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Articles

Reactions of Ti^+ with CH_3PH_2. Metal-Catalyzed Oligomerization of Phosphorus in the Gas Phase

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The reactions of Ti^+ with methylphosphine in the gas phase have been characterized using the technique of Fourier transform mass spectrometry. Elimination of H_2 is the initial reaction of the metal ion with CH_3PH_2. Using CH_3PD_2 as the substrate resulted in a loss of D_2, which supports the initial formation of $[Ti{=}PMe]^+$. Collision-induced dissociation (CID) and ion−molecule reactions, however, give evidence for a rapid conversion to the presumably more stable $[TiP(H){=}CH_2]^+$. The product from the primary reaction reacts further in successive steps with the neutral methylphosphine to form a variety of higher order ionic reaction products, including the series $TiP_2^+ \rightarrow TiHP_3^+ \rightarrow TiP_4^+ \rightarrow TiHP_5^+ \rightarrow TiP_6^+$. CID and general bonding principles are not inconsistent with the formation of titanium phosphacycles, in particular TiP_4^+ with a five-membered ring structure, but other possible structures are also discussed.

Introduction

The syntheses of polyphosphacycle ligands, either neutral or anionic, such as P_4, P_5^-, P_4CH^-, and P_6^{2-}, have been reported.[1] P_4CH^- has a structure analogous to the one for P_5^-, but one phosphorus atom has been replaced by CH. We report here a study of the reactions of Ti^+ with methylphosphine and our attempts to characterize the product ions, not only from the primary but also from higher order reactions. In particular, we were intrigued by the observation of the formation of a series of ions, $TiP_2^+ \rightarrow TiHP_3^+ \rightarrow TiP_4^+ \rightarrow TiHP_5^+ \rightarrow TiP_6^+$, and made an effort to elucidate the structures of those as well as other product ions from the reactions. We propose cyclic structures for these ions, but also discuss other possible structures consistent with collision-induced dissociation (CID) studies. A particular effort was made to establish the structure of the product ion from the primary reactions of Ti^+ with the neutral methylphosphine.

Reactions of metal ions with various substrates in the gas phase have been extensively studied in past years by several research groups,[2] as evidenced by recent reviews.[3] Organic substrates have been the subjects in most of those studies; in contrast, inorganic species have received much less attention. Some work has been reported on the reactions of metal ions with ammonia and amines,[4] but to the best of our knowledge, no studies have been performed on the reactions of metal ions with phosphines.

Experimental Section

The experimental approach has been described elsewhere,[5,6] but briefly, the experiments were done by employing an EXTREL FTMS-2000 Fourier transform mass spectrometer equipped with a pulsed CO_2 laser and a laser desorption interface.

Ti^+ was generated from the pure metal using the laser desorption method developed by Freiser and co-workers[7] and isolated using double-resonance techniques[8] prior to monitoring the reactions with the neutral phosphines, which were present in the cell of the mass spectrometer at a static pressure. All reaction paths were confirmed by using double-resonance techniques.

Argon or nitrogen buffer gas, maintained at roughly 40−100 times the pressure of the sample gas, was used in a duplicate set of experiments to avoid misinterpretations due to the presence of electronically or kinetically excited titanium ions. It should be noted, however,

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Table 1. Reactions of Ti^+ with Methylphosphine (CH_3PH_2)

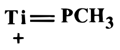
reactant ion	reaction products	% yield
Ti^+	$TiCH_3P^+ + H_2$	95
	$TiCHP^+ + 2H_2$	5
$TiCH_3P^+$	$TiCH_2P_2^+ + [CH_4 + H_2]$	50
	$TiP_2^+ + [2CH_4 \text{ or } C_2H_6 + H_2]$	40
	$TiP_2H_2^+ + [C_2H_4 + H_2]$	10
$TiCH_2P_2^+$	$TiCH_3P_3^+ + CH_4$	50
	$TiCHP_3^+ + [CH_4 + H_2]$	30
	$TiP_3^+ + [C_2H_7]$	20
TiP_2^+	$TiP_3H^+ + CH_4$	60
	$TiCH_3P_3^+ + H_2$	35
	$TiP_3^+ + [CH_5]$	5
TiP_3H^+	$TiP_4^+ + [CH_4 + H_2]$	100
$TiCH_3P_3^+$	$TiP_4^+ + [C_2H_6 + H_2]$	30
	$TiCH_4P_4^+ + CH_4$	20
	$TiCH_5P_4^+ + CH_3$	50
TiP_4^+	$TiP_5H^+ + CH_4$	100
TiP_5H^+	$TiP_6^+ + [CH_4 + H_2]$	100

that operating only slightly above the threshold laser fluence for metal ion production led to low production of ions in excited states, much lower than that produced by electron impact. This was verified by a comparative study of the reactions of $Fe(CO)_5$ with Fe^+ produced by electron impact and laser desorption (varying the power density) and by comparing the results to those of a study of the reactions of $Fe(CO)_5$ with Fe^+ in excited states, which was reported by Oriedo and Russell.[9] It is assumed that Ti^+ behaves in a similar manner, such that the observed reactions are predominantly due to ground state titanium ions.

The labeled and unlabeled methylphosphines were prepared according to the literature and characterized by NMR and FTMS prior to use. The deuterium-labeled water, ethene, and ethane were commercially obtained and used without further purification.

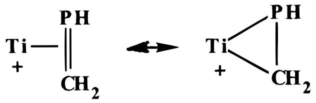
Results and Discussion

The ionic products from the primary and several higher order reactions of Ti^+ with CH_3PH_2 are listed in Table 1. The main reaction product is $TiCH_3P^+$, and two probable structures are shown in **1** and **2**. The single dehydrogenation reaction with CH_3PD_2 reveals elimination of D_2 only and, thus, strongly supports **1** in favor of **2**. The structure of this ion was further probed by CID and ion−molecule reactions. The three CID channels that were observed are shown in (1)−(3), and Figure 1 shows the variation of CID product ion intensities as a function of ion kinetic energy for $TiCH_3P^+$. A loss of CH_3 would have been expected as a main CID product for structure **1**, and to appear at lower energies than Ti^+, but is only observed at very high energies and is always a minor CID product, even at high energies. The CID results, thus, point to structure **2** in favor of structure **1**. The rationale for this is that if the structure was $Ti{=}PCH_3^+$ (**1**), then to produce Ti^+ upon CID, one would have to break the presumably strong Ti=P bond, whereas to produce TiP^+, one would only have to break the $P-CH_3$ bond. Thus, one would expect TiP^+ to appear at lower energies than Ti^+, which is not the case.



$$\overset{}{\underset{+}{Ti}}{=}PCH_3$$

1



2

$$TiCH_3P^+ \xrightarrow{CID} TiCHP^+ + H_2 \qquad (1)$$

$$\longrightarrow Ti^+ + CH_3P \qquad (2)$$

$$\longrightarrow TiP^+ + CH_3 \qquad (3)$$

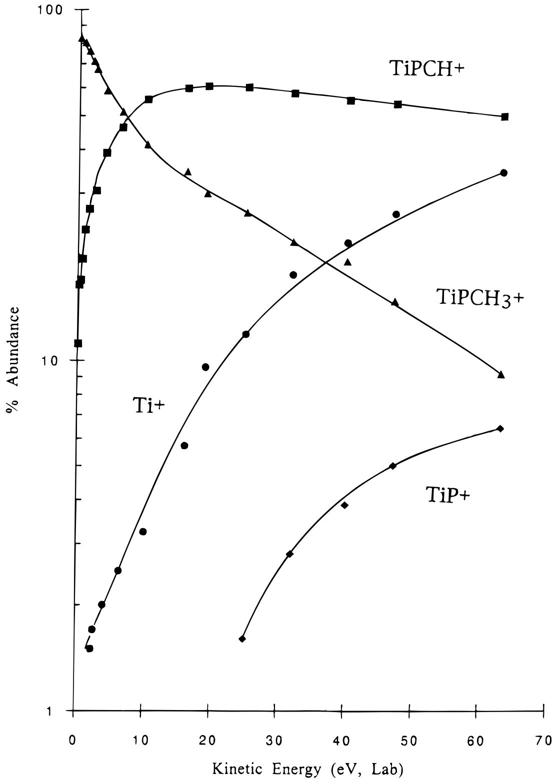


Figure 1. Collision-induced dissociation (CID) product intensities vs ion kinetic energy for $TiCH_3P^+$ ions generated in the main primary reaction of Ti^+ with CH_3PH_2.

Reactions of $TiCH_3P^+$ with perdeuterated samples, such as C_2D_4, C_2D_6, and D_2O, resulted only in a single H/D exchange, most clearly evidenced in the D_2O case. It is well-known in mass spectrometry studies that hydrogen atoms bound to nitrogen are relatively labile, compared to, for example, hydrogen atoms bound to carbon atoms. This is evidenced in relatively rapid D/H exchanges when deuterium-labeled ammonia or amines are used. During the course of the experiments described in this report, it became evident that D/H exchanges for the labeled methylphosphine, CH_3PD_2, were even more rapid than those for the analogous CH_3ND_2. Thus, it is clear that hydrogen atoms bound to phosphorus are very labile, much more so than methyl-group hydrogen atoms. Thus, a single, rapid H/D exchange between $TiCH_3P^+$ and D_2O points to a single phosphorus bound hydrogen atom plus two hydrogen atoms on the carbon, rather than three identical methyl-group hydrogen atoms. The single H/D exchange of $TiCH_3P^+$, in addition to the CID results, clearly points to structure **2** for this ion, even though the exclusive D_2 elimination from $MePD_2$ had originally supported structure **1**.

Further experimental evidence for structure **2** in favor of structure **1** is derived from the observation of the reaction of $TiCH_2DP^+$, produced in the H/D exchange with D_2O, with the neutral methylphosphine, CH_3PH_2. Only the production of an ion at *m*/*z* 124 is observed, which is assigned as $TiCH_2P_2^+$. There is, thus, an exclusive loss of the deuterium atom, which has two possible explanations: The deuterium atom is attached to the phosphorus atom and is not one of the three connected to the carbon atom. This would point to structure **2** in favor of **1**. The other explanation is that if the deuterium is connected to the carbon atom and the structure is **1**, rather than **2**, then

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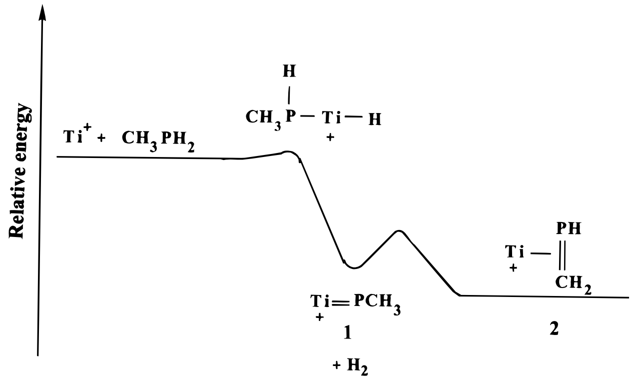


Figure 2. Qualitative potential energy surface for the reaction of Ti^+ with CH_3PH_2 to produce $TiCH_3P^+$ and H_2.

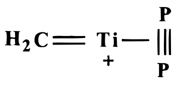
the methyl group from **1** is lost upon the reaction with the neutral methylphosphine to produce $TiCH_2P_2$. CID studies could not be performed on $TiCH_2PD^+$ due to low abundance of this ion.

The three independent experimental observations are all consistent with structure **2** for the product ion in the primary reactions of Ti^+ with CH_3PH_2.

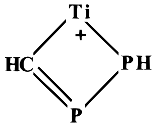
On the basis of these findings, we suggest that **1** is an intermediate in the formation of **2**, the latter being more stable. Upon high-energy CID, **2** may again rearrange over an activation barrier to form **1**, which explains the loss of CH_3 only observed from the highly excited ion. For comparison, see the discussion below on $TiCH_3P_3^+$ where the exclusive loss of a methyl group was observed upon CID. The initial step in the reaction is believed to be insertion into a P−H bond followed by transfer of the other phosphorus-connected hydrogen and elimination of molecular hydrogen to form **1**. Rearrangement to the more stable **2** follows. Figure 2 shows a qualitative potential energy surface for this proposed reaction scheme. It should be noted here that in the FTMS the CID is usually a multicollision process, even though, by maintaining a low pressure of the collision gas, one can approach the single-collision regime. Thus, CID in the FTMS suffers from the inherent possibility of rearrangements prior to bond cleavages. It is exactly this fact that makes ion−molecule reactions (such as the reactions with D_2O) often more informative about ion structure than CID.

Unfortunately, critically evaluated thermodynamic data are unavailable for CH_3P, so that the dissociation energy for the metal ion/ligand bond cannot be calculated. The TiP double bond proposed in structure **1** is, however, not without precedent. Fenske et al.[10] have reported the synthesis of a compound claimed to contain a TiP double bond, and Ehrig et al.[11] have reported a theoretical investigation supporting this assumption.

The main ionic products in the secondary reactions of $TiCH_3P^+$ with the neutral methylphosphine were $TiCH_2P_2^+$ and TiP_2^+. The latter exclusively loses P_2 upon CID, and P_2 is therefore assumed to be a ligand on Ti^+, probably in a side-on configuration. $TiCH_2P_2^+$ was found to yield $TiCH_2^+$, TiP_2^+, and $TiCP_2^+$ upon CID, and we present three probable structures for this ion: **3a**−**c**. Although not inconsistent with the CID results, **3a** may be least likely, as carbenes are rarely produced in the gas-phase chemistry of small transition metal ions, although more commonly observed for larger transition metal ions.[3b]



3 a



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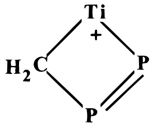
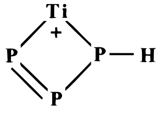


3 c

TiP_2^+ reacted in tertiary reactions to form TiP_3H^+ and $TiCH_3P_3^+$, and by the use of CH_3PD_2, only the elimination of CH_3D was observed in the formation of the former product ion whereas only elimination of D_2 was observed in the formation of the latter ion. $TiCH_3P_3^+$ is also the main product ion in the reaction of $TiCH_2P_2^+$ with the neutral methylphosphine. CID on $TiCH_3P_3^+$ only yields TiP_3^+ with the elimination of CH_3, and we present structures **4a**,**b** as probable candidates for TiP_3H^+ and $TiCH_3P_3^+$, respectively.



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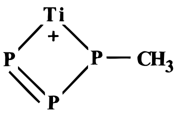
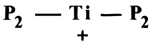
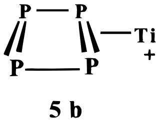


4 b

TiP_4^+ was formed from two precursors, two-thirds from TiP_3H^+ and one-third from $TiCH_3P_3^+$, as determined by double-resonance experiments. No evidence (CID or ion−molecule reactions) was found for two different structures for TiP_4^+ from these two precursors. TiP_4^+ can have several different structures, five possibilities being **5a**−**e**.



5 a



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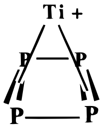

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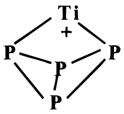
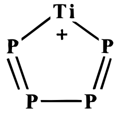


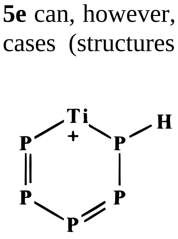
5 d



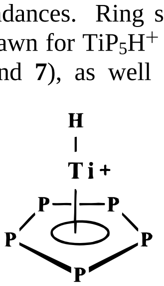
5 e

Three major fragment ions, TiP_3^+, TiP_2^+, and Ti^+, were observed upon CID, the first two being the dominant fragments and produced in similar yields. Structures **5a**,**b** are unlikely because TiP_3^+ would not be expected to be a major CID product in those cases. Loss of Ti^+ upon CID would be expected to dominate for structure **5b**, which is not the case. Losses of P_2 and 2 P_2 would be expected to be the main CID channels for structure **5a**, but not loss of P. The CID results are, however, not inconsistent with structures **5c**−**e**.

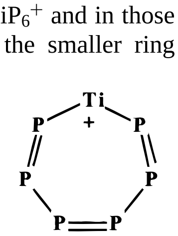
TiP_4^+ reacts further to form TiP_5H^+, which in turn forms TiP_6^+ upon reactions with the neutral methylphosphine. CID experiments could not be performed for these ions because of their low relative abundances. Ring structures, analogous to **5e** can, however, be drawn for TiP_5H^+ and TiP_6^+ and in those cases (structures **6a** and **7**), as well as in the smaller ring structures, it becomes clear why TiP_n^+ ions are predominantly formed for even values of *n* and $TiHP_n^+$ or $TiCH_3P_n^+$ ions are predominantly formed for odd values of *n* (the only exception being TiP_3^+, produced in small abundances). Both the condition



6 a



6 b



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of stable leaving groups and the requirement that general bonding principles be obeyed are fulfilled in the formation of the cyclic structures, which include the Ti cation in the ring structures, depicted above. The cyclic structures involving titanium as part of the ring skeleton are presented here as logical possibilities, consistent with the experimental facts, even though ligands such as, or similar to, those shown in **5d**, **5c**, and **6b** have been reported in the literature[1,12] and need also be considered. Theoretical studies on P_n clusters[13] and in particular P_6 have shown that even though planar benzene-like P_6 ring ligands are known, isolated P_6 has several other energetically more favorable structures.[14] In fact, the benzene-like structure is the least favorable on the basis of these calculations.

Conclusion

This report describes our efforts to elucidate the structure of the primary product ion from the reaction of Ti^+ with CH_3PH_2 and CH_3PD_2. Using the previously accepted deduction method, frequently seen in the literature, to assign the structure of this ion as $[Ti{=}PCH_3]^+$, on the basis of the fact that Ti^+ only eliminates D_2 from CH_3PD_2, was found to be erroneous. Detailed studies of the primary reaction product by CID, H/D exchanges with D_2O and other substrates, and ion−molecule reactions of the product ion after the H/D exchange all gave convincing evidence that $[Ti{=}PCH_3]^+$ is only an intermediate, which rearranges to the presumably more stable $[TiP(H){=}CH_2)]^+$. This finding should caution researchers not to rely entirely on results from reactions with deuterated samples in drawing conclusions about the structures of product ions. The titanium-catalyzed oligomerization of phosphorus, also described in this report, is of particular interest, and studies of the formation and structures of metal polyphospha complexes involving other metal ions are in progress, as well as a study of other, related phosphines.

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