

Production of $C_6O_6^-$ from Oligomerization of CO on Molybdenum Anions

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The $C_nO_n^{2-}$ ($n = 3, 4, 5, 6, \dots$) series of high-symmetry oxocarbon dianions has been the subject of considerable interest¹ because of the question of aromaticity,² their capacity as bridging ligands and building blocks in interesting materials,³ and their usefulness in various analytical applications.⁴ Most computational⁵ and experimental⁶ studies on the structure of these oxocarbons have been confined to the dianion. The neutral species have been largely left uncharacterized, and it has been proposed that the neutrals may be unstable with respect to loss of CO.⁷ The singly charged radical anions have recently been observed in mass spectrometric studies for $n = 3-6$.⁸ Isolated dianions have not been observed and are probably not stable with respect to the $C_nO_n^-$ plus free electron continuum.

In this communication, we describe the results of our continuing studies on the reactivity of small molybdenum suboxide clusters ($Mo_xO_y^-$, $y < 3x$), in which mass spectrometry, anion photoelectron (PE) spectroscopy, and density function theory calculations have been applied toward determining the structures of small $Mo_xO_y^-$ clusters⁹ and their size- and oxidation state-dependent reactivity toward methane and ethane.¹⁰ Reactions between CO and $^{98}Mo_xO_y^-$ are the subject of the present study. The results suggest that a series of reactions occurs involving oxidation of CO until the oxygen content of the clusters is depleted, followed by metal carbonyl formation and, ultimately, free $C_6O_6^-$ formation.

The experiment has been described in detail elsewhere.¹⁰ Briefly, cluster ions are generated in a pulsed laser ablation/molecular beam valve source adapted to accommodate a pressed powder of ^{98}Mo (Oak Ridge National Laboratory, Isotope Business Office).¹⁰ The source is coupled to a fast-flow reactor where neat CO is injected using a second molecular beam valve, the duration of which is varied to increase CO exposure. The resulting anions are mass analyzed in a beam-modulated time-of-flight mass spectrometer. While in the ion drift tube, the PE spectra of selected anions are measured by photodetachment using the one of the harmonic outputs of a Nd:YAG laser (3.493 eV, or 355 nm; 4.657 eV, or 266 nm). Electron kinetic energy (e^-KE) analysis is carried out by field-free time-of-flight of the photoelectrons. Calibrated e^-KE is converted to electron binding energy. The resolution of the apparatus is 6 meV at 0.5 eV e^-KE , and deteriorates with e^-KE .³²

Figure 1 shows the mass spectrum of bare molybdenum oxide cluster anions (bottom trace) along with a series of snapshots taken with increasing CO-valve duration. At lower CO concentration, species with single CO additions are observed, particularly within the $Mo_2O_y^-$ series. A peak at 168 amu/e^- is observed in small quantities. This mass corresponds to $C_6O_6^-$, as well as $C_{10}O_3^-$ and C_{14}^- . However, in the absence of other carbon clusters and lower oxide carbon clusters, we assert that $C_6O_6^-$ is a more reasonable assignment. It is the only free oxocarbon observed. As the CO exposure is increased, MoO_2CO^- appears, along with $Mo(CO)_5^-$ and $Mo_2O_2(CO)_5^-$. No MoO_3CO^- is observed. No masses below $^{98}Mo^-$ were observed, and ion signal in the higher mass region

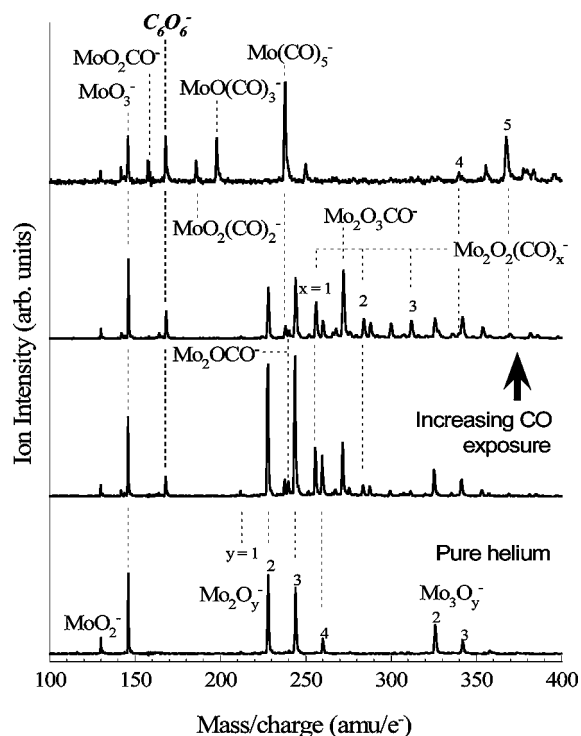


Figure 1. Mass spectra of (a) bare molybdenum oxide clusters and (b–d) increasing CO duration on the second valve.

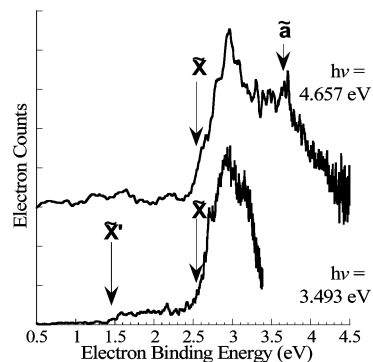


Figure 2. Photoelectron spectra of $C_6O_6^-$ obtained using 3.493 eV (lower trace) and 4.657 eV (upper trace) photon energies.

was insignificant over 400 amu/e^- under these experimental conditions.

Figure 2 shows the PE spectrum of $C_6O_6^-$ using 3.493 eV (lower trace) and 4.657 eV (upper trace) photon energies. The onset of significant electron signal occurs at 2.54(5) eV (band \tilde{X}), which is taken to be the adiabatic EA of neutral C_6O_6 . In the 3.493 eV spectrum, the baseline is free from background electrons, so a lower-intensity band, \tilde{X}' , is also observed originating at 1.45(5) eV. This may be due to the population of an excited electronic state of

the anion or a second isomer of $C_6O_6^-$ having a lower electron affinity. At least one excited neutral state is observed in the 4.657 eV spectrum, labeled \tilde{a} with a vertical detachment energy of 3.67(3) eV.

Band \tilde{X} is broad (~ 0.6 eV fwhm) and congested, and no clean vibrational progressions are resolved. However, there is a 1100-(100) cm^{-1} spacing between shoulders in both spectra. Additionally, there are both 1700(100) cm^{-1} and 400(30) cm^{-1} spacings apparent in the higher-resolution 3.493 eV spectrum. These correspond to *neutral* vibrational frequencies. Existing Raman spectra are only of the dianion in solid or solution phases.¹¹ Although the spectra are broad, there is no strong evidence of dissociation upon photodetachment. The neutral signal observed when the anion is detached does not show kinetic energy spread, and the reproducible shoulders in the spectra show that multiple vibrational levels are supported on the neutral potential energy surface, in addition to an excited electronic state.

We now consider the implications of the trends observed in the mass spectra. Because of the prevalence of carbonyl complexes in which the metal oxide portion is in a very low oxidation state, it appears that CO may initially be oxidized by the $Mo_xO_y^-$ clusters via $CO + Mo_xO_y^- \rightarrow CO_2 + Mo_xO_{y-1}^-$. For instance, $MoO(CO)_3^-$ and $Mo(CO)_5^-$ are abundant after CO exposure, but neither bare Mo^- or MoO^- are observed in the mass spectra of the unreacted clusters. Oxidation of CO by gas-phase transition metals with O_2 has been observed by Castleman and co-workers.¹² A mechanism for $C_6O_6^-$ production cannot be inferred definitively from the mass spectra. However, on the basis of the abundance of both $Mo(CO)_5^-$ and $Mo_2O_2(CO)_5^-$, saturation followed by oligomerization is suggested. Rhodizonate has formed via oligomerization of CO on the (low-valence) edges of several metal oxides,¹³ and more recently, the delatate and squarate species were observed to form on organouranium complexes.¹⁴ Though not entirely analogous, we note that gas-phase production of benzene from the addition of ethylene to tungsten atomic cations has been observed.¹⁵

$Mo(CO)_5^-$ is a reactive 17-electron radical,¹⁶ and the addition of a sixth CO is necessarily destabilizing. It is plausible that $Mo(CO)_6^-$ is unstable with respect to $C_6O_6^-$ loss [or autodetachment, or CO loss, as in the case of $Ni(CO)_4^-$].¹⁷ C_6O_6 , based on the PE spectrum, has a higher EA than both Mo (0.748 eV)¹⁸ and Mo_2O_2 (2.24 eV),⁹ so it is conceivable that $C_6O_6^-$ results from addition of CO to either $Mo(CO)_5^-$ or $Mo_2O_2(CO)_5^-$. We have initiated a series of calculations on the addition of CO to Mo^- to evaluate the tenability of both scenarios.

To our knowledge, this is the first PE spectrum of $C_6O_6^-$ to be recorded, and a qualitative assignment follows. The neutral is closed-shell. The LUMO is analogous to the a_{2u} aromatic orbital in benzene but composed of the totally symmetric combination of C–O out-of-plane π^* orbitals. A higher EA is therefore possible and consistent with preliminary calculations (the subject of a subsequent paper). Note that in rhodizonate salts, the presence of counterions localizes the electrons outside of the ring.⁵

Most calculations to date on the dianion predict distortion from D_{6h} .⁵ If the same holds true for the anion and neutral, a vibrationally congested PE spectrum is expected. Confined to D_{6h} symmetry, however, band \tilde{X} corresponds to the ${}^1A_{1g} + e^- \rightarrow {}^2A_{2u}$ transition. Detachment from the HOMO accesses the first excited (triplet) state,

the term energy of which is approximately 1.0(1) eV. The large uncertainty is due to ambiguity in the origin of band \tilde{a} . We suggest that band \tilde{X}' is an isomer, possibly a polymeric form¹⁹ or one of the other suggested neutral structures.²⁰

To summarize, we have observed the formation of $C_6O_6^-$ in the gas-phase reactions between CO and small molybdenum suboxide cluster anions. It appears that the process first involves oxidation of CO, followed by addition of CO to the reduced cluster anions. Free $C_6O_6^-$ formation may be occurring on saturated molybdenum oxide species in lower oxidation states. The PE spectrum of $C_6O_6^-$ gives an EA of 2.54(5) eV for the neutral, with an excited triplet state observed at $T_e = 1.0(1)$. Electron signal observed at 1.45(5) eV is attributed to either an excited anion state or a structural isomer of $C_6O_6^-$. To our knowledge, this marks the first observation of isolated, neutral $C_6O_6^-$.

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