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Reactions of first-row transition metal ions with propargyl alcohol in the gas phase

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The gas-phase reactions with propargyl alcohol (PPA) of all the singly charged ions of the first-row transition metals, generated by laser ablation in an external ion source, were studied by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICRMS.). The reactivities of the metal ions change irregularly across the periodic table, and the reactivity of each ion is a function of its electronic configuration and corresponding metal-oxygen (M-O) bond energies. The 10 metal ions were classified into three categories according to their reactivities: Sc^+, Ti^+ and V^+ are the most reactive ions which react with PPA to give many kinds of oxygen-rich products due to stronger M-O bonds; Fe^+, Co^+ and Ni^+ are less reactive; Cr^+, Mn^+, Cu^+ and Zn^+ are the most unreactive ions, due to the half and completely occupied valence electronic configurations. The order of reactivity is $Ti^+ > V^+ > Sc^+ \gg Co^+ > Fe^+ \approx Ni^+ > Zn^+ > Cr^+ \approx Mn^+ \approx Cu^+$.

Studies of the gas-phase reactions of 'bare' transition metal ions have attracted much attention. This is due to the fact that the gas phase offers a unique possibility to probe the intrinsic properties of reactive organometallic species, without any solvation, ion-pairing and other 'bulk' effects, and to evaluate the detail in the initial steps of the activation of C-H and C-C bonds,[1–4] which is of fundamental interest in catalysis and has attracted considerable attention.[5–7]

Transition metal ions are reactive toward many organic substrates because their valence electron configurations make it possible for the metal ions to insert into organic bonds.[8] Following insertion, migration of hydrogen and other functional groups occurs to yield new organic species. It has been proposed that thermodynamics is a major factor governing the reactions; however, the electronic configuration of the metal ion and the polarization of the accompanying organic molecules may also need to be considered.

Although thermodynamic measurements of bond energies, proton affinities, heats of formation, etc., are important approaches in the study of gas-phase metal ion-molecule reactions, a complete study of the relationship between the metal ion electronic configurations and the corresponding reactivities will help understanding of the intrinsic rules of metal ion chemistry.

There have been many reports concerning the reaction of the first-row transition metal ions with organic molecules in gas phase, but the ions investigated have been mainly focused on Fe^+, Co^+, Ni^+ and Cu^+.[9–11] A systematic study of the electronic structure effect on metal ion reactivities has not been published to date, to our knowledge. Therefore, we studied the gas-phase chemistry of all 10 first-row transition metal ions from Sc^+ to Zn^+ with propargyl alcohol. It is hoped that this work can help unravel the reaction patterns of transition metal ions with propargyl alcohol, as well as the relationship between the electronic configurations of the metal ions and their reactivities.

EXPERIMENTAL

All experiments were performed using a Bruker APEX II FT-ICR mass spectrometer, equipped with external ion source and 4.7 T superconducting magnet.[12] Metal ions were produced in the external source using a Nd:YAG laser (532 nm, ~10 mJ/pulse) to ablate metal oxides or metal-containing salts. The metal ions were then injected into the ICR cell after electrostatic focusing. The ions of interest were mass-selected by resonant frequency ejection techniques, and allowed to react with static pressures of propargyl alcohol (PPA) in the range of 1–15 $\times 10^{-7}$ mbar. All reactions were monitored up to 5 s.

RESULTS

The general reactions between singly charged first-row transition metal ions and propargyl alcohol (PPA) are dehydrogenation and dehydration in which the common products $[C_3H_3O]^+$, $[C_3H_5O]^+$, $[C_5H_{5,7}]^+$, $[C_6H_{5,7}]^+$, $[C_6H_7O]^+$, $[M \cdot C_3H_2]^+$ and $[M \cdot PPA]^+$ are produced;

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Table 1. Product species for the reactions between first-row transition metal cations M^+ and PPA

M^+	D_{M-O}*	$[C_3H_3O]^+$ $[C_3H_5O]^+$	$[C_5H_{5,7}]^+$ $[C_6H_5]^+$ $[C_6H_7O]^+$	M^+, $[MC_3H_2]^+$ [M-PPA]$^+$	Other products
Sc^+	673.0	√			$[ScO]^+$, $[OScOH_2]^+$, $[OScC_2H_2]^+$, [OSc-PPA]$^+$, $[(H_2O)OScPPA]^+$, $[ScC_4H_{6,8}O_3]^+$, $[(H_2O)_{1,2}ScPPA]^+$, $[Sc(OC_3H_3)_2]^+$, $[OSc(PPA)_2]^+$, $[H_2OSc(PPA)_2]^+$
Ti^+	675.9	√	√		$[TiO]^+$, [Ti-OH]$^+$, $[OTiOH]^+$, $[OTi\text{-}C_2H_2]^+$, $[O_2Ti\text{-}OCH_3]^+$, $[OTi(C_3H_{3,5}O)]^+$, $[O_2TiOC_3H_{1\sim5}]^+$, $[HOTi(OC_3H_3)_2]^+$, $[Ti\text{-}(OC_3H_3)_3]^+$
V^+	643.7	√	√		$[C_4H_7O]^+$, $[VO]^+$, $[OVOH]^+$, $[OVC_2H_2]^+$, [OV-PPA]$^+$
Fe^+	391.2	√	√	√	[Fe-OH]$^+$, $[Fe\text{-}C_4H_2]^+$, $[Fe\text{-}OC_3H_3]^+$, $[Fe\text{-}C_6H_4]^+$, $[Fe\text{-}C_5H_5O]^+$, $[C_3H_3O\text{-}Fe\text{-}PPA]^+$
Co^+	426.4	√	√	√	$[C_7H_7]^+$, $[CoOH]^+$, $[Co\text{-}C_2H_2]^+$, $[Co\text{-}C_4H_2]^+$, $[Co\text{-}C_5H_{4,5,6}]^+$, $[Co\text{-}C_6H_4]^+$, $[Co\text{-}C_3H_8O]^+$
Ni^+	401.3	√	√	√	$[Ni\text{-}OH_2]^+$, $[Ni\text{-}C_2H_2]^+$, $[Ni\text{-}C_6H_4]^+$, $[Ni\text{-}C_6H_6O]^+$
Cr^+	409.6	√	√	√	
Mn^+	367.8	√	√	√	
Cu^+	342.8	√	√	√	
Zn^+	275.9	√	√	√	$[C_4H_4O_2]^+$, $[C_5H_5O]^+$

* Unit of D_{M-O} is kJ/mol.

however, for Sc^+ only $[C_3H_3O]^+$ and $[C_3H_5O]^+$ from this list were produced (Table 1). The reactivities of the metal ions were found to change irregularly across the periodic table. Generally, they can be classified into three categories according to reactivity. Sc^+, Ti^+ and V^+ belong to the first category. They can react with PPA to give many kinds of O-rich products besides the common products $[C_3H_3O]^+$ and $[C_3H_5O]^+$. The second category includes the three VIIIB group ions, Fe^+, Co^+ and Ni^+, which react with PPA to give $[M{\cdot}OH]^+$, $[M{\cdot}C_3H_{2,4}]^+$, $[M{\cdot}C_6H_4]^+$ and C-C bond cleavage products, $[M{\cdot}C_2H_{2,4}]^+$ and $[M{\cdot}C_4H_2]^+$, in addition to the common products $[C_3H_3O]^+$, $[C_3H_5O]^+$, $[C_5H_{5,7}]^+$, $[C_6H_{5,7}]^+$, $[C_6H_7O]^+$, $[M{\cdot}C_3H_2]^+$ and $[M{\cdot}PPA]^+$. The remaining four ions, Cr^+, Mn^+, Cu^+ and Zn^+, are the most unreactive among the 10 ions. The main products of these ions with PPA are the common products except for Zn^+, which gives additional C-C bond dissociation products $[C_4H_4O_2]^+$ and $[C_5H_{5,7}O]^+$.

Sc^+, Ti^+ and V^+

Figure 1(a) shows a typical mass spectrum of the product ions from the reactions of Ti^+ with PPA. The detailed product assignments of all the 10 ions with PPA are listed in Table 1. One can see from Fig. 1(a) that the highest peak of the product ions is *m/z* 81, corresponding to $[OTiOH]^+$. In the lower mass region, the $[C_3H_3O]^+$, $[C_3H_5O]^+$ and $[TiO]^+$ ions can also be seen. In the higher mass region, $[OTiC_2H_2]^+$, $[O_2Ti(OCH_3)]^+$, $[O_2TiC_3H_{1-5}O]^+$, $[HOTi(OC_3H_3)_2]^+$, $[HOTi(OC_3H_3)_2]^+$ and $[Ti(OC_3H_3)_3]^+$ ions were found. However, some trace ions can also be seen in the mass spectrum, such as $[C_5H_{5,7}]^+$, $[C_6H_{5,7}]^+$, $[C_6H_7O]^+$ and $[OTi(C_3H_{3,5}O)]^+$. In the case of Sc^+/PPA, the most abundant ion is $[OScOH_2]^+$. $[ScO]^+$, $[C_3H_3O]^+$, $[C_3H_5O]^+$, $[ScOC_2H_2]^+$, $[ScCH_4O_3]^+$, $[OScPPA]^+$, $[H_2OScPPA]^+$ and $[Sc(OC_3H_3)_2]^+$ are present at normal abundance, with $[(H_2O)_2ScPPA]^+$, $[ScC_4H_{6,8}O_3]^+$, $[O_2Sc(PPA)_2]^+$ and $[(H_2O)_2Sc(PPA)_2]^+$ at trace levels (Table 1). The main products of V^+/PPA are $[C_3H_3O]^+$, $[C_3H_5O]^+$, $[C_5H_{5,7}]^+$, $[VO]^+$, $[C_6H_{5,7}]^+$, $[C_6H_7O]^+$ and $[OVC_2H_2]^+$.

Fe^+, Co^+ and Ni^+

Fe^+, Co^+ and Ni^+ are less reactive toward PPA than Sc^+, Ti^+ and V^+. As can be seen from the mass spectrum of the product ions of the reaction of Ni^+ with PPA shown in Fig. 1(b), the highest peak is Co^+, showing that Co^+ is less reactive and remained largely unreacted after same reaction time. The mass spectra of the products from the reactions of Fe^+ and Ni^+ with PPA are similar to that of Co^+. However, in the reactions of Sc^+, Ti^+ and V^+ with PPA, no metal ions remained unreacted under the same experimental conditions (same PPA pressure and same reaction duration), indicating that Sc^+, Ti^+ and V^+ are far more reactive than Fe^+, Co^+ and Ni^+. The main products of Fe^+, Co^+ and Ni^+ with PPA include $[C_3H_3O]^+$, $[C_3H_5O]^+$, $[M{\cdot}C_3H_{2,4}]^+$, $[M{\cdot}PPA]^+$ and $[M{\cdot}C_6H_{4,6}]^+$. Some trace of other species can also be found, such as $[C_6H_7]^+$(*m/z* 79), $[C_7H_7]^+$(*m/z* 91) and $[M{\cdot}PPA]^+$ (*m/z* M + 54).

Cr^+, Mn^+, Cu^+ and Zn^+

Similar to the second category of ions, Cr^+, Mn^+, Cu^+ and Zn^+ cannot react completely under the same experimental conditions. The product species of these four ions are quite simple compared with those of the other two category ions, as shown in Fig. 1(c), indicating that these four ions are the most inert of all of the 10 metal ions. The main products are $[C_3H_3O]^+$ and $[C_3H_5O]^+$, as well as small amounts of $[C_5H_{5,7}]^+$, $[C_6H_{5,7}]^+$, $[M{\cdot}C_3H_{2,4}]^+$ and $[M{\cdot}PPA]^+$.

DISCUSSION

General characteristics of the reactions between first-row transition metal ions and PPA molecules

It should be noted that the laser-ablated metal ions might not necessarily be in their ground electronic states. While we cannot exclude possible reactions of electronically excited-state metal ions, we believe that the contribution from the excited states can be ignored because the lifetimes for the

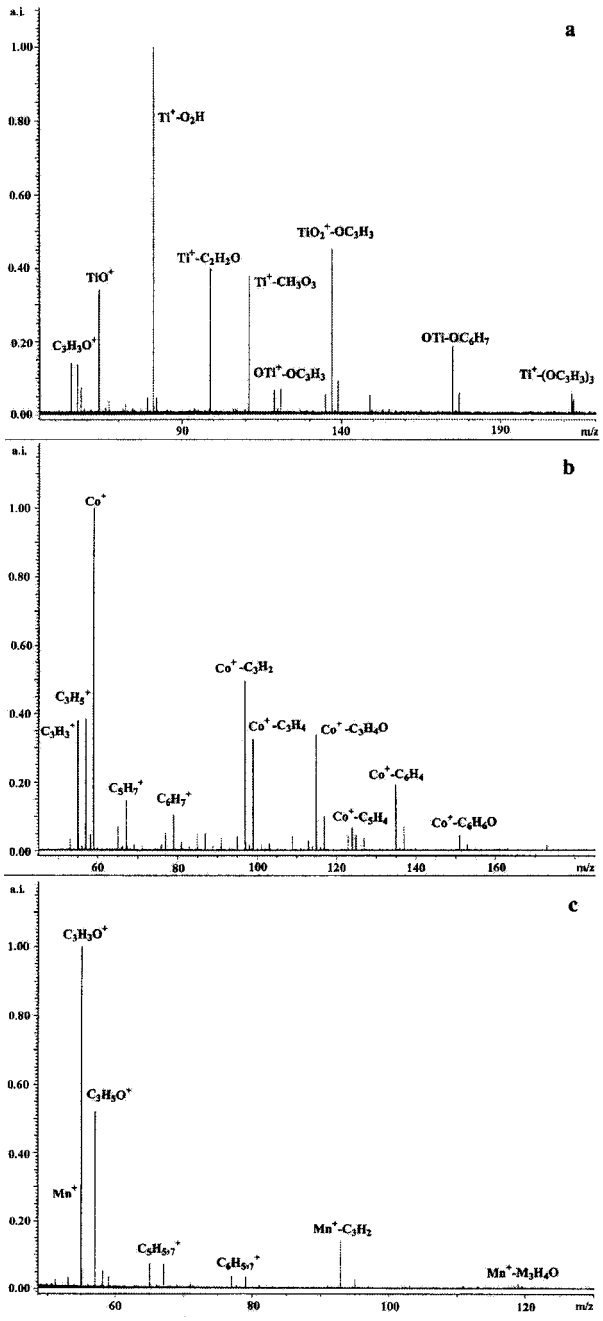


Figure 1. Typical mass spectra of the product ions from the reactions of (a) Ti^+, (b) Co^+, and (c) Mn^+ with PPA.

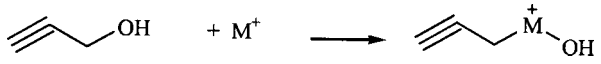
excited states of the first-row transition metal ions are all very short compared to the reaction duration.[13]

Huang *et al.* studied the reactions of Fe^+, Cr^+ and Mo^+ with various saturated alcohols.[14] They classified the reactions into three types: (a) C-H or O-H bond insertions (dehydrogenation), (b) C-O bond insertions (dehydration), and (c) C-C bond insertion. In our experiments, all of the three types of metal insertion occurred since dehydrogenation, dehydration and C-C bond cleavage products were all found. The C-O bond insertion appears to be the most energetically favorable, based on the following facts. (a) The dehydration products $[C_5H_{5,7}]^+$ and $[C_6H_{5,7}]^+$ are formed in all the reactions of M^+ with PPA, (b) the main reaction products of Sc^+, Ti^+ and V^+ with PPA are O-rich species, which are produced from dehydration; and (c) $[M\text{-}C_3H_2]^+$ is formed in all the reactions of the second and third category ions with PPA. The products of metal ions with PPA are much more complicated compared with these of metal ions with saturated alcohols. This is attributed to the activation of the hydroxyl group by the C≡C bond.

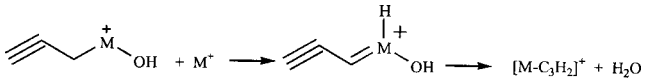
In our experiments, all of the 10 metal ions reacted with PPA to give $[C_5H_{5,7}]^+$, $[C_6H_{5,7}]^+$ and $[C_6H_7O]^+$, except for Sc^+/PPA which gave only $[C_3H_3O]^+$ and $[C_3H_5O]^+$. The second and third category ions reacted with PPA to give $[M{\cdot}C_3H_2]^+$ and $[M{\cdot}PPA]^+$. The reactions of M^+ with PPA molecules can form $[M{\cdot}PPA]^+$ at least in the initial stage, since ion-molecule association reactions are generally believed to proceed without an activation barrier.[16] In these initial products, M^+ is expected to bond to the oxygen by an end-on bond with weak side-on interaction with C≡C in the PPA molecules, and the interaction is essentially electrostatic in nature. The association products may be stabilized by evaporation of solvent or collision with a third body. All of the ions react with PPA to give $[C_3H_3O]^+$, showing that the metal ions insert into the O-H bond, as follows:

$$M^+ + CHCCCH_2OH \rightarrow [CHCCH_2O \cdot MH]^+ \rightarrow [C_3H_3O]^+ + M\text{-}H$$

The $[M{\cdot}C_3H_2]^+$ product can be attributed to the following proposed mechanism. M^+ inserts into the C-O bond to form $[CHCCH_2\text{-}M\text{-}OH]^+$,

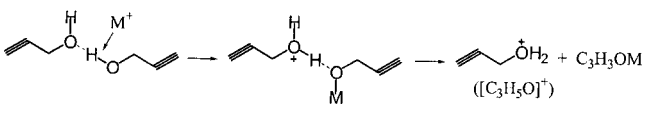


followed by an α-H shift and H_2O-elimination to give $[M\text{-}C_3H_2]^+$ as show below:



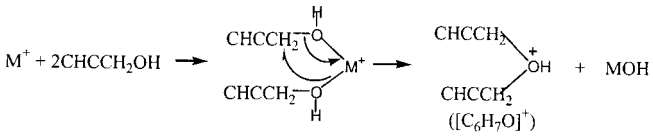
The bond energy of C-OH in PPA is lower than that in saturated alcohols due to the conjugate effect, and this promotes $[CHCCH_2\text{-}M\text{-}OH]^+$ formation. Two possible geometries of $[M{\cdot}C_3H_2]^+$ are $[M{=}CHC{\equiv}CH]^+$ and $[M\text{-}\eta\text{-}C_3H_2]^+$. In order to explore the final geometry of $[M\text{-}C_3H_2]^+$, we optimized the two possible geometries, $[M{=}CHC{\equiv}CH]^+$ and $[M\text{-}\eta\text{-}C_3H_2]^+$, using density functional theory. The Berny algorithm used was B3LYP, and the basis set used for C and H was 6–31G**, and the pseudo basis set LANL2DZ for M^+. The calculated results showed that the energy of $[M{=}CHC{\equiv}CH]^+$ is lower than that of $[M\text{-}\eta\text{-}C_3H_2]^+$ by 30.3, 98.6, and 96.1 kJ/mol for Cr, Fe and Cu, respectively, indicating that the geometry of ground-state $[M\text{-}C_3H_2]^+$ is $[M{=}CHC{\equiv}CH]^+$.

In the gas phase, the PPA molecules can form molecular clusters by hydrogen bonding. $[C_3H_5O]^+$ could be formed by M^+ attacking the O-H bond of the PPA dimer.



while $[C_6H_7O]^+$ could be formed by eliminating M-OH from

$[M\text{-}(PPA)_2]^+$, as show below:



Reactivity order of first-row transition metal ions towards PPA molecules

As mentioned above, the 10 first-row transition metal ions can be classified into three categories according to their reactivities toward PPA molecules. However, it is difficult to assign the exact reactivity order of these 10 metal ions, all of which react with PPA molecules leading to many product species. Nevertheless, we can exploit the relationship between the reactivities and the product species. We assume that the more reactive is M^+, the less the reactant, M^+, survived and the greater was the abundance of the product species. In our experiments, the metal ions react with PPA molecules and produce various product species. The intensity of the remaining unreacted M^+, and the number of products, are then used to compare the reactivities. Table 1 summarizes the product species observed in the mass spectra for all of the first-row transition metal ions reacting with PPA. Among the 10 ions, Ti^+ might be regarded as the most reactive because Ti^+ reacts with PPA completely and gives the maximum number of product species. Sc^+ and V^+ are less reactive toward PPA than Ti^+ since, though they react with PPA completely, they give fewer product species than Ti^+. Under the same experimental conditions, all of the first category ions react with PPA completely, while the ions in the other two categories do not. This indicates that the first category ions are more reactive than those in the others. The products of Ni^+/PPA are similar to those of Fe^+/PPA, and are less complex than those of Co^+/PPA, suggesting a reactively order: $Co^+ > Fe^+ \approx Ni^+$. The reactivities of Cr^+, Mn^+ and Cu^+ are close since all of them react with PPA to give $[M{\cdot}C_3H_2]^+$ and $[M{\cdot}PPA]^+$ besides the common products, $[C_3H_3O]^+$, $[C_3H_5O]^+$, $[C_5H_{5,7}]^+$ and $[C_6H_{5,7}]^+$. However Zn^+ is somewhat more reactive than Cr^+, Mn^+ and Cu^+ as it reacts with PPA not only to give the corresponding products as for Cr^+, Mn^+ and Cu^+, but also to give $[C_5H_7O]^+$, $[C_4H_4O_2]^+$ and $[Zn{\cdot}C_3H_6]^+$. Summarizing the above considerations, we obtain the following reactivity order: $Ti^+ > V^+ > Sc^+ \gg Co^+ > Fe^+ \approx Ni^+ > Zn^+ > Cr^+ \approx Mn^+ \approx Cu^+$. Although the work presented here is only focused on the propargyl alcohol substrate, we expect that such an approach is applicable to the other substrates such as hydrocarbons.

Correlation between reactivities and M-O bond energies and electronic configurations of M^+ ions

The different reactivities of metal ions M^+ toward PPA are likely to be related to their electronic configurations and corresponding M-O bond energies. As can be seen from Table 1, the M-O bond energies for Sc, Ti and V are all larger than 640 kJ/mol. Though we do not know the exact bond energies of $[M\text{-}O]^+$ in the initial association products, $[M\text{-}PPA]^+$, we are sure that they are stronger than that of C-OH and O-H in PPA based on the following considerations. The normal bond energies of C-OH and O-H are ~395 and ~435 kJ/mol, respectively, which are all 200 kJ/mol lower than the M-O bond energies for Sc, Ti and V. Furthermore, the conjugation effect in PPA decreases the energy of C-OH and O-H. It can be presumed that these three ions are energetically favored to insert into C-OH and O-H, and the main products of these ions with PPA will be O-rich species, as confirmed by our experiments. Because the bond energy of C-OH is ~40 kJ/mol stronger than that of O-H in PPA,[15] the energetically prefered M^+ insertion site would be C-OH. As mentioned above, Ti^+, V^+ and Sc^+ are far more reactive than the other ions and have stronger M-O bonds. This implies that the controlling step of the M^+/PPA reactions is the M^+-O bonding. Co^+ is somewhat more reactive than its neighboring ions Fe^+ and Ni^+ as shown in Table 1. This is because the Co-O bond is stronger than Fe-O and Ni-O by 35 and 25 kJ/mol, respectively.

It is clear that M-O bond strength considerations cannot be used to explain completely the reactivity order of the first-row transition metal ions toward PPA. The second factor affecting the ion reactivities is the electronic configurations of the ions. Also we cannot completely exclude possible reactions of the electronically excited-state metal ions, but we believe that the observed reaction products are mainly from the ground-state reactions due to lifetime considerations. It has been suggested that bonding between first-row transition metals and organic substrates involves only s orbital electrons.[17] However, it seems that not only 4s electrons, but also 3d electrons, must be involved in the bonding in our experiments since if the 3d electrons are not involved, Cr^+ and Cu^+ would be unreactive toward PPA. This prediction is contradictory to the fact that their reactivities are close to those of Mn^+ and Zn^+. The low reactivity of Cr^+, Mn^+, Cu^+ and Zn^+ is attributed to their complete and half-occupied 3d orbitals which are less reactive than the other configurations. Similar results were found in the reactions of Fe^+, Mo^+ and Cr^+ with various alcohols by Huang,[14] who found that Cr^+ is the most unreactive ion among these three ions.

CONCLUSIONS

All the 10 first-row transition metal ions (singly charged) were generated by laser ablation, and their reaction with propargyl alcohol (PPA) was studied. It was found the reactivities of the metal ions change irregularly across the periodic table, and that the reactivity of each ion is a function of its electronic configuration and corresponding M-O bond energy. Sc^+, Ti^+ and V^+ are the most reactive ions, as they react with PPA completely and give many kinds of O-rich products; an observation that is attributed to the higher M-O bond energies. Fe^+, Co^+ and Ni^+ are less reactive, and Cr^+, Mn^+, Cu^+ and Zn^+ are the most unreactive ions due to their different valence electronic configurations. The order of reactivity is $Ti^+ > V^+ > Sc^+ \gg Co^+ > Fe^+ \approx Ni^+ > Zn^+ > Cr^+ \approx Mn^+ \approx Cu^+$.

Acknowledgements

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