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2. Project Title: Earth Abundant Transition Metal Oxides and Carbides as Super-Atom Molecular Analogs to Platinum.
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There are two specific aims to this research. The first is to spectroscopically study a transition metal oxide (MO) cation to determine electronic similarities between the superatom / atom pair. Having verified a similar ground state electronic structure, the second aim is to measure the reactivity of the pair toward an organic molecule. The goal of the research is to identify MO species that could potentially replace M species in industrially catalyzed chemical reactions. Photodissociation action spectroscopy and the single photon initiated dissociative rearrangement reactions (SPIDRR) technique will be employed in these studies. Here we detail our progress toward these aims. Our first study is to prove concept.

Comparative Studies of the TiO^+ / Ni^+ atom / superatom pair toward reactions with CH_3COCH_3 and its deuterium analog CD_3COCD_3

We have already kinetically characterized the single photon excited, Ni^+ mediated decomposition of CH_3COCH_3 and its deuterium analog. Here, the photo-excited system decarbonylates through an oxidative addition / reductive elimination sequence producing $NiCO^+ + C_2H_6$. Thus, TiO^+ reactive studies against CH_3COCH_3 is a logical starting point since both TiO^+ and Ni^+ contain nine valence electrons. Moreover, theory suggests that these nine electrons are angular momentum coupled to yield a 2D ($3d^9$) ground electronic state in Ni^+ and a $^2\Delta$ ($\dots 8\sigma^2, 3\pi^4, 1\delta^1$) ground electronic state in TiO^+ . To gain an understanding of the TiO^+ electronic structure, and to verify the electronic structure calculations, we have measured a portion of the photodissociation action spectrum of TiO^+ -Ar. Argon tagging is required because of the appreciable strength of the Ti-O⁺ bond making direct dissociation impossible with our current lasers. The photodissociation action spectrum is shown in Figure 1. Our early results indicate a band origin around 1.90 eV with vibrational quantum number assignment confirmed by monitoring isotopic shifts in $^{50}TiO^+$ relative to the $^{48}TiO^+$ isotopomer. These assignments are consistent with theoretical studies, which determine a $^2\Pi \leftarrow ^2\Delta$ TiO^+ electronic transition with the band origin predicted to lie at 1.91 eV. Thus, spectroscopic studies supported by computation suggests similar electronic structures observed between TiO^+ and Ni^+ , indicating their superatomic natures.

Results from the photo-excited TiO^+ mediated decomposition of CH_3COCH_3 , is presented in Figure 2. Here a 16000 cm^{-1} photon is absorbed by the TiO^+ chromophore to initiate the chemical reaction. Electronic excitation is likely the same $^2\Pi \leftarrow ^2\Delta$ transition observed in the spectroscopic study of the argon tagged species. The expected outcome of these studies was to mimic the action of Ni against acetone since their electronic ground structures are so similar (each with nine valence electrons coupled so that they have identical quanta of unquenched spin and angular momenta). However, that was not observed.

Three products are observed in the decay of the precursor $TiO^+[CH_3COCH_3]^*$: one associated with isomerization and two with dehydration. Isomerization likely follows an oxidative addition / reductive elimination sequence reforming TiO^+ + either a terminal ketone or alcohol. The analogous study into CD_3COCD_3 was used to verify exit channel assignment by monitoring the slightly heavier fragment masses in two of the three channels. The results of Figure 2 suggest that two dissociative pathways exist with one terminating in the dehydration products and the other in an apparent isomerization reaction. The

dehydration kinetics are nearly the same while the isomerization reaction is nearly twice as fast. This indicates that the minor intensity channel, by a ratio of ~80:20, has the largest rate constant. This is an unexpected result. The relative exit channel fractions and associated rate constants remained unchanged while varying the activating photon's power, ruling out multiphoton transitions as the reason for the unexpected kinetics. The chemical reactivity and reaction dynamics measured between Ni^+ and its superatomic analog, TiO^+ , toward CH_3COCH_3 are markedly different, despite the similarities in their ground electronic states.

We believe that these differences may be caused by the reactivity of the excited TiO^+ state. The $\pi \leftarrow \delta$ promotion of the valence electron reduces the bond order from three to two. Weakening and lengthening the Ti-O bond during electronic excitation likely increases the oxophilicity of titanium, making the excited state more strongly reducing than the ground state and initiating the consequent dehydration reaction. Thus, the cause of the unusual kinetic response of TiO^+ toward CH_3COCH_3 may be due to the two different reaction pathways propagating on different potential energy surfaces. The two observed pathways are not competitive in the traditional kinetic sense, where ratios of rate constants govern exit channel fractions on an adiabatic surface, but rather, relative intensities are determined by the nonadiabatic coupling between the ground and excited PESs and this provides a reason why the minor channel is observed to have the larger rate constant: the reactions do not progress on the same surfaces.

We have continued to explore this interesting chemistry initiated by excited state dynamics in TiO^+ mediated reactions. The science funded by the PRF have yielded results that form the basis of a funding application to the NSF. Exploring nonadiabatic effects caused by excited state dynamics has significantly increased the groups abilities. We are now looking into how these nonadiabatic effects influence the behavior of molecular photocatalytic active sites.

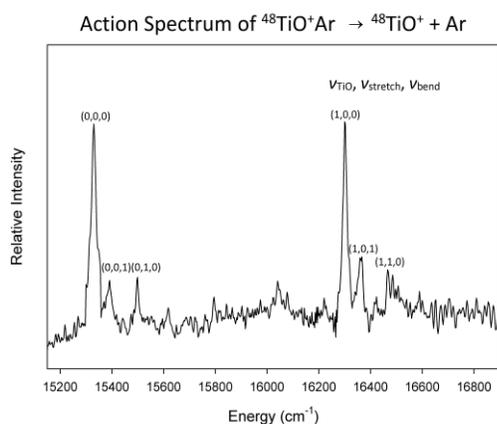


Figure 1. Photodissociation action spectrum of argon tagged TiO^+ .

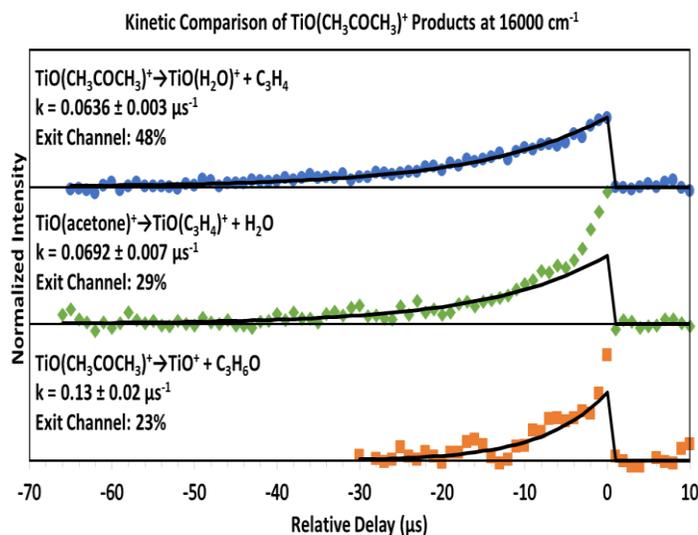


Figure 2. Current progress toward measuring the photo-excited TiO^+ mediated decay of CH_3COCH_3 .