

Decomposition of Phosphonate Esters Adsorbed on Aluminum Oxide

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Abstract: Inelastic electron tunneling spectroscopy has been used to examine the adsorption and reaction of three phosphonate esters on aluminum oxide surfaces which were synthesized by the plasma oxidation of metallic aluminum films. The phosphonate esters were diisopropyl methylphosphonate (DIMP), dimethyl methylphosphonate (DMMP), and diphenyl methylphosphonate (DPMP). The adsorption temperatures ranged from 200 to 673 K. The exposures of gaseous DIMP and DMMP were 1.0 torr-s, while DPMP was exposed to the surface as a 0.025 M solution in hexane. DIMP was found to adsorb molecularly in low coverages at 295 K, whereas at 373 K, DIMP was found to adsorb dissociatively in low coverages as isopropyl methylphosphonate. Above 373 K the isopropyl methylphosphonate decomposed to the metastable hydroxy methylphosphonate, which, in turn, decomposed completely to the methylphosphonate above 573 K. Although the dissociative adsorption temperature was lower (295 K), adsorbed DMMP decomposed similarly through the hydroxy methylphosphonate to form the methylphosphonate. However, in this case the hydroxy methylphosphonate was a short-lived intermediate. DPMP was found to adsorb dissociatively at 295 K, and the phenyl methylphosphonate that is formed is stable to at least 673 K. Consistent with these observations, mechanisms for the adsorption and decomposition of phosphonate esters on aluminum oxide are proposed that involve P-O bond cleavage upon adsorption but O-C bond cleavage upon further decomposition of the adspecies.

I. Introduction

By studying the interaction of various adsorbates with aluminum oxide, the surface chemistry of this important material may be clarified. Previously, we have examined the interaction of gaseous dimethyl methylphosphonate with aluminum oxide over a wide range of temperatures (200 to 673 K) and exposures (5×10^{-5} to 10 torr-s).¹ The gaseous phosphonate ester adsorbs molecularly at 200 K in high coverages. On the other hand, increasing the temperature of adsorption to 295 K causes the phosphonate ester to adsorb dissociatively in low coverages to form methyl methylphosphonate. If the temperature of adsorption is increased further to 573 K, then the dissociatively adsorbed phosphonate ester decomposes to methylphosphonate.

The previous work emphasized the spectroscopic identification of the various adsorbed species and, in this way, confirmed that the transformations indeed took place. This paper is an extension of the previous work in that it examines the interaction of similar phosphonate esters with the surface of aluminum oxide via tunneling spectroscopy. However, issues concerning the mechanisms for the dissociative adsorption and decomposition of the phosphonate esters are emphasized here.

Our conclusions are based on the vibrational spectra of three diesters of methylphosphonic acid adsorbed on aluminum oxide between 200 and 673 K. The particular phosphonate esters are diisopropyl methylphosphonate $[(CH_3)_2CHO]_2(CH_3)P(O)$, dimethyl methylphosphonate $(CH_3O)_2(CH_3)P(O)$, and diphenyl methylphosphonate $(C_6H_5O)_2(CH_3)P(O)$. These three esters have chemically very different ester moieties. Hence, depending on the reaction mechanism, they can display either very different or rather similar reactivities. This feature will be useful in drawing conclusions concerning reaction mechanisms on the surface.

Aside from our previous work,¹ there are few accounts in the literature of the adsorption of phosphonate esters on aluminum oxide. An infrared spectroscopic study of the adsorption of diisopropyl methylphosphonate on hydroxylated alumina powders at 295 K concluded that although adsorption was predominantly molecular, a small concentration of the dissociatively adsorbed phosphonate ester was present as well.² Evidently, the adsorption of diphenyl methylphosphonate has not been reported on any surface.

II. Experimental Procedures

1. **Adsorbates** Diisopropyl methylphosphonate (DIMP) was obtained from Alfa Products in 98% purity. Dimethyl methylphosphonate

(DMMP) was obtained from Aldrich Chemical Co. in 97%+ purity. Diphenyl methylphosphonate (DPMP) was synthesized by the reaction of triphenyl phosphite methiodide with ethanol following a previously published procedure.³ The purity of the final product was confirmed by a comparison between the ¹H NMR spectrum of the product and one reported in the literature.⁴

2. **Tunnel Junction Fabrication Procedure.** The tunnel junction fabrication and measurement procedures have been documented elsewhere.¹ Nevertheless, it is important to emphasize the nature of the aluminum oxide surfaces being studied here. They are formed by oxidizing the surfaces of evaporated metallic aluminum films with a glow discharge in approximately 0.2 torr of O₂ (99.999% purity). The similarity of this surface oxide to γ -alumina has been demonstrated with X-ray photoelectron spectroscopy.⁵

The procedure for dosing the surfaces varied depending upon the vapor pressure of the adsorbate. For DIMP and DMMP, the surfaces were contacted with the gaseous adsorbate. With this procedure, the surface temperature during exposure could be varied arbitrarily. On the other hand, the vapor pressure of DPMP is approximately 10^{-7} torr at 295 K.⁶ Consequently, a 0.025 M solution of DPMP in spectral grade *n*-hexane was freshly prepared for each of the experiments with DPMP. A few drops of this solution were then pipetted onto the surface at room temperature and atmospheric pressure. The solvent evaporated in a few minutes, and then the surface was returned to vacuum where it could be heated arbitrarily. Again, more detailed specifications for these procedures are found elsewhere.¹

III. Results and Discussion

1. **Dissociative Adsorption.** DMMP, in exposures of 1.0 torr-s, adsorbs dissociatively on aluminum oxide between 295 and 473 K.¹ A key factor in determining this was the positions of the P-O stretching vibrations of the adsorbed species, since from these it is easily possible to distinguish dissociative from molecular adsorption. Therefore, selectively deuterium labeled dimethyl methylphosphonate (DDMMP) was used extensively in these experiments, since it was free from modes that occluded the extraordinarily weak P-O stretching vibrations in the unlabeled compound. Without use of similarly labeled forms of DIMP and DPMP, it is doubtful whether the positions of the P-O stretching vibrations could be ascertained. Rather, we will rely on a combination of less direct spectroscopic data and information in the literature to infer that, on the one hand, DIMP adsorbs molecularly at 295 K while, on the other hand, DPMP adsorbs dissociatively at 295 K. The evidence for this will be discussed below in connection with results for adsorption of these esters between 373 and 673 K.

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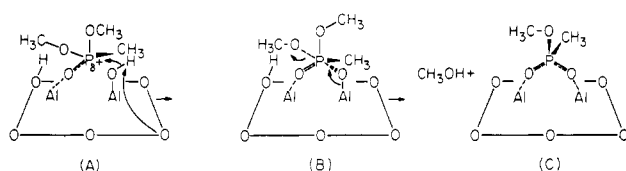
Table I⁶

ester	alkaline hydrolysis, 353 K		acid hydrolysis, 383 K	
	E_a (kcal·mol ⁻¹)	A (L·mol ⁻¹ ·s ⁻¹)	E_a (kcal·mol ⁻¹)	A (s ⁻¹)
[(CH ₃) ₂ CHO] ₂ (CH ₃)P(O)	14.9	2.24×10^5	25.6	1.83×10^{11}
(CH ₃ O) ₂ (CH ₃)P(O)	13.5	1.75×10^7	26.7	4.23×10^{10}
(C ₆ H ₅ O) ₂ (CH ₃)P(O)	12.4	4.66×10^7	26.0 (assumed)	2.62×10^8

Table II¹²

ester	alkaline hydrolysis, 298 K		acid hydrolysis	
	E_a (kcal·mol ⁻¹)	A (L·mol ⁻¹ ·s ⁻¹)	E_a (kcal·mol ⁻¹)	A (s ⁻¹)
(CH ₃)COO-CH(CH ₃) ₂ ¹³	11.1	3.03×10^6		
(CH ₃)COO-CH ₃ ¹⁴	12.2	1.43×10^8		
(CH ₃)COO-C ₂ H ₅ ¹⁵	11.5 (assumed)	3.28×10^8		
(CH ₃)COO-C(CH ₃) ₃ ¹⁶			27.5	1.0×10^{16}

Scheme I



These results are also consistent with our proposed mechanism for the dissociative adsorption of phosphonate esters on aluminum oxide, which is based on previous results with DMMP, and which is depicted in Scheme I.¹ At this point, it is convenient to discuss this mechanism, which is similar to nucleophilic substitution occurring in phosphonate esters under neutral and alkaline conditions.^{6,7} A somewhat similar mechanism has been proposed previously for the dissociative adsorption of isopropyl methylphosphonofluoridate.² The mechanism consists of adsorption of the neutral phosphonate ester on a coordinately unsaturated aluminum site [Scheme IA]. This destabilizes the phosphorus center and leads to nucleophilic attack by a lattice oxygen at the phosphorus to form the pentacoordinate intermediate [Scheme IB]. This is followed by the transfer of a proton from the surface to the leaving group oxygen and elimination of the alcohol [Scheme IC].

This mechanism is supported by all available data. The initial step of the mechanism is consistent with the similarity between the number of coordinately unsaturated aluminum atoms, as determined by titration with gaseous trimethylphosphine oxide, and the surface coverage of the dissociatively adsorbed DMMP.¹ The nucleophilic behavior of the lattice oxygen, as in the second step, has been demonstrated clearly in other reactions on aluminum oxide, such as the conversion of acetaldehyde and acetone to acetate.^{8,9} Furthermore, several carboxylic acid esters adsorb dissociatively on aluminum oxide,¹⁰ and the mechanistic similarity between homogeneous nucleophilic substitution at an acyl carbon and homogeneous nucleophilic substitution at the phosphoryl phosphorus has been emphasized.¹¹

The dissociative adsorption mechanism (Scheme I) indicates a bimolecular nucleophilic substitution taking place at the phosphorus [$S_N2(P)$] leading to P-O bond cleavage. As mentioned, this is consistent with the behavior of phosphonate esters under neutral and alkaline hydrolysis.^{6,7} For comparison, the preexponential factors and activation energies for homogeneous hydrolysis of the phosphonate esters under study are given in Table I.⁶ Two principal effects explain the relative ordering of the alkaline hydrolysis rates shown in Table I.^{6,7} First, because the

mechanism is bimolecular and takes place via a trigonal-bipyramidal transition state, steric hindrance will render the alkaline hydrolysis of DIMP unfavorable compared to DMMP and DPMP. Second, because the basicity of the phenoxy, methoxy, and isopropoxy anions increases in that order, the hydroxide ion will more easily displace the phenoxy as compared to the isopropoxy, and thus again the alkaline hydrolysis of DIMP is unfavorable compared to DMMP and DPMP. Consequently, the combination of these two effects accounts for the two to three orders of magnitude lower rate of alkaline hydrolysis for DIMP vs. DMMP and DPMP. Moreover, it is a consequence of this much lower activity toward nucleophilic substitution at the phosphorus that DIMP adsorbs molecularly at 295 K, whereas both DMMP and DPMP adsorb dissociatively at 295 K. Rates and activation energies for the alkaline hydrolysis of analogous esters of acetic acid are given in Table II.¹² In this case, the hydrolysis mechanism is a bimolecular nucleophilic substitution taking place at the acyl carbon [$S_N2(Ac)$].¹² Note the similar activation energies and preexponential factors in comparison with phosphonate hydrolysis. The acid catalyzed hydrolysis of these carboxylic acid esters also takes place by a $S_N2(Ac)$ reaction, and the activation energy is expected to be approximately 5 kcal/mol higher.¹²

However, as will be important later, phosphonate esters can also be hydrolyzed by nucleophilic substitution at the alkyl carbon of the ester moiety, leading to C-O bond cleavage.⁶ This occurs in acidic media. For comparison, the relative rates and activation energies for the acidic hydrolysis of the phosphonate esters under study are given also in Table I. The relative ordering of the rates for acidic hydrolysis can be explained in terms of differences in mechanism. Under these conditions, the decomposition of DIMP proceeds by a unimolecular nucleophilic substitution at the alkyl carbon of the ester [$S_N1(Ak)$].⁶ On the other hand, in DMMP it is unfavorable for the methyl of the ester to form a carbocation. Consequently, DMMP probably decomposes by a bimolecular nucleophilic substitution at the alkyl carbon of the ester [$S_N2(Ak)$], which is apparently less favorable under these conditions.⁶ Even less favorable is the decomposition of DPMP, the difficulty of nucleophilic substitution at the phenyl carbon being well-known. Note that the order of increasing relative rates is reversed in going from alkaline hydrolysis to acidic hydrolysis and that the activation energy for hydrolysis by attack at the phosphorus is approximately half the activation energy for attack at the alkyl carbon.

Esters of carboxylic acids will undergo hydrolysis by unimolecular nucleophilic substitution at the alkyl carbon of the ester only if the resulting carbocation formed is sufficiently stable. For example, *tert*-butyl acetate hydrolyzes in water, yielding the (CH₃)₃C⁺ carbocation. The activation energy is 27.5 kcal/mol,¹⁶ and this compares favorably with the activation energy for the

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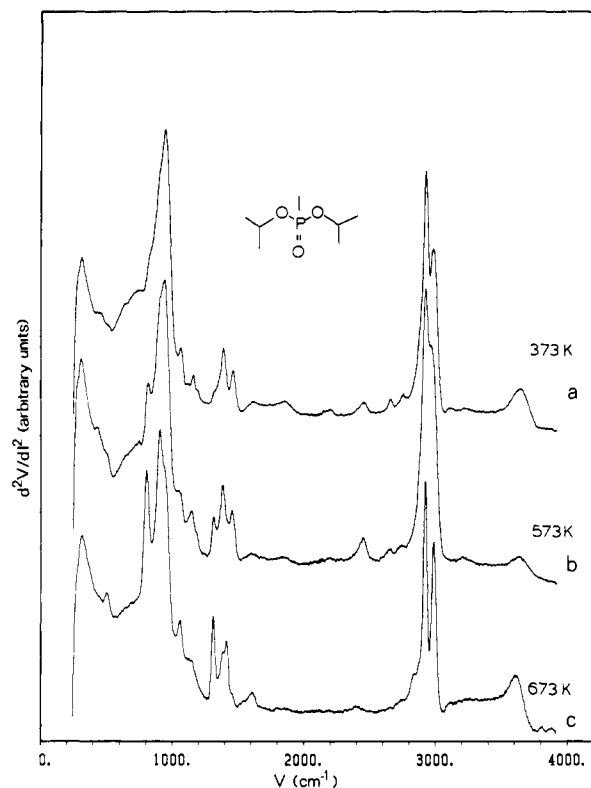


Figure 1. Inelastic electron tunneling spectra resulting from the exposure of 1.0 torr-s of diisopropyl methylphosphonate to aluminum oxide at various temperatures: (a) 373 K, (b) 573 K, and (c) 673 K.

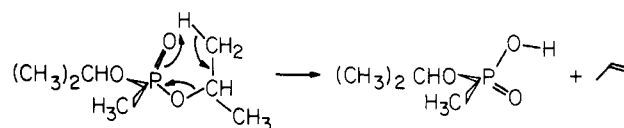
mechanistically similar hydrolysis of phosphonate esters in acidic media (see Table I).

The phosphonate ester is likely to adsorb dissociatively on the aluminum oxide surface as the bidentate bridging phosphonate (rather than the bidentate chelating), as shown in Scheme IC. This is attested to by the close match in the frequencies of the $\nu_s(\text{O}-\text{P}-\text{O})$ and $\nu_a(\text{O}-\text{P}-\text{O})$ stretching modes between adsorbed hydroxy isopropoxy methylphosphonate [1090 and 1180 cm^{-1}],² which produces a surface species identical to dissociatively adsorbed DIMP, and the homogeneous metal complex $\text{Al}(\text{IMP})_3$ [1088 and 1179 cm^{-1}],¹⁷ which is known to consist largely or entirely of the bidentate bridging homogeneous analogue of dissociatively adsorbed DIMP.

Other work suggests that either the (100) or the (110) planes of γ -alumina are the actual surfaces synthesized.^{18,19} Both the (100) and (110) γ -alumina surfaces contain adsorption sites that equally well accommodate the geometry of the bidentate bridging, dissociatively adsorbed phosphonate, as judged from crystallographic determinations of the structure of homogeneous metal phosphonates.²⁰ However, the adsorption site picture in Scheme I is tentatively located on the (100) plane, since this site also provides a more favorable geometry for further decomposition of the adsorbed phosphonate.

2. The Adsorption and Decomposition of DIMP. The interaction of aluminum oxide with gaseous DIMP is discussed first since relevant information on this phosphonate ester is available in the literature. An infrared spectroscopic study of the adsorption of gaseous DIMP on aluminum oxide powders concluded that DIMP adsorbs predominantly molecularly at 295 K.² In addition, a small concentration of the dissociatively adsorbed species was present. In view of the proposed mechanism for dissociative

Scheme II



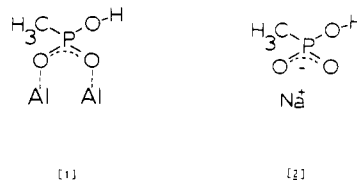
adsorption, the low susceptibility of DIMP to homogeneous alkaline hydrolysis supports these conclusions.

On the other hand, the tunneling spectrum of an aluminum oxide surface exposed to 1.0 torr-s of DIMP at 373 K is shown in Figure 1a. A comparison between Figure 1a and the spectrum of DIMP adsorbed molecularly at 200 K (not shown) reveals that the relative ratio of the number of isopropoxy groups to the number of methyl groups bound to the phosphorus decreases in going from adsorption at 200 K to adsorption at 373 K, as judged from changes in the relative intensities of the appropriate vibrational modes. This is consistent with a change from molecular adsorption to dissociative adsorption, which would ideally cause this ratio to fall from 2 to 1. Thus the molecularly adsorbed DIMP must decompose to dissociative adspecies between 295 and 373 K.

The tunneling spectra of aluminum oxide exposed to 1.0 torr-s of DIMP at 573 and 673 K are shown in Figure 1, parts b and c, respectively. From these spectra it is clear that the decomposition of adsorbed DIMP proceeds in a fashion somewhat analogous to the decomposition of adsorbed DMMP.¹ As the adsorption temperature is increased from 373 K (Figure 1a) to 573 K (Figure 1b), the dissociatively adsorbed DIMP begins to decompose, as evidenced by substantial changes taking place in the shapes of the CH stretching and deformation regions. Increasing the adsorption temperature to 673 K produces a spectrum (Figure 1c) that is virtually identical with the tunneling spectrum of DMMP adsorbed at 673 K.¹ Since the latter has been identified as characteristic of adsorbed methylphosphonate, it is clear that the decomposition of adsorbed DIMP also yields the methylphosphonate.¹

The gaseous hydrocarbon evolved during the decomposition of adsorbed DIMP is propene. This can be surmised for the following reasons. It was found that isopropyl methylphosphonofluoroidate (IMPF) adsorbs dissociatively on alumina to form isopropyl methylphosphonate, which is identical with the species formed when DIMP adsorbs dissociatively on the aluminum oxide.² At 295 K, the adsorbed IMPF produces gaseous propene corresponding to a decomposition rate of 2% per week.² Heating the adsorbed IMPF increased the rate of production of gaseous propene.² In addition, the pyrolysis of liquid diisopropyl *n*-hexylphosphonate begins at approximately 480 K and produces gaseous propene and *n*-hexylphosphonic acid.²¹ This is in agreement with the tunneling spectra of adsorbed DIMP, which begins to show decomposition of DIMP at 473 K (not shown).

The tunneling spectra of Figure 1 also indicate the presence of a heretofore unidentified, stable intermediate in the decomposition of adsorbed DIMP to MP. In going from 373 K (Figure 1a) to 573 K (Figure 1b), the intensity of the mode at 2440 cm^{-1} increases concomitantly with the increase in the extent of decomposition of the adsorbed DIMP. Then in going from 573 K (Figure 1b) to 673 K (Figure 1c), the intensity of this mode declines concomitantly with the increase in surface coverage of MP. The 2440-cm^{-1} mode is due to the bidentate hydroxy methylphosphonate adspecies (1). This identification is based on a



homogeneous analogue of this species, the monobasic sodium salt

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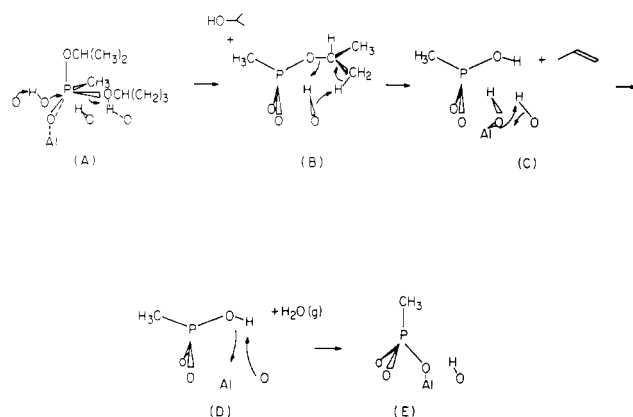
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Scheme III



of hydroxy methylphosphonic acid (**2**), which has an OH stretching mode at 2440 cm^{-1} .²² In addition, the same mode was observed in connection with the incomplete dissociative adsorption of methylphosphonic acid on aluminum oxide to give adsorbed hydroxy methylphosphonate.¹ Note that it is difficult to detect the presence of this species by any vibrational mode other than the one at 2440 cm^{-1} , since both this species and methylphosphonate have strongly overlapping spectral signatures, and a mixture of these two species coexists on the surface.

From these observations, the decomposition of adsorbed DIMP is proposed to proceed as in Scheme II. At 295 K, DIMP is adsorbed molecularly (Scheme IIA). Increasing the temperature to 373 K results in the decomposition of the molecularly adsorbed DIMP via nucleophilic substitution at the phosphorus atom by a surface oxygen, to produce isopropyl methylphosphonate (IMP) and gaseous isopropyl alcohol (Scheme IIB). This is a very reasonable occurrence in view of the alkaline hydrolysis rates given in Table I. At 373 K the alkaline hydrolysis rate of DIMP is comparable to the alkaline hydrolysis rate of DMMP at 295 K. Since DMMP adsorbs dissociatively at 295 K, it follows that the hydrolysis rate is an approximate measure of the dissociative adsorption threshold. (Admittedly, this assumes that the nucleophilic reactivity of the surface does not decrease upon heating to 373 K. This is a reasonable approximation in view of the limited dehydroxylation occurring at these temperatures.¹⁹) The decomposition of the isopropyl methylphosphonate proceeds further at 473 K by the surface catalyzed elimination of propene (Scheme IIB) to produce the hydroxy methylphosphonate (Scheme IIC). The mechanism indicated (Scheme IIB) for this transformation is only tentative and is similar to mechanisms proposed for the dehydration of alcohols.²³ On the other hand, the pyrolytic elimination of propene in liquid diisopropyl *n*-hexylphosphonate, which begins above 480 K,²¹ may proceed as depicted in Scheme III by analogy to pyrolytic eliminations of alkenes in carboxylic acid esters and xanthate esters.²⁴

Although the six-membered-ring transition state is common to both Schemes III and IIB, it is impossible to carry all the aspects of the former mechanism to the latter. Although base catalyzed elimination mechanisms are observed in the dephosphorylation of some phosphate esters, such mechanisms cannot be operative here since they would result in a methylphosphonate anion rather than the hydroxy methylphosphonate that is observed.^{7,25} In addition, the decomposition mechanism shown (Scheme IIB) is much favored over mechanisms involving a nucleophilic attack at the phosphorus by lattice oxygen, as occurs in the dissociative adsorption mechanism (Scheme I). These latter mechanisms are improbable for the following two reasons. First, compared to the neutral phosphonate ester, the IMP adspecies now has more negative charge on the phosphorus which makes it a poorer

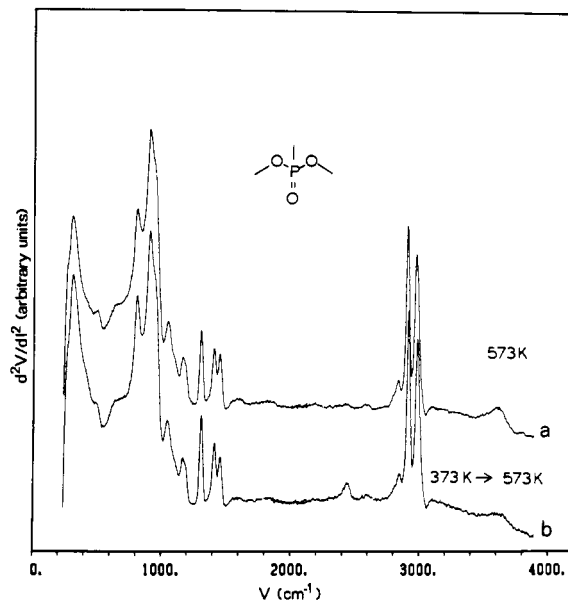


Figure 2. (a) Inelastic electron tunneling spectrum resulting from the exposure of 1.0 torr-s of dimethyl methylphosphonate to aluminum oxide at 573 K. (b) Inelastic electron tunneling spectrum resulting from the exposure of 1.0 torr-s of dimethyl methylphosphonate to aluminum oxide at 373 K, followed by heating the surface in vacuo to 573 K.

electrophile.²⁶ For example, the alkaline hydrolysis of phosphonate esters only proceeds through formation of the monoester.²⁷ Second, because IMP is constrained by two points of attachment to the surface, it would be difficult for the phosphorus center to accommodate the trigonal-bipyramidal transition state needed for a bimolecular nucleophilic substitution. The hydroxy methylphosphonate (Scheme IIC) persists on the surface until further dehydroxylation of the surface (Scheme IIC) produces a neighboring coordinately unsaturated aluminum (Scheme IID). The hydroxy methylphosphonate then reacts with this site (Scheme IID) to form a methylphosphonate and a surface hydroxyl (Scheme IIE). A direct reaction between a surface hydroxyl and the hydroxy methylphosphonate would be unfavorable because of the relatively low acidity of the hydroxy methylphosphonate proton ($\text{p}K_{\text{A}} \approx 7.9$),²⁸ in comparison to surface hydroxyls on the partially dehydroxylated surface ($\text{p}K_{\text{A}} > 7.2$).²⁹

Decomposition of the MP adspecies is expected to occur only above 750 K, since aluminum phosphonate polymers do not decompose below this temperature.³⁰ However, this temperature regime was inaccessible due to physical limitations of our experiments.

3. The Adsorption and Decomposition of DMMP. The identification of a probable mechanism for the decomposition of adsorbed DIMP was facilitated by knowledge of the gaseous products of decomposition. For DMMP, this information is presently unavailable. Nonetheless, it is still possible to delineate the most plausible decomposition mechanisms.

The dissociative adsorption and decomposition of DMMP on aluminum oxide has been studied previously.¹ Like DIMP, the stable surface species resulting from the adsorption of DMMP at 673 K is the methylphosphonate.¹ However, unlike dissociatively adsorbed DIMP, which shows significant signs of further decomposition at 473 K and is virtually completely decomposed to MP at 673 K, dissociatively adsorbed DMMP showed significant signs of decomposition beginning only at 573 K, and only

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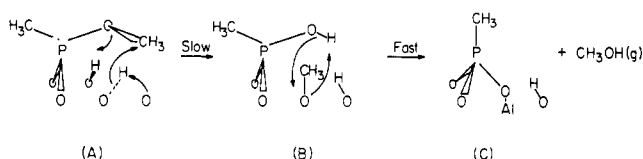
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Scheme IV



approximately 50% of the total adspecies population consists of MP at 673 K.¹

Figure 2a is the tunneling spectrum of 1.0 torr-s of DMMP adsorbed on the aluminum oxide surface at 573 K. Of particular significance is the near absence of a mode at 2440 cm^{-1} in Figure 2a as compared with the spectrum of DIMP adsorbed under similar conditions (Figure 1b). Since this mode is characteristic of the hydroxy methylphosphonate, this implies that this species is much stable intermediate in this case compared to the decomposition of DIMP. That the hydroxy methylphosphonate is in fact an intermediate in the decomposition of DMMP is verified by the tunneling spectrum of an aluminum oxide surface that is exposed to 1.0 torr-s of DMMP at 373 K and then heated in vacuo to 573 K (Figure 2b). Following this treatment, the hydroxy methylphosphonate is clearly present on the surface, as evidenced by the considerable intensity of the mode at 2440 cm^{-1} .

Although the presence of the hydroxy methylphosphonate is not surprising, it is somewhat surprising that there is a pronounced and reproducible difference between heating the dissociatively adsorbed species to its decomposition temperature vs. adsorbing the DMMP at the decomposition temperature. Furthermore, aside from the absence of the 2440- cm^{-1} mode in Figure 2a, there do not appear to be any significant differences between parts a and b of Figure 2, with the possible exception that the surface hydroxyl stretching mode is of stronger intensity in the former than in the latter. Thus the alteration of the preparation procedure perturbs the final surface species distribution only slightly. Consequently, we would argue that the hydroxy methylphosphonate in Figure 2b was produced not by a completely new reaction pathway but rather by a subtle perturbation in the already existing reaction pathway for the decomposition of DMMP, following adsorption directly on the surface at 573 K (Figure 2a). This leads to the conclusion that the hydroxy methylphosphonate is a transient species in this latter reaction (Figure 2a) and that the effect of the alternative preparation procedure (Figure 2b) was to quench the complete decomposition of this species.

The homogeneous chemistry of phosphonate esters gives several important clues as to how the decomposition mechanism proceeds. As discussed earlier in connection with the decomposition of adsorbed DIMP, the phosphorus center of the dissociatively adsorbed DMMP will not be susceptible to nucleophilic substitution. However, unlike the isopropoxy moiety of dissociatively adsorbed DIMP, the methoxy moiety of dissociatively adsorbed DMMP cannot undergo facile elimination to form a gaseous alkene. Therefore, the only reasonable possibility is for decomposition to proceed by nucleophilic substitution at the alkyl carbon of the ester moiety, as occurs in the hydrolysis of phosphonate esters under acidic conditions (see section III.1). Furthermore, this must be a bimolecular nucleophilic substitution since the methyl group of the ester moiety does not tend to form a carbocation. This leads us to propose a mechanism for the decomposition of DMMP which is consistent with these observations (Scheme IV). Scheme IVA depicts the base-catalyzed nucleophilic substitution by a lattice oxygen at the alkyl carbon center of the dissociatively adsorbed DMMP to form the hydroxy methylphosphonate intermediate and a surface methoxide (Scheme IVB). The hydroxy phosphonate and methoxide eliminate rapidly to form gaseous methyl alcohol and methylphosphonate, as shown in Scheme IVC. This last step is tentative, but it is in accordance with the observation that additional hydrocarbons do not accumulate on the surface during the decomposition of adsorbed DMMP. At the decomposition temperature, the surface methoxide is unstable and would be oxidized to a formate. However, the formate so produced would be exceedingly difficult to remove from the surface and would

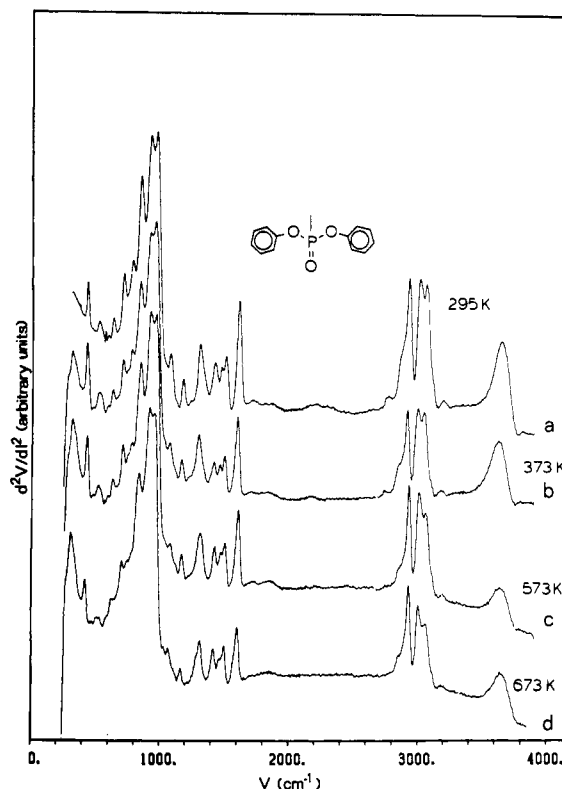


Figure 3. Inelastic electron tunneling spectra of aluminum oxide surfaces exposed to a 0.025 M solution of diphenyl methylphosphonate at 295 K and subsequently heated in vacuo to various temperatures: (a) 295 K, (b) 373 K, (c) 573 K, and (d) 673 K.

therefore be indicated in the spectra. Since it is not, the reaction depicted in Scheme IVB seems to be the most reasonable. Data concerning the gaseous decomposition products could confirm this, but unfortunately they are currently unavailable. Nevertheless, we feel that Scheme IV correctly shows an important feature of the decomposition in that it must proceed not by nucleophilic attack at the phosphorus but by nucleophilic attack at the methoxy carbon.

4. The Adsorption and Decomposition of DPMP. The tunneling spectra of diphenyl methylphosphonate (DPMP) adsorbed on aluminum oxide at 295 K and heated to 373, 573, and 673 K are shown in Figure 3, parts a–d, respectively. The interpretation of these spectra is facilitated by recognizing the three majority surface species present: surface hydroxyls, adsorbed phenol, and dissociatively adsorbed DPMP (i.e., phenyl methylphosphonate). The adsorbed phenol is the product of the dissociative adsorption of DPMP.

The relative surface coverages of these three species can be assessed independently from different regions of the tunneling spectrum. The surface hydroxyl coverage can be monitored by the peak at approximately 3630 cm^{-1} which is due to the (Al)O–H stretching vibration. The adsorption of phenol on thermally pretreated alumina powders has been studied with infrared spectroscopy.³¹ Adsorption between 420 and 573 K produced a surface phenoxide coordinated to a surface aluminum.³¹ A similar conclusion was reached concerning the nature of phenol adsorption at 295 K in a tunneling spectroscopic study.³² The adsorption conditions and instrumental technique in the latter study are similar to those employed here. A comparison between the tunneling spectrum in Figure 3a and the tunneling spectrum of adsorbed phenol in this previous work³² indicates that the prominent low-energy shoulder at approximately 2850 cm^{-1} in Figure 3a is due to a surface phenoxide. The phenoxide of the phenyl methylphosphonate will not contribute to this mode since each of its CH stretching modes should lie above 3000 cm^{-1} , in

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analogy with the spectrum of liquid phenol.³³ Finally, the mode at 2925 cm⁻¹, which is due to the $\nu_s[(P)CH_3]$ vibration, can be used to characterize the surface coverage of the phenyl methylphosphonate. However, care must be taken in judging the intensity of this mode since it is partially superposed on the broad surface phenoxide mode appearing as a shoulder at 2850 cm⁻¹.

The tunneling spectra in Figure 3 are consistent with these assignments. In going from the spectrum of DPMP adsorbed at 295 K (Figure 3a) to the spectrum of DPMP adsorbed at 295 K and heated to 373 K (Figure 3b), the relative intensities of all CH modes remain virtually unchanged (the absolute intensity difference between parts a and b of Figure 3 is attributed to a difference in the initial adsorbate concentrations). This is consistent with the dissociative adsorption of DPMP at 295 K, because if there had been a large concentration of molecularly adsorbed DPMP on the surface at 295 K, the subsequent heating to 373 K would almost certainly have caused some of this to desorb, or decompose, which would have then resulted in a change in the CH stretching mode intensities. Rather, only the hydroxyl mode is observed to decrease in intensity, probably due to the desorption of associatively bound water. The dissociative adsorption of DPMP is also in accord with the extremely high rates of homogeneous alkaline hydrolysis for DPMP compared with DMMP, since DMMP adsorbs dissociatively, and the dissociative adsorption and homogeneous alkaline hydrolysis reactions appear to be mechanistically very similar.

In going from the spectrum of adsorbed DPMP heated to 373 K (Figure 2b) to the spectrum of adsorbed DPMP heated to 573 K (Figure 2c), the changes observed are due to increasing dehydroxylation caused by the higher temperature and to the desorption of some of the surface phenoxide as gaseous phenol, which accompanies this more extensive dehydroxylation. These changes are most clearly visible in terms of the decrease in the amplitude of the low-energy shoulder at 2850 cm⁻¹ in going from part b to part c in Figure 3. Since the intensity of this shoulder is proportional only to the surface phenoxide coverage, this coverage must be decreasing. However, the decrease in surface phenoxide coverage also causes all of the other phenyl-related modes to decrease in intensity, and this causes the overall spectrum to change shape somewhat. For example, the CH stretching modes at 3004 and 3055 cm⁻¹ also decrease in intensity. However, since the latter is purely due to a phenyl vibration, it decreases more substantially than the former, which has a partly alkyl character. Nevertheless, all changes observed in going to the higher temperature can be related to either the desorption of the surface phenoxide as gaseous phenol and/or further dehydroxylation.

These same trends persist in going to the spectrum of adsorbed DPMP heated to 673 K (Figure 3d). Specifically, the spectrum does not reflect the appearance of the methylphosphonate, which

would be evident from the appearance of a mode at 750 cm⁻¹ that is not observed. In addition, the intensities in the 1300 to 1500 cm⁻¹ spectral region are properly accounted for by assuming only the presence of phenyl methylphosphonate. Thus it appears that the phenyl methylphosphonate is stable on the surface at 673 K and does not decompose to the methylphosphonate. This is consistent with the mechanisms that were proposed earlier for the decomposition of adsorbed DIMP and adsorbed DMMP (Schemes II and IV). In analogy with these, the DPMP must necessarily decompose by nucleophilic substitution at the phenyl carbon. This is an unfavorable reaction, as discussed earlier in connection with the homogeneous hydrolysis of DPMP in acidic media (section III.1). Thus, the lack of reactivity of the phenyl methylphosphonate is strong confirmation that decomposition of adsorbed phosphonate esters proceeds either by elimination (DIMP) or nucleophilic attack at the alkyl carbon of the ester (DMMP), resulting in C-O bond cleavage rather than P-O bond cleavage.

IV. Conclusions

This work should perhaps be viewed as representing both important conceptual and instrumental achievements. Most previous studies employing tunneling spectroscopy to study chemisorption and surface reactions can be categorized as survey studies, where several different compounds are adsorbed at 295 K. Although important, this type of work represents only the first step in studying surface and catalytic chemistry, since much of the latter occurs at significantly higher temperatures. When considered as a whole with the previous study of DMMP,¹ this study represents an advance in the application of tunneling spectroscopy to study the chemistry of adsorption and reaction, because, unlike survey studies, we have focused in detail on the adsorption of one phosphonate ester, DMMP, over a wide temperature range, 200–673 K. This in turn has led to significant general conclusions concerning the chemistry of phosphonate esters on oxide surfaces. It was shown that the appropriate homogeneous reaction chemistry could explain the observed decomposition reactions of phosphonate esters on aluminum oxide. This is a consequence of localized bonding interactions that occur on the oxide surface. Two important reactions were identified: (1) nucleophilic substitution at the phosphorus atom and (2) nucleophilic substitution at the alkyl carbon of an alkoxy. The relative ease of C-O bond cleavage in isopropoxy, methoxy, and phenoxy groups on the aluminum oxide was found to decrease in that order. Finally, these ideas were incorporated into mechanisms for surface reactions. It is hoped that this success with tunneling spectroscopy will stimulate further work with this promising vibrational spectroscopic technique.

Acknowledgment. This work was supported by the Army Research Office under Grant No. DAAG29-83-K-0094.

Registry No. DIMP, 1445-75-6; DMMP, 756-79-6; DPMP, 7526-26-3; alumina, 1344-28-1.

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