2985 vs	3630 m, vbr	2989 w	ν <sub>a</sub> (CH <sub>3</sub> )	ν(AlO-H)
2920 vw	2915 vs		2921 w	ν <sub>s</sub> (CH <sub>3</sub> )	
	2820 w		2800 s	fermi resonance	
		2710 vw			
		2605 vw			
		2440 m, vbr	2450 m		ν(PO-H)
			2300 s		
		1805			ν(Al-H)
			1680 m		ν(PO-H)
		1550			
1429 w	1418 s		1419 w	δ <sub>a</sub> (CH <sub>3</sub> )	
1304 m	1308 s		1314 m	δ <sub>s</sub> (CH <sub>3</sub> )	
			1234 s		δ(PO-H)
1085 vs, vbr	1145 w, sh, vbr		1160 s	ν(PO <sub>3</sub> )	
			1093 m	ρ(CH <sub>3</sub> )	
1050	1035 w, sh		1038 s	ν(PO <sub>3</sub> )	
972 m		940 s, vbr		ν(PO <sub>3</sub> )	ν(Al-O)
			930 s	ν(PO <sub>3</sub> )	
			920 s		
880 vw	902 s		868 m	ρ(CH <sub>3</sub> )	
750 w	809 vs		765 s	ν(P-C)	
515 w	497 m, vbr		524 s	δ <sub>s</sub> (PO <sub>3</sub> )	
480 vw, sh			478 s	δ <sub>a</sub> (PO <sub>3</sub> )	
			461 m		
336 m	310		330 m	ρ(PO <sub>3</sub> )	
			300 m		
			240 m		

Scheme VIII



The decomposition mechanism of the MMP is discussed more extensively in a related publication.<sup>43</sup> However, some of the pertinent conclusions are the following. Although the initial dissociative adsorption of the phosphonate ester to form the MMP proceeds by attack at the phosphorus by a nucleophilic surface oxygen (as shown in Scheme VI), an identical reaction is not responsible for the subsequent decomposition of the MMP at 573 K. Rather, the decomposition of the MMP proceeds via attack at the methoxy carbon by a nucleophilic surface oxygen and simultaneous protonation of the methoxy oxygen by a hydroxyl (Scheme VIIIA). This results in cleavage of the C-O methoxy bonds and the formation of a surface methoxide and a hydroxy methylphosphonate (Scheme VIIIB). The hydroxy methylphosphonate reacts rapidly with the surface methoxide to eliminate gaseous methyl alcohol and to form the tridentate MP (Scheme VIIIC). A detailed discussion of the evidence for this mechanism is presented elsewhere.<sup>43</sup> The MP is expected to decompose further only above 750 K, which is unattainable in our experiments.<sup>44</sup>

**c. Dependence of the Surface Coverage on Exposure and Temperature.** Only a modest increase in the surface coverage of MMP results when the aluminum oxide surface is held at 295 K and exposed to progressively larger fluxes of DDMMP, as may be seen from the tunneling spectra in Figure 8. These spectra correspond to aluminum oxide surfaces that were held at 295 K and exposed to the following fluxes of DDMMP: 0.10 torr-s (Figure 8a), 1.0 torr-s (Figure 8b), and 10 torr-s (Figure 8c). While the exposure to DDMMP increases by a hundredfold in

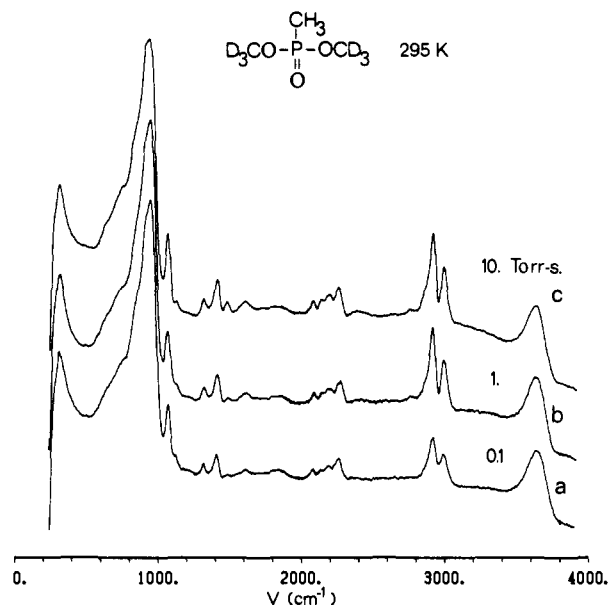


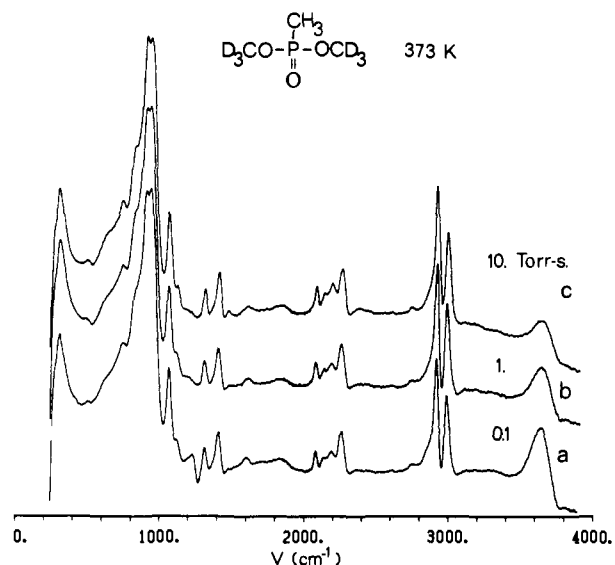
Figure 8. Inelastic electron tunneling spectra of aluminum oxide subjected to increasing exposures of DDMMP at 295 K: (a) 0.1 torr-s, (b) 1.0 torr-s, (c) 10 torr-s.

going from Figure 8a to Figure 8c, there is only a twofold increase in the concentration of dissociatively adsorbed DDMMP. Thus, the aluminum oxide is highly active for the dissociative adsorption of DDMMP at exposures below 0.1 torr-s and much less active for the dissociative adsorption of DDMMP at exposures higher than this.

Whereas saturation coverage is unattained with exposures of 0.1 torr-s at 295 K, Figure 9 indicates that saturation coverage is achieved already at 0.1 torr-s when the adsorption temperature is increased to 373 K. There are two possible explanations for this strong dependence of the surface coverage on the temperature that is maintained during the exposure. One is that the dissociative adsorption reaction is slightly activated. The other explanation

(43) M. K. Templeton and W. H. Weinberg, *J. Am. Chem. Soc.*, to be published.

(44) E. E. Flagg and D. L. Schmidt, *J. Polym. Sci., Part A-1*, **8**, 1 (1970).



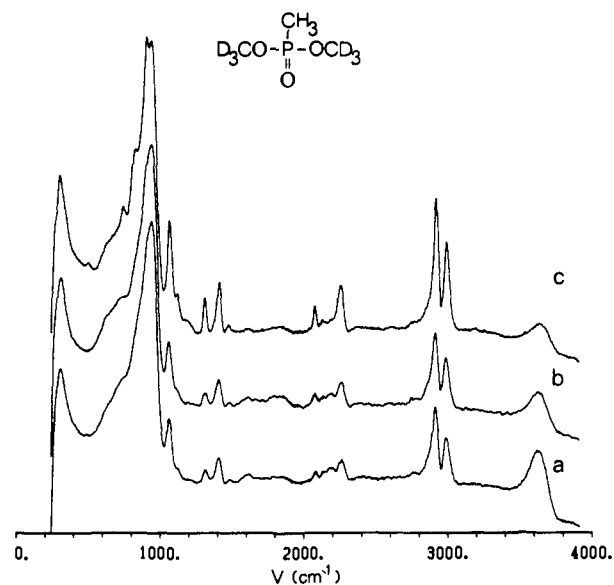
**Figure 9.** Inelastic electron tunneling spectra of aluminum oxide subjected to increasing exposures of DDMMP at 373 K: (a) 0.1 torr-s, (b) 1.0 torr-s, (c) 10 torr-s.

is that the dehydroxylation of the aluminum oxide, which results from the increase in surface temperature, produces coordinatively unsaturated sites that are active for the dissociative adsorption of DDMMP. To decide between these two explanations, the following experiment was performed. An aluminum oxide surface was dehydroxylated at 473 K (in a vacuum of  $1 \times 10^{-7}$  torr) prior to exposure to 1.0 torr-s of DDMMP at 295 K. The tunneling spectrum of this surface is shown in Figure 10b. Unpretreated surfaces were also exposed to 1.0 torr-s of DDMMP at 295 K (Figure 10a) and 473 K (Figure 10c). Since the surface coverages of MMP are more similar between the pretreated surface exposed at 295 K (Figure 10b) and the unpretreated surface exposed at 295 K (Figure 10a) than between the pretreated surface exposed at 295 K (Figure 10b) and the unpretreated surface exposed at 473 K (Figure 10c), the dehydroxylation pretreatment did not appreciably influence the surface coverage. Hence, an activated adsorption reaction is the proper explanation for the observed dependence of the surface coverage of MMP on the temperature of exposure.

Furthermore, the intensities of the hydroxyl stretch on the pretreated surface (Figure 10b) and the surface exposed at 473 K (Figure 10c) compare favorably. Thus, the thermal pretreatment did dehydroxylate the surface, and the experiment compared the proper variables. It also indicates that the observed dehydroxylation is due principally to a thermal effect and not to chemical effects associated with dissociative adsorption. It is likely that thermal pretreatment temperatures of 473 K are inadequate to produce the type of adsite necessary for unactivated dissociative adsorption.

#### IV. Conclusions

In this investigation, the extremely high sensitivity and wide spectral range inherent to tunneling spectroscopy have been used to study the chemisorption of dimethyl methylphosphonate (DMMP) and a number of related phosphorus compounds on aluminum oxide surfaces at coverages ranging from submonolayer to saturation and over a temperature range from 200 to 673 K. Together, this information has led to a number of important conclusions concerning the adsorption of dimethyl methylphosphonate on alumina. This can be summarized as follows:



**Figure 10.** Inelastic electron tunneling spectra of aluminum oxide exposed to 1.0 torr-s of DDMMP at various temperatures: (a) 295 K, (b) as in part a except prior to exposure, surface was heated in vacuo to 473 K, (c) 473 K.

1. At 200 K, dimethyl methylphosphonate adsorbs molecularly, with exposures as low as 300 L producing saturation coverage. For molecular adsorption, the adsorbate/surface complex consists of a Lewis base/Lewis acid adduct between DMMP and a surface hydroxyl.

2. With exposures of less than 10 torr-s between 295 and 473 K, DMMP adsorbs dissociatively to form the methyl methylphosphonate (MMP) adspecies via cleavage of a phosphorus-oxygen bond. The dissociative adsorption sites consist of coordinatively unsaturated aluminum. The methoxy fragment formed during the dissociative adsorption reaction is more likely to remain on the surface as a methoxide at lower adsorption temperatures.

3. Saturation coverage is unattained at 295 K with exposures of 10 torr-s. However, saturation coverage is achieved at 373 K with exposures below 0.10 torr-s. An activated adsorption reaction is responsible for the strong temperature dependence of the surface coverage. Although significant surface dehydroxylation occurs upon increasing the surface temperature from 295 to 473 K, this influences the surface coverage of MMP only slightly.

4. Above 573 K, the methyl methylphosphonate adspecies decomposes to yield the tridentate methyl phosphonate adspecies. The other fragment of decomposition was not identified but presumably consists of gaseous methyl alcohol. The surface coverage consists of approximately equal concentrations of MP and MMP when DDMMP is adsorbed at 673 K. The total surface coverage is estimated to be less than 20% of a monolayer.

**Acknowledgment.** We thank Nadeem Tufail for his competent and exacting preparation of many of the tunnel junctions used in this study. In addition, we are indebted to Steve Buchwald for synthesizing the deuterated dimethyl methylphosphonate and to Steve Blair for measuring the Raman spectra of the phosphonate esters. This work was supported by the Army Research Office under Grant No. DAAG29-83-K-0094.

**Registry No.**  $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{P}(\text{O})$ , 756-79-6;  $(\text{CD}_3\text{O})_2(\text{CH}_3)\text{P}(\text{O})$ , 80014-34-2;  $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ , 676-97-1;  $(\text{CH}_3\text{O})(\text{CH}_3)\text{P}(\text{O})(\text{OH})$ , 1066-53-1; TMPO, 676-96-0;  $\text{CD}_3\text{OD}$ , 811-98-3; aluminum oxide, 1344-28-1; methyl phosphonate, 13590-71-1; methyl phosphinic acid, 993-13-5.