Binding Energies of Terminal and Bridging Carbonyls in $Pt_3(CO)_6^-$

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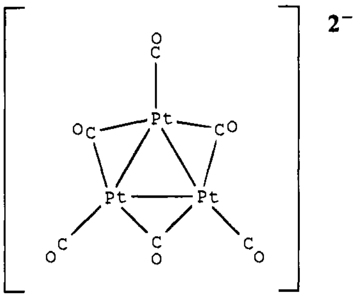
Metal carbonyl species are of great interest to organometallic chemists as model systems for catalysis reactions. For example, the catalytic oxidation of carbon monoxide on a platinum surface can be modeled, in part, by platinum carbonyl clusters. One of the earliest and most intriguing platinum carbonyls to be investigated is the $Pt_3(CO)_6^{2-}$ species synthesized by Longoni and Chini.[1] This complex ion was characterized as having structure **I**, which has six equatorial carbonyls: three in terminal positions and three in edge-bridging positions. While the structures of many metal cluster carbonyls have been characterized using spectroscopic techniques, the metal carbonyl binding energies are generally unknown with the exception of some monometal carbonyl clusters[2,3] and average bond energies from decomposition calorimetry for stable iron and cobalt cluster carbonyls.[3] The subject of this communication is the gas phase examination of the platinum cluster series $Pt_3(CO)_m^-$, $m = 1-6$. We use a new guided ion beam apparatus to perform collision-induced dissociation (CID) experiments on these clusters. The binding energies of individual carbonyl groups are determined from collision energy thresholds of reaction 1, with $m = 1-6$.



I

$$Pt_3(CO)_m^- + Xe \rightarrow Pt_3(CO)_{m-1}^- + CO + Xe \quad (1)$$

The binding energies we determine are characteristic of terminal and bridging carbonyl ligands.

Recent flow tube reactor experiments in our laboratory have examined the gas phase reaction kinetics of small platinum cluster anions with carbon monoxide.[4,5] In the case of the triplatinum anion, it was observed that the initial addition of CO is moderately fast, 16% of the collision rate, and sequential addition of further CO's proceeds at similar rates. Triplatinum clusters with six carbonyl ligands were observed in the saturation limit. Several $Pt_3(CO)_m^-$ anions have also been investigated recently by photoelectron spectroscopy;[6] the same saturation limit was found.

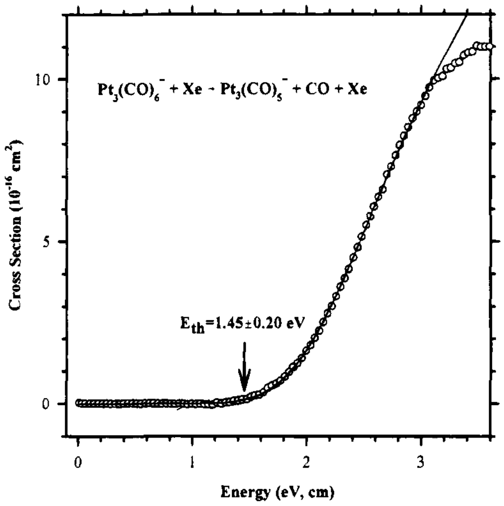


Figure 1. Cross section for the reaction $Pt_3(CO)_6^- + Xe \rightarrow Pt_3(CO)_5^- + CO + Xe$ as a function of collision energy in the center-of-mass frame. Circles represent the measured reaction cross section; the line is a fit using an empirical threshold law.

The guided ion beam tandem mass spectrometer and data analysis procedures used in this work will be described in detail in a future publication. Similar instruments are in use by other research groups.[7−12] Thermalized (300 K) platinum carbonyl cluster anions were produced using the same flow tube reactor source as in our previous kinetics experiments.[4,5] The cluster ions of interest are selected by mass using a magnetic sector and are then injected into an octopole beam guide[7] at a known translational energy, where they collide with the xenon target gas in a gas cell. Fragmentation products are collected with high efficiency by the octopole and are then detected by a quadrupole mass spectrometer. CID cross sections are obtained as a function of collision energy at several xenon pressures (0.05−0.20 mTorr) and are extrapolated to zero pressure to obtain the CID cross section in the single-collision limit. The laboratory ion energy is determined using retarding potential analysis and then converted to the collision center-of-mass frame.[8]

As an example, Figure 1 shows the single-collision CID cross section for the formation of $Pt_3(CO)_5^-$ from $Pt_3(CO)_6^-$. For each of the $Pt_3(CO)_m^-$ anions, the loss of CO is observed as the lowest energy channel. To extract a threshold energy, E_{th}, we fit the cross section data to an empirical threshold law (eq 2) as described by Armentrout *et al.*,[9]

$$\sigma(E) = \sigma_0 \sum_i g_i (E + E_i - E_{th})^n / E \quad (2)$$

where E is the collision energy, E_i are the vibrational energies of the cluster, and g_i are the Boltzmann populations of those vibrations. Equation 2 is convoluted over the experimental translational energy distribution, and RRKM theory is used to model the dissociation probability within the experimental time window between collision and detection.[9] For convolution over the vibrational energy distribution and the RRKM analysis, we

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Table 1. Threshold Energies for $Pt_3(CO)_m^- \rightarrow Pt_3(CO)_{m-1}^- + CO$

m	E_{th} (kJ mol^{-1})	*m*	E_{th} (kJ mol^{-1})
1	215 ± 30	4	82 ± 10
2	203 ± 50	5	90 ± 14
3	189 ± 17	6	140 ± 19

estimate the vibrational frequencies[13] of the clusters. The measured threshold energies are given in Table 1. Errors quoted in Table 1 reflect the sensitivity of the threshold energy to the fit parameters (*e.g.*, energy range and vibrational frequencies) and the reproducibility of the experiments under different conditions. Sources of systematic error due to ion detection efficiency, effective gas cell length, and pressure measurement may affect the absolute measured cross section by as much as 50%, but have no effect on the determination of the threshold energy.

At higher energies, additional product channels open up, including loss of more than one CO and metal atom loss. In the case of the formation of Pt_3CO^- from $Pt_3(CO)_2^-$ there exists a competing reaction, namely, the formation of $Pt_2CO^- + PtCO$. This second reaction has only a slightly higher threshold energy than that for the loss of CO, but it appears to have a higher efficiency. As a result of this competing reaction, we were not able to obtain a precise threshold energy for the loss of CO from $Pt_3(CO)_2^-$.

The threshold energy is equal to the dissociation energy if there is no reverse activation barrier. Comparing the effective bimolecular addition rate for $Pt_3^- + CO$ measured in our flow tube study[4] to the collision rate, we obtain an Arrhenius activation energy of 4.5 kJ mol^{-1} as an upper limit. The actual barrier is probably less because the measured rate is affected by the efficiency of collisional stabilization of the intermediate complex in the termolecular addition process.[4,5] In CID of cluster ions there are usually no activation barriers in excess of the reaction endothermicities.[9] We therefore equate E_{th} with the carbonyl binding energy, within other experimental uncertainties.

The most striking feature of the results given in Table 1 is the sharp drop in binding energy from the third to the fourth carbonyl. NMR experiments[16] have indicated that there are two types of carbonyls on **I**, terminal and bridging, and that no exchange of the carbonyls occurs up to 330 K. Our observed bond energies also fall into two groups; the first three have binding energies of 189–215 kJ mol^{-1}, the second three, 82–140 kJ mol^{-1}. Longoni and Chini[1] assigned the carbonyl stretching frequencies of 1740 and 1945 cm^{-1} observed for **I** to the bridging and terminal carbonyls, respectively. The lower frequency of the bridging carbonyl ligands reflects the stronger π back-bonding for bridging carbonyls.[17] Therefore, we surmise that the bridging carbonyls are more strongly bound than the terminal ligands. From this we hypothesize that, in $Pt_3(CO)_m^-$, $m=1-3$ are bridging and $m = 4-6$ are terminally bound. It is reasonable to expect that the more strongly bound sites are filled first in the flowing afterglow source. Extended Hückel molecular orbital calculations[18a] indicate that $Pt_3(\mu\text{-}CO)_3(CO)_3^{2-}$ is more stable than $Pt_3(CO)_6^{2-}$ by >400 kJ mol^{-1}, which also suggests that bridging carbonyls are more tightly bound than terminal carbonyls (although the greater stability of the bridged system is attributed[18b] to lower energies for both the metal–metal and metal–carbon bonding orbitals). The binding energy of the sixth carbonyl ligand is slightly elevated over the bond energies of the fourth and fifth ligands. This might be attributed to extra stability of the $Pt_3(CO)_6^-$ cluster because it is saturated, with respect to addition of CO in the gas phase.[4,6] Since little is known quantitatively about carbonyl binding energies in multimetal species, our assignments of terminal and bridging binding energies are tentative. High-level *ab initio* calculations of geometries and bond energies for $Pt_3(CO)_m^-$ species would be most helpful to test our interpretations.

The possibility that the carbonyls are in the 3-fold face-capping positions for clusters such as Pt_3CO^- and $Pt_3(CO)_2^-$ needs to be considered. Most triplatinum complexes have the structure $Pt_3L_3(\mu\text{-}L)_3$, as in **I**, but Puddephatt and co-workers[19,20] have successfully added up to three carbonyl ligands to axial positions in unsaturated cluster species of the type $Pt_3(\mu\text{-}dppm)_3^{2+}$ (dppm = $Ph_2PCH_2PPh_2$). However, the dppm or other phosphorous donor ligands are necessary to stabilize the cluster against fragmentation upon axial carbonyl addition. Furthermore, the axial carbonyls are fluxional, exchanging between 3-fold, 2-fold, and terminal positions on the NMR time scale. These observations imply that the axial carbonyls are relatively weakly bound. Calculations[18] indicate that, in planar Pt_3L_6 species, the out-of-plane platinum p orbitals are high-lying. The relative inaccessibility of those orbitals for donation from ligands is the reason for the saturation of Pt_3^- at six carbonyls in the gas phase and the stability of $Pt_3(CO)_3(\mu\text{-}CO)_3^{2-}$ in solution. For these reasons, we expect that all our $Pt_3(CO)_m^-$ clusters are quasiplanar with the carbonyls in equatorial positions.

We can compare the $Pt_3(CO)_m^-$ binding energies with CO adsorption energies on platinum surfaces. On Pt(100), the on-top (terminal) and 2-fold bridging sites are about equally favorable,[21] while on Pt(111) the on-top site is actually more strongly bound than the 2-fold bridge site,[22] with binding energies of 131 ± 5 and 95–110 kJ mol^{-1}, respectively. Thus, the higher binding energy for the bridging carbonyls in the triplatinum clusters does not hold for surfaces, and the binding energies at both surface sites are comparable to those of the terminal carbonyls in $Pt_3(CO)_m^-$. Calculations by Anderson and Awad[23] indicate that the energy of the valence d band of the Pt(111) surface is significantly below the CO π^* orbital energy, which precludes strong π back-donation that would favor higher coordination sites and promotes σ donation instead. It will be interesting to determine whether larger platinum clusters approach the surface behavior by exhibiting a decrease in the favorability of the bridging sites.

In summary, we have measured the sequential bond dissociation energies of each carbonyl in the gas phase $Pt_3(CO)_6^-$ cluster anion. These results are the first measurements of individual CO binding energies in a multiple metal species. We have found that the carbonyl ligands fall into two categories, assigned as three bridge-bound (189–215 kJ mol^{-1}) and three terminally bound (82–140 kJ mol^{-1}), consistent with the structure[1] of the $Pt_3(CO)_3(\mu\text{-}CO)_3^{2-}$ species in solution.

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(13) The carbonyl stretching vibrational frequencies of 1740 and 1945 cm^{-1} are taken from the study[1] of $Pt_3(CO)_6^{2-}$. Pt_3 vibrational frequencies (191, 161, and 112 cm^{-1}) are estimated using the treatment of Jarrold and Bower.[14] The Pt–CO vibrational frequencies (600, 561 × 2, and 200 × 2 cm^{-1}) are taken from a calculation.[15]

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