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Gas-Phase Reactions of M^+ and MO^+ (M = Sc, Ti, V) with Toluene

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The reactions of M^+ and MO^+ (M = Sc, Ti, V) with toluene in the gas phase have been characterized by employing Fourier transform mass spectrometry. Dehydrogenation is the main reaction channel for Sc^+ and Ti^+ in the reactions with toluene producing $MC_7H_6^+$, but V^+ is unable to dehydrogenate toluene and only forms an adduct product. To further characterize these reactions, $C_6H_5CD_3$ and toluene-α-^{13}C were also studied, and unexpectedly, different behavior was observed in their reactions with Sc^+ compared with Ti^+. In the reactions with $C_6H_5CD_3$, Sc^+ predominantly eliminates HD (90%) and to a lesser extent H_2 (8%), and D_2 (2%), whereas Ti^+ exhibits lesser specificity and eliminates HD (50%), H_2 (20%), and D_2 (30%). Ion/molecule reactions (IMR) of the three different product ions, $TiC_7H_{6-n}D_n^+$ (n = 1, 2, and 3) point to a common structure for all three. IMR of the products from the reactions with the ^{13}C-labeled toluene provide evidence for a common structure but some differences in the reaction mechanisms for $ScC_7H_6^+$ and $TiC_7H_6^+$. Collision-induced dissociation (CID) and ligand exchange reactions provide evidence that the structure of $MC_7H_6^+$ is $CpM(CCH)^+$. The reactions were very fast, proceeding at close to collision rates. MO^+ were found to be unreactive with toluene and only formed the adducts $MO(toluene)^+$.

Introduction

The reactions of bare and ligated metal ions with organic and inorganic substrates have received considerable attention in recent years.[1] Metal-catalyzed reactions are of both fundamental and applied interest, and the development of ion-beam and Fourier transform mass spectrometry techniques has allowed researchers to probe the elementary steps in the gas-phase reactions of metal and metal-containing ions with various substrates.

Several reports have appeared of studies of the reactions of transition-metal ions with aromatic compounds. Dietz, Chatellier, and Ridge originally reported the reactions of Fe^+ with chlorobenzene,[2] and those studies were later expanded by Bjarnason et al.[3] and Huang and Freiser.[4] Bjarnason also investigated the metal-catalyzed oligomerization of the related naphthalene halides.[5] Bjarnason et al. studied the reactions of Fe^+ with a variety of benzene derivatives including toluene[6a] and developed a method for isomer discrimination for disubstituted benzene derivatives using metal-ion reactions.[6b] Similarly, Stepnowski and Allison studied the reactions of Ni^+ with a large group of aromatic substrates.[7] Only a few reports have, however, dealt with the reactions of the smaller, more reactive ions, Sc^+, Ti^+, and V^+, but Staley and co-workers studied the reactions of Ti^+ with chlorobenzene.[8] Recently, a report emerged from this laboratory on the reactions of V^+ and VO^+ with the isomers of xylene.[9]

Toluene has been the subject of several studies involving the gas-phase chemistry of transition metal ions. Previous work has found toluene to be inert with V^+,[10] Fe^+ and Ni^+, [6a,7,11] Cu^+,[10] and Nb^+,[10] but it is dehydrogenated by Rh^+.[11] Au^+ afforded charge-transfer and hydride abstraction in reactions with toluene.[12] The reactions of the oxides of the above mentioned metal ions have received little attention. Clemmer, Aristov, and Armentrout[13] studied the reactions of ScO^+, TiO^+, and VO^+ with D_2. Closely related to this study, Schröder et al. have investigated the reactions of FeO^+ with

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toluene and deuterium-labeled toluene and observed a highly selective benzylic C−H bond activation (>92%).[14]

Experimental Section

The experimental approach has been described elsewhere,[3,5,6] but briefly, the experiments were done by employing a Finnigan FT/MS-2000 (originally a Nicolet FTMS-2000) Fourier transform mass spectrometer equipped with a pulsed CO_2 laser and a laser desorption interface.

The metal ions were generated using the laser desorption method developed by Freiser and co-workers[15] and isolated using double resonance techniques[16] prior to monitoring the reactions with the neutral toluene, which was present in the cell of the mass spectrometer at a static pressure. MO^+ was generated by reacting M^+ with the instruments background gases (mostly air and water from the direct insertion probe).

All reaction paths and ion formulas were confirmed by using double resonance techniques and accurate mass measurements. Argon or nitrogen buffer gas, maintained at 50−200 times the pressure of the sample gas, was used in a duplicate set of experiments to avoid misinterpretations due to the presence of “hot” metal ions. In addition, the metal ions were allowed to react with the substrate, in the presence of argon, for about 4 half-lives and then reisolated and their reactions monitored by collecting mass spectra at different time intervals. This method should minimize the abundance of metal ions in excited states and give results that can be attributed to the behavior of the ground state. It should be noted, however, that by operating only slightly above the threshold laser fluence for metal ion production, the production of ions in excited states is low, much lower than that produced by electron impact. This was confirmed by examining the reactions of $Fe(CO)_5$ with Fe^+ produced by electron impact and with Fe^+ produced by laser desorption (varying the power density). Comparing these results with the reactions of $Fe(CO)_5$ with Fe^+ in excited states reported by Russel’s group[17] confirmed that predominantly ground-state Fe^+ was used in the present study. It is assumed that the other transition-metal ions generated in these experiments behave in the same fashion. The kinetic analysis of the reactions studied here as well as the results obtained by employing buffer gases do not indicate the presence of an appreciable abundance of “hot” ions, unless their reactive behavior is identical to the ground state ions.

Mass spectra were acquired in the broad band mode with bandwidth of 1200 kHz employing 32k or 64k data points. The sample pressure was varied from 2×10^{-8} to 2×10^{-7} Torr, and spectra were acquired after reaction times ranging from 0.003 to several seconds. The toluene and the isotopically labeled toluene samples were commercially obtained and used without further purification, except for a few freeze−pump−thaw cycles to remove dissolved gases.

Results and Discussion

The primary reaction products from the reactions of the metal ions with the unlabeled and isotopically labeled toluene are shown in Table 1. The only primary reaction of Sc^+ and Ti^+ with toluene is dehydrogenation. V^+ only forms an adduct $VC_7H_8^+$ that reacts in secondary reactions with toluene to give $VC_{14}H_{16}^+$. The reactions of Sc^+ and Ti^+ with toluene are very fast, the measured rate constants being $k_1 = 2.3$ and $k_2 = 2.1$ for Sc^+ and Ti^+, respectively (in units of 10^9 cm^3 $molecule^{-1}$ s^{-1}). These values are close to and actually higher than the collision rates, as k_{coll} are 1.8 and 1.7, respectively for these two ions (same units as above).[18] The uncertainty in the experimental values for the rate constants is estimated to be around 30%, mainly due to uncertainty in the pressure measurements. This puts the collision rates within the uncertainty range of the measured rates.

Table 1. Products Ion Distribution from the Primary Reactions of Sc^+, Ti^+, and V^+ with Toluene and Toluene-d_3[a]

	substrate				
	$C_6H_5CH_3$		$C_6H_5CD_3$		
metal ion	$-H_2$	M(toluene)$^+$	$-H_2$	−HD	$-D_2$
Sc^+	100	0	8	90	2
Ti^+	70	30	20	50	30
V^+	0	100			

[a] A relative error of 5−10% was observed in the abundances of the reaction products in repeated sets of the experiments.

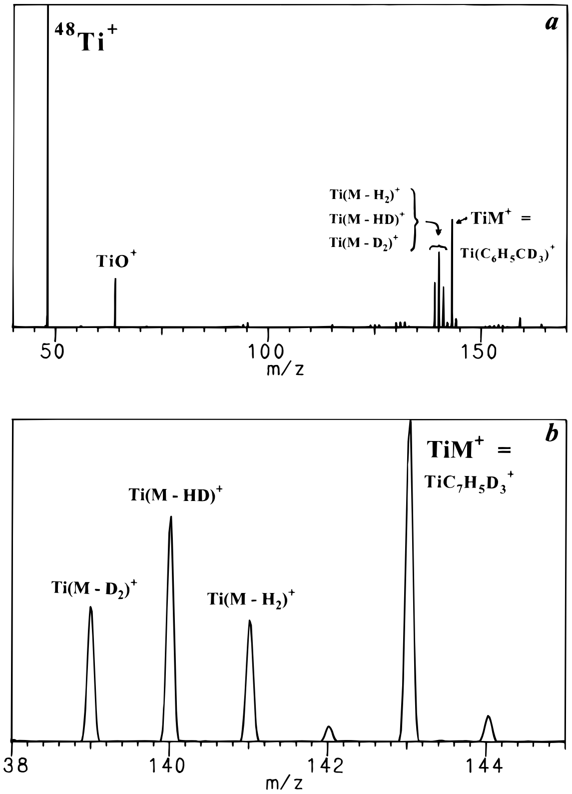

Figure 1. Mass spectra showing (a) the ionic reaction products resulting from the reactions of $^{48}Ti^+$ with neutral $C_6H_5CD_3$ after a suitable reaction time and (b) an expanded region of the products from the dehydrogenation reactions.

Figure 1 shows mass spectra obtained after the reactions of $^{48}Ti^+$ with $C_6H_5CD_3$ for a reaction time of 0.3 s with the pressure of the labeled toluene at 1×10^{-7} Torr. Figure 1a shows the ionic products of the reactions, including some TiO^+ due to background

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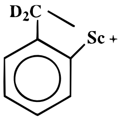
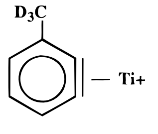
impurities, and Figure 1b shows the expanded region of the spectrum focusing on the ionic products resulting from the dehydrogenation reactions. The spectrum in Figure 1b is characterized by good resolution and very high signal-to-noise ratio, and the significant elimination of H_2, HD, and D_2 is clearly evident, in striking contrast with the results obtained for Sc^+ as tabulated in Table 1. This ratio of H_2, HD, and D_2 elimination did not change markedly with varied experimental conditions, such as pressure of the neutral reactant or with the incorporation of buffer gases at relatively high pressures. The main effect of the buffer gas on the spectra was to increase the relative abundance of $TiC_7H_8^+$ (the adduct complex ions) compared with the H_2 elimination product ion, $TiC_7H_6^+$. This is in accordance with the expected behavior for an association reaction responsible for the production of $TiC_7H_8^+$.

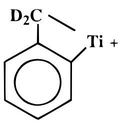
The dominant elimination of HD by Sc^+ from the labeled toluene allows us to suggest a speculative structure **I** for $ScC_7H_4D_2^+$. The different results obtained in the case of Ti^+ point to a different structure or structures for the dehydrogenation product ion(s). One might speculate, based on the reactions with the labeled toluene, that three different product ions are formed, shown in (the speculative) structures **IIa**−**c**, corresponding to elimination of H_2, HD, and D_2, respectively. To test this, we isolated each ion $TiC_7H_{6-n}D_n^+$ ($n = 1, 2, 3$) from the reactions of Ti^+ with the labeled toluene and allowed these ions to react with several substrates, but no significant differences could be observed in the reactivity of these ions with respect to those substrates. These results point to an identical structure for these three ions.



I



a



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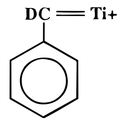


c

II

Collision-induced dissociation (CID) studies were performed on $TiC_7H_6^+$ (**1**). Figure 2 shows the experimental approach used for this CID study. The ion of the most common isotope of Ti, ^{48}Ti, is first isolated and then allowed to react with the neutral toluene. Figure 2a shows a mass spectrum obtained after a suitable reaction time for the reactions of $^{48}Ti^+$ with toluene. Figure 2b shows a mass spectrum obtained after the isolation of **1**, by ejecting all other ions from the cell, and Figure 2c shows the CID spectrum of **1** obtained after excitation of **1** to 85 eV prior to collisions with argon. The losses of C_nH_n with $n = 2$, 4, and 5 are observed as the main reactions in the CID spectrum. A CID study was also performed on $ScC_7H_6^+$ (**2**) at similar excitation energies, and the CID products for both **1** and **2** are listed in Table 2. As is usually the case, the relative ratio of CID products was heavily dependent on excitation energy. Over a wide range of excitation energies the two ions, **1** and **2**, yielded the same CID reaction products, but H_2 loss and C_2H_4 loss were consistently more important for **2**.

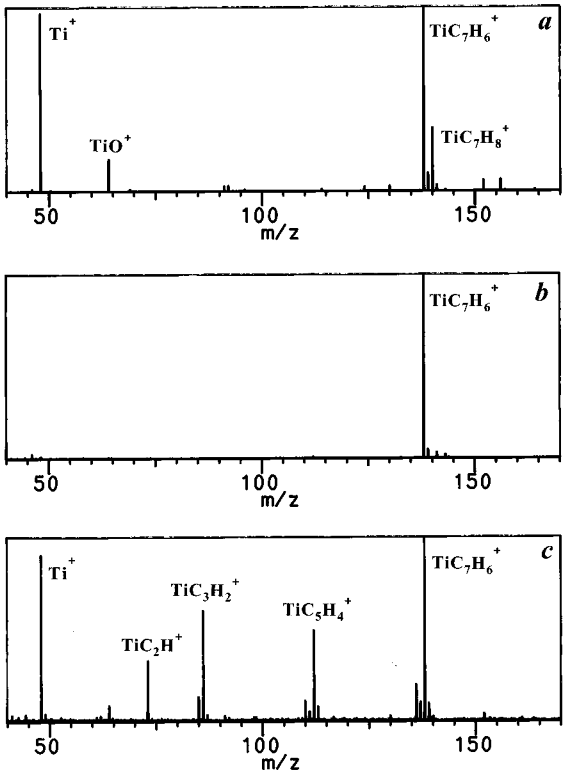


Figure 2. Mass spectra showing the experimental approach to the collision-induced dissociation (CID) study of $TiC_7H_6^+$ (**1**) formed in the reactions of $^{48}Ti^+$ with toluene. The spectrum in (a) shows the ionic products from the reactions of $^{48}Ti^+$ with toluene for a suitable reaction time. The spectrum in (b) was obtained after isolation of **1**, by ejecting all other ions from the cell. The spectrum in (c) shows the CID products after exciting **1** to 85 eV (Lab) prior to collisions with argon.

Table 2. Collision-Induced Dissociation (CID) of $ScC_7H_6^+$ (2) and $TiC_7H_6^+$ (1) Formed from Toluene, Normalized to the Largest Value[a]

elimination of	$ScC_7H_6^+$	$TiC_7H_6^+$
H_2	100	10
C_2H_2	75	60
$C_2H_4/[C_2H_2 + H_2]$	50	8
$[C_4H_4]$	32	70
$[C_5H_5]$	9	40
$[C_7H_6]$	45	100

[a] Ions were excited to 85 eV (lab) kinetic energy prior to dissociation collisions.

The reactions of **1** with several substrates was investigated to further gain information regarding the structure of **1**. These reactions are listed as follows:

$$\mathbf{1} + H_2O \rightarrow C_5H_5TiOH^+ + C_2H_2 \quad (1)$$

$$\mathbf{1} + D_2O \rightarrow C_5H_5TiOD^+ + C_2HD \quad (2)$$

$$\mathbf{1} + H_2{}^{18}O \rightarrow C_5H_5Ti^{18}OH^+ + C_2H_2 \quad (3)$$

$$\mathbf{1} + HCl \rightarrow C_5H_5TiCl^+ + C_2H_2 \quad (4)$$

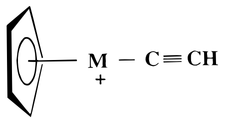
$$\mathbf{1} + DCl \rightarrow C_5H_5TiCl^+ + C_2HD \quad (5)$$

$$\mathbf{1} + C_2D_2 \rightarrow \text{no ligand exchange} \quad (6)$$

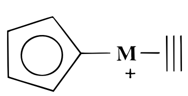
The reactions of **2** give the same product ions as **1** in reactions analogous to eqs 1−6, but in the reaction with water, the main product ion is ScO^+. Thus, aside form the oxide ion formation, the $ScC_7H_6^+$ and $TiC_7H_6^+$ behave identically, which again points to common structures for **1** and **2** as was the conclusion from the CID studies.

It should be noted that kinetically excited **2** did not participate in reaction 4. Furthermore, continuous ejection of *m/z* 171 (the mass of **2** + HCl) during the entire reaction time did not affect the course of reaction 4. This means that the lifetime of the intermediate complex ion is shorter than the ejection time, which in turn is on the order of a few microseconds. This points to a fast rearrangement and elimination of C_2H_2 in reaction 4. Although the other reactions were not investigated in the same manner, similar behavior would be expected in those cases. This is of interest due to the fact that by using the product ions from the reactions of the metal ions with the deuterium-labeled toluene instead of **1** and **2** and reacting with HCl and water, we observed the following: There is evidence for considerable hydrogen scrambling in the initial elimination reaction and more profoundly so in the case of titanium than scandium. Further support for the different behavior of titanium and scandium came from employing toluene-α-^{13}C as explained below.

By employment of toluene-α-^{13}C, the reactions of Ti^+ and Sc^+ gave $TiC_6{}^{13}CH_6^+$ (**3**) and $ScC_6{}^{13}CH_6^+$ (**4**). The reactions of **4** with HCl resulted in the exclusive loss of $^{12}C^{13}CH_2$, whereas **3** reacted with H_2O, $H_2{}^{18}O$, and HCl, analogous to reactions 1, 3, and 4, by eliminating a mixture of $^{12}C^{13}CH_2$ and $^{12}C_2H_2$ in a ratio of roughly 3:2. These experimental facts prove two things. First, the carbon atoms in the ligand that are removed in the IMR are not randomly chosen, which eliminates the possibility of a tropylium type intermediate in the reaction mechanism. Second, there is a difference in the behavior of the Sc- and Ti-containing ions. This result alone points either to different structures for the ions and/or to different mechanisms for their production. Coupled with the results reported above, the conclusion is that **1** and **2** have common structures but somewhat different formation mechanisms. It is clear that the speculative structures **I** and **II** do not fit the experimental evidence, in particular reactions 1−5, and therefore, we offer structure **IIIa** as our proposed structure for **1** and **2**, which we feel is strongly supported by the various experimental evidence described above. It may still be feasible that structures **I** and/or **II** are initially formed but then rearrange to the more stable structure **IIIa**.



IIIa

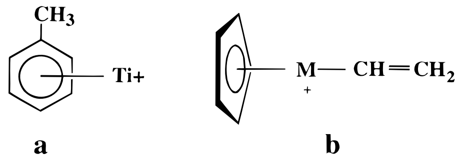


IIIb

Structure **IIIb** needed to be considered, however. It is not inconsistent with the CID results, although one would have expected to see the loss of C_2H_2 dominate to a greater extent. Structure **IIIb** was dismissed for two reasons. First, because no ligand exchange was observed for **1** or **2** reacting with C_2D_2 as would be expected for structure **IIIb**. Second, structure **IIIb** would not be compatible with the results obtained from reactions 2 and 5.

The behavior of Sc^+ and Ti^+ is unexpected, especially in view of the fact that Sc^+ has been found to eliminate H_2 from benzene, indicating that it readily inserts into an aromatic C−H bond,[19] whereas Ti^+ is unable to dehydrogenate benzene. Sc^+ predominantly eliminates HD, which does not point to an insertion into an aromatic C−H bond. As the insertion of Ti^+ into an aromatic C−H bond is unlikely, in view of the results for benzene, we propose that the initial step in the reaction of both metal ions is an insertion into a benzylic C−H bond. We can only speculate on what follows along the reaction coordinates. At least two C−H and two C−C bonds must be broken, suggesting a complex surface with a number of local minima. While the shapes of the PES's for Ti and Sc are probably similar, the relative heights of barriers between local minima must differ somewhat. As a result of these barrier height differences, the Ti system proceeds more slowly from reactants to products sampling more of the potential surface along the way resulting in the observed isotope scrambling. It is obvious from the labeling results that, in the case of Sc^+ the methyl group carbon and one of the carbon atoms from the benzene ring are contained in the acetylide ligand. Least disruption in terms of bond braking and bond formation suggests that the second carbon atom is the one that was originally connected to the methyl group. It is also clear from the labeling results that in the case of Ti^+, an intermediate is formed in the reaction that allows close to a 50/50 chance of the methyl group carbon to be incorporated into the acetylide ligand suggesting complex and perhaps reversible steps in the mechanism. Further discussion of possible mechanisms would be highly speculative and will not be put forth here. It may be that further insight into the reaction mechanisms would result from studying the behavior of additional ^{13}C-labeled toluene derivatives with the heavy carbon atoms strategically placed at particular places in the benzene ring skeleton, but such species are not available to us.

The adduct ion, $TiC_7H_8^+$ (**5**), from the reactions of Ti^+ with toluene could, analogous to the results described above, have two different structure as shown in structures **IVa**,**b**. Structure **IVa** is a simple adduct complex ion, whereas structure **IVb** involves a C−C bond insertion by the titanium. CID studies on **5** showed only the loss of Ti^+, and ion−molecule reactions with H_2O and HCl showed no ligand exchange. Both of these results point to structure **IVa** for **5**.



a **b**

IV

The product ions from the primary reactions, $MC_7H_6^+$ (M = Sc, Ti), reacted again with the toluene in secondary and tertiary dehydrogenation reactions to produce $MC_{14}H_{12}^+$ and $MC_{21}H_{18}^+$, respectively. No larger dehydrogenation product ions could be observed.

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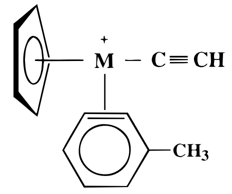
The structure of $ScC_{14}H_{12}^+$ (**6**) was probed by CID. Three different CID product ions were observed, shown in reactions 7−9. At 10 eV (lab) only the first reaction

$$ScC_{14}H_{12}^+(\mathbf{6}) \xrightarrow{CID} ScC_7H_6^+ + C_7H_6 \quad (7)$$

$$\rightarrow ScC_{12}H_{10}^+ + [C_2H_2 + H_2] \quad (8)$$

$$\rightarrow ScC_5H_5^+ + C_9H_7 \quad (9)$$

(eq 7) was observed, and at 17 eV the first two were observed (eqs 7 and 8). The product ion from (9), $CpSc^+$, could only be seen at excitation energies of 25 eV or higher. We propose structure **V** for **6** that is consistent



V

with the CID results and logical considering the proposed structure for **2** (structure **IIIa**), which is the precursor of **6**. Experimental difficulties precluded us from obtaining as clear information regarding the structure of $TiC_{14}H_{12}^+$, but the evidence that could be collected pointed to similar results as obtained for **6**.

Conclusion

While none of the other first-row transition metal atomic ions react with toluene other than to form addition complexes, the dehydrogenation reactions of Sc^+ and Ti^+ with toluene are very fast, proceeding at collision rates. The reactions result in the formation of one product ion, $MC_7H_6^+$, in the case of each metal ion, which behave as if they have identical structures and are probably formed by a similar mechanisms. While both reactions proceed through intermediate ion−neutral collision complexes, a very short-lived intermediate Sc−toluene complex ion results in little or no scrambling of hydrogen and carbon atoms, whereas the longer lived Ti−toluene complex ion results in product ions that exhibit significant scrambling when using the deuterium- or ^{13}C-labeled toluene samples. The structure of the metal-containing product ion from the dehydrogenation reaction is indicated to be of the form $Cp{-}M^+{-}CCH$ by collision-induced dissociation and ion−molecule reaction studies. We are in the process of examining other, related aromatic compounds to further investigate the phenomenon of Cp-ligand formation from benzene derivatives.

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