perimental data provide an unambiguous answer in favor of the second alternative; thus, we have to conclude that the isomerization 10 $\rightarrow$ 9a-Fe$^*$ is rapid in comparison to the production of molecular hydrogen.

The behavior of the [M - C2H4]+ species generated from 9a-Fe$^*$ was also probed by using FTICR. If, for example Fe(C2H4)+, generated from Fe$^*$ and C2H4Cl, is reacted with CD3(CH2)3OC3H7 (Sc), the primary reaction products are the pressure of experimental data provide an unambiguous answer in favor of the hydrogen. Was also probed by using FTICR. If, for example Fe(C2H4)+, 10 173 (36), exhibit higher metal/ligand ratios than most saturated transfer clusters and metal surfaces lies in the fact that metal surfaces. The breakdown between transition-metal clusters. An understanding of the chemical and physical properties of "catalysis/ surface chemistry" will be enhanced if the factors which alter the information essential to a complete description of adsorbatemetal be delineated. Thus, the study of transition-metal clusters provides essential to a complete description of adsorbate-metal surface interactions. The breakdown between transition-metal clusters and metal surfaces lies in the fact that metal surfaces exhibit higher metal/ligand ratios than most saturated transition-metal clusters. Consequently, the current trends in much of cluster chemistry is centered around so-called bare metal clusters.

An important aspect is the study of gas-phase ion clusters. Gas-phase transition-metal clusters is the ability to study highly unsaturated cluster (both cationic and anionic) fragments which have higher metal-to-ligand ratios. Our work is directed toward developing methods for measuring metal–metal and metal–ligand binding energies as a function of cluster size as well as a function of metal-to-ligand ratio. For example, ions of the type Mx(CO)yx/x = 2–8, y = 0–3x can be synthesized and probed by ion-molecule reaction chemistry, collisional activation methods, and photodissociation. Ridge and Russell studied the ion-molecule clustering reactions of anionic and cationic transition-metal species and reported on the formation of highly unsaturated ionic cluster fragments, and proposed that the reactivities of the cluster fragments directly correlate with the electron deficiencies. Because electron deficiency is an indication of the number of open coordination sites of the metal atoms within the cluster fragment, a change in the electron deficiency (number of open coordination sites) is observed as a change in the reactivity.

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Ion-Molecule Reaction Chemistry of Ionic Transition-Metal Carbonyl Cluster Fragments. 1. Ligand-Exchange Reactions of Cr2(CO)y+y+ Ions

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Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received November 15, 1989

Abstract: The ligand-exchange ion-molecule reaction chemistry of Cr2(CO)y+y+ ionic transition metal cluster fragments has been investigated by using a two-section ion cell Fourier transform ion cyclotron resonance mass spectrometer. Simple ligand-exchange reactions involving ligand (L) addition followed by metal–ligand (M – CO) bond cleavage (i.e., an associative ligand-exchange mechanism) as well as ligand exchange involving metal–metal bond cleavage (i.e., addition of L to Cr2(CO)y+y+ followed by metal–metal bond cleavage) are observed. The branching ratios for reactions involving metal–metal bond cleavage increase as the metal-to-ligand ratio decreases. In addition, the ratio for simple ligand exchange to metal–metal bond cleavage is strongly dependent upon the nature of the reacting ligand (L). These data combined with collision-induced dissociation data for Cr2(CO)y+y+ionic cluster fragments suggest that the Cr–Cr bond strength decreases as y is increased; i.e., the Cr--Cr bond order is strongly dependent upon the ligand environment.

Introduction

Studies of the chemical and physical properties of gas-phase transition-metal ions are a subject of growing research interest. An understanding of the chemical and physical properties of transition-metal ions and unsaturated ionic cluster fragments is fundamental to continued development in several areas of inorganic chemistry. Studies of transition-metal clusters is partially motivated by the similarities between transition-metal clusters and bulk-metal surfaces. Although one can argue the merits of studies aimed toward bridging the gap between atomic/molecular properties and bulk materials, our understanding of "catalysis/ surface chemistry" will be enhanced if the factors which alter the chemical and physical properties of transition metal species can be delineated. Thus, the study of transition-metal clusters provides information required for a complete description of adsorbate–metal surface interactions. The breakdown between transition-metal clusters and metal surfaces lies in the fact that metal surfaces exhibit higher metal/ligand ratios than most saturated transition-metal clusters. Consequently, the current trends in much of cluster chemistry is centered around so-called bare metal clusters.

An important aspect is the study of gas-phase ionic transition-metal clusters. Gas-phase transition-metal clusters is the ability to study highly unsaturated cluster (both cationic and anionic) fragments which have higher metal-to-ligand ratios. Our work is directed toward developing methods for measuring metal–metal and metal–ligand binding energies as a function of cluster size as well as a function of metal-to-ligand ratio. For example, ions of the type Mx(CO)yx/x = 2–8, y = 0–3x can be synthesized and probed by ion–molecule reaction chemistry, collisional activation methods, and photodissociation. Ridge and Russell studied the ion–molecule clustering reactions of anionic and cationic transition-metal species and reported on the formation of highly unsaturated ionic cluster fragments, and proposed that the reactivities of the cluster fragments directly correlate with the electron deficiencies. Because electron deficiency is an indication of the number of open coordination sites of the metal atoms within the cluster fragment, a change in the electron deficiency (number of open coordination sites) is observed as a change in the reactivity.
The calculated (using the 18-electron rule) electron deficiencies of Cr$_2$(CO)$_4^{+}$ ($\gamma = 4-6$) are 7.5, 6.5, and 5.5, respectively. However, the reactivities of Cr$_2$(CO)$_4^{+}$ and Cr$_2$(CO)$_5^{+}$ are much lower than that for Cr$_2$(CO)$_6^{+}$, suggesting that the cluster fragments have much smaller electron deficiencies, 3.5 and 4.5, respectively. Because the reactivity of Cr$_2$(CO)$_6^{+}$ is low relative to the predicted electron deficiency, it was suggested that higher order metal-metal or metal-ligand bonds could compensate the electron deficiencies.

On the basis of ion-molecule reactivity data, the electron deficiencies of the Cr and Fe ionic cluster fragments are found to be of two types: (i) electron deficiencies that are typical for simple polyhedra structures (e.g., systems that obey the 18-electron rule) and (ii) electron deficiencies that deviate from the 18-electron rule. It was proposed that deviations from the 18-electron rule are attributable to high bond orders for either the metal-metal and/or metal-ligand binding.

Ligand-exchange reaction chemistry of unsaturated ionic cluster fragments is of fundamental interest as well as an informative probe of chemical properties. Although addition of ligands to coordinatively unsaturated metal centers might be expected to be rapid and efficient, recent studies show that some ligand-exchange reactions are slow and inefficient. For example, CO addition reactions to coordinatively unsaturated, neutral metal carbonyls have been examined by Weitz et al. Large variations in the reaction rate for CO addition to Fe(CO)$_5$ were observed, and the slow rate for CO addition to Fe(CO)$_4$ was attributed to a spin-forbidden transition: Fe(CO)$_4$ (triplet ground state) $\rightarrow$ Fe(CO)$_3$ (singlet ground state). Conversely, the rapid rate for CO addition to Fe(CO)$_5$ and Fe(CO)$_4$ suggest these processes are spin-allowed. Thus, the first step in ligand-exchange reactions, e.g., ligand addition as illustrated by reaction 1, and, consequently $M_i$(CO)$_4^{+}$ + L $\rightarrow$ $[M_i$(CO)$_4^{+}$-$L$]$^*$ $\rightarrow$ $M_i$(CO)$_3^{+}$L$^*$ + aCO

the overall rate for ligand exchange, may be exceedingly sensitive to the spin state of the ionic cluster fragment. Similar trends in the rates of ligand-exchange reactions have been observed for gas-phase ionic species. Specifically, Beauchamp and co-workers showed that CO addition reactions for some gas-phase cationic metal species are also quite slow.

Experimental Section

All experiments were carried out by using a Fourier transform ion cyclotron resonance built at TAMU. The system consists of a Nicolet 1280 data system, a 3-tesla Oxford superconducting magnet, a home-built vacuum system, and a two-section ion cell. Samples were introduced into the system with a leak valve maintained at ambient temperature with typical pressures of 1-3 $\times$ 10$^{-7}$ Torr. The electron impact ionization of the sample was performed by using a pulsed electron beam (pulse duration 1-3 ms) at 50 eV (nominal) exciting energy and 200 $\mu$A emission current. The ion cell trapping voltage was maintained at 500 V. Temperature with typical pressures of 1-3 Torr. The temperature of the neutrals is corrected for the sensitivity of the ionization gauge to the particular ligand (relative to nitrogen) by multiplying the pressure by the sensitivity factors. The reaction rate constants obtained in this manner are good to $\pm$10%, determined by comparing reaction rate constants for C$_2$H$_4^{+}$ + CH$_3$H$_2$ $\rightarrow$ C$_2$H$_5^{+}$ + CH$_4$ with literature values.

Collision-induced dissociation spectra of the Cr$_2$(CO)$_4^{+}$ ions were obtained by using a Kratos MS-50TA tandem mass spectrometer. The instrument and the details of the experiment have been described previously.

Results

This work investigates the ion-molecule ligand-exchange reactions for Cr$_2$(CO)$_4^{+}$ ($\gamma = 4, 5, 6$) ionic cluster fragments with several ligands ($^{13}$CO, O$_2$, C$_2$H$_2$, NH$_3$, and CH$_4$). The Cr$_2$(CO)$_4^{+}$ ionic cluster fragments are formed by ion-molecule reactions of Cr$^+$ with neutral Cr(CO)$_4$ (12b). The ligand-exchange reactions proceed by an associative reaction mechanism (reaction 2) where L is some ligand. Thus, addition Cr$_2$(CO)$_4^{+}$ + L $\rightarrow$ [Cr$_2$(CO)$_3^{+}$+L$^*$] $\rightarrow$ Cr$_2$(CO)$_3^{+}$+L$^*$ + a(CO) (2)

of L to Cr$_2$(CO)$_4^{+}$ occurs because open coordination sites are available for ligand binding to form a collision complex Cr$_2$(CO)$_3^{+}$+L$^*$.$^{12}$ Dissociation of the collision complex to the final products, Cr$_2$(CO)$_3^{+}$+L$^*$ + a(CO), corresponds to unimolecular dissociation of the ion-molecule collision complex. In the following sections a detailed description of the ligand-exchange reactions for Cr$_2$(CO)$_4^{+}$, Cr$_2$(CO)$_5^{+}$, and Cr$_2$(CO)$_6^{+}$ with several ligands are presented. Although the general ligand-exchange reactions were used to mass select a particular ionic cluster fragment for ligand-exchange studies. The mass-selected ionic cluster fragment was then partitioned to the analyzer side of the two-section cell which contains the neutral ligand at a static pressure of 1-3 $\times$ 10$^{-7}$ Torr. The ligand-exchange products for a particular ionic cluster fragment and a particular ligand were then monitored as a function of time. The complete experimental sequence has been described in detail previously. The data for each reaction are represented as relative total ion intensity versus time to produce temporal plots which can be fitted and used to extract reaction rate constants.

The rate of disappearance of the ionic cluster fragment is defined as $ln(I/I_0) = -exp(nkT)$ where $I$ is the intensity of the ionic cluster fragment at any time, $T$ is the initial intensity of the ionic cluster fragment, $n$ is the number density of neutral molecules, and $k$ is the rate constant for the reaction. Therefore, a plot of $[ln(I/I_0)]$ versus time would have a slope of $-nk$, where $k$ is the rate constant for disappearance of the ionic cluster fragments. The number density is calculated using the ideal gas law. The pressure of the neutrals is corrected for the sensitivity of the ionization gauge to the particular ligand (relative to nitrogen) by multiplying the pressure by the sensitivity factors. The reaction rate constants obtained in this manner are good to $\pm$10%, determined by comparing reaction rate constants for C$_2$H$_4^{+}$ + CH$_3$H$_2$ $\rightarrow$ C$_2$H$_5^{+}$ + CH$_4$ with literature values.

Collision-induced dissociation spectra of the Cr$_2$(CO)$_4^{+}$ ions were obtained by using a Kratos MS-50TA tandem mass spectrometer. The instrument and the details of the experiment have been described previously.


Figure 1. Temporal plot for the ligand-exchange ion-molecule reactions of Cr$_2$(CO)$_4^{+}$ with $^{13}$CO.
Ligand-Exchange Reactions of $\text{Cr}_2(\text{CO})_x^+$ Ions

Table I. Ion–Molecule Reaction Rate Constants* for Disappearance of $\text{Cr}_2(\text{CO})_x^+$ for Ligand-Exchange Reactions with Various Ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) $\times 10^9$ for</th>
<th>$\text{Cr}_2(\text{CO})_x^+$</th>
<th>$\text{Cr}_2(\text{CO})_y^+$</th>
<th>$\text{Cr}_2(\text{CO})_z^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp</td>
<td>induced dipole</td>
<td>ADQ exp</td>
<td>induced dipole</td>
</tr>
<tr>
<td>$^{13}\text{CO}$</td>
<td>0.5</td>
<td>0.7</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>oxygen</td>
<td>0.6</td>
<td>0.7</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>methanol</td>
<td>0.7</td>
<td>0.8</td>
<td>1.4</td>
<td>0.6</td>
</tr>
<tr>
<td>ammonia</td>
<td>1.6</td>
<td>0.9</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>benzoene</td>
<td>0.3</td>
<td>1.0</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>l,3-butadiene</td>
<td>0.3</td>
<td>1.1</td>
<td>1.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Reaction rate constants are reproducible (based on three replicate measurements) to ±10% in each case. See Experimental Section for further discussion on methods.

for the $\text{Cr}_2(\text{CO})_x^+$ ions are quite similar, each ionic cluster fragment manifests characteristic differences.

**Ligand-Exchange Reactions with $^{13}\text{CO}$ (Thermoneutral Exchange Reactions).** $\text{Cr}_2(\text{CO})_x^+$ and $\text{Cr}_2(\text{CO})_y^+$ react (stepwise) with $^{13}\text{CO}$ to displace all of the $^{12}\text{CO}$ ligands. Figure 1 contains a temporal plot for the ligand-exchange reaction products of $\text{Cr}_2(\text{CO})_x^+$ and $^{13}\text{CO}$. The $\text{Cr}_2(\text{CO})_x^+$ ionic cluster fragment does not undergo a ligand-exchange reactions with $^{13}\text{CO}$. There is no significant amount (<10%) of $^{12}\text{CO}$ ligand-exchange reaction product(s) detected for the $\text{Cr}_2(\text{CO})_x^+$ ion for reaction times of up to 800 ms (~20 ion–neutral collisions).

The rate constants for the disappearance of the $\text{Cr}_2(\text{CO})_x^+$ ionic cluster fragments by $^{13}\text{CO}$ ligand-exchange reactions are contained in Table I. The rate for the disappearance of $\text{Cr}_2(\text{CO})_x^+$ ($k = 5 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) is approximately 20% faster than that for $\text{Cr}_2(\text{CO})_y^+$ ($k = 4 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$). The experimental reaction rates are compared with calculated collision frequencies (Langevin and averaged-dipole orientation theories). Note that in each case the reaction with $^{13}\text{CO}$ is relatively efficient (70–80%). Assuming that all CO ligands of the collision complex are equivalent, loss of both $^{12}\text{CO}$ and $^{13}\text{CO}$ is possible; thus the measured reaction rate will deviate significantly from the calculated collision rate.

**Ligand-Exchange Reactions with Oxygen.** The ligand-exchange reactions of $\text{Cr}_2(\text{CO})_x^+$ and $\text{Cr}_2(\text{CO})_y^+$ with $\text{O}_2$ proceed with the displacement of all the CO ligands by a single O$_2$ ligand (reaction 3).

$$\text{Cr}_2(\text{CO})_x^+ + \text{O}_2 \rightarrow [\text{Cr}_2(\text{CO})_x(\text{O}_2)_y]^+ \rightarrow \text{Cr}_2(\text{O}_2)^+ + \gamma(\text{CO})$$

($\gamma = 4, 5$) (3)

S=10 ion–neutral collisions), the $\text{Cr}_2(\text{O}_2)^+$ ion reacts with $\text{O}_2$ to form $\text{Cr}_2(\text{O}_2)_2^+$ or $\text{Cr}_2(\text{O}_2)_y^+$. The $\text{Cr}_2(\text{O}_2)^+$ and $\text{Cr}_2(\text{O}_2)_y^+$ are both present in low (<20%) relative abundances. Figure 2a contains temporal plots for the ligand-exchange reaction for $\text{Cr}_2(\text{CO})_x^+$ reacting with $\text{O}_2$; this temporal plot is representative of both the $\text{Cr}_2(\text{CO})_x^+$ and $\text{Cr}_2(\text{CO})_y^+$ ions.

The ligand-exchange reaction of $\text{Cr}_2(\text{CO})_y^+$ with $\text{O}_2$ is similar to those observed for $\text{Cr}_2(\text{CO})_x^+$ and $\text{Cr}_2(\text{CO})_y^+$. That is, the initial ligand-exchange reaction yields $\text{Cr}_2(\text{O}_2)^+$ ions by displacement of all six CO ligands by a single O$_2$ ligand (reaction 4; $y = 6$). Also, the $\text{Cr}_2(\text{O}_2)_y^+$ ion reacts with $\text{O}_2$ to form $\text{Cr}_2(\text{O}_2)_2^+$ or $\text{Cr}_2(\text{O}_2)_y^+$. However, there are significant differences in the ion–molecule reaction rates, as well as the observed ion–molecule products. For example, the relative abundances of $\text{Cr}_2(\text{O}_2)_y^+$ and $\text{Cr}_2(\text{O}_2)_y^+$ are approximately twice that observed for the $\text{Cr}_2(\text{O}_2)_x^+$ and $\text{Cr}_2(\text{O}_2)_y^+$ with $\text{O}_2$ (Figure 2b). The product ion yield for $\text{Cr}_2(\text{O}_2)_y^+$ (formed by reactions of $\text{Cr}_2(\text{CO})_y^+$ with $\text{O}_2$) is probably due to differences in internal energies of the $\text{Cr}_2(\text{O}_2)_y^+$ ion. In addition, a new product ion,

$$\text{Cr}_2(\text{O}_2)_y^+ + \gamma(\text{O}_2) \rightarrow \text{Cr}_2(\text{O}_2)_y^+ + \gamma(\text{CO})$$

($\gamma = 4, 5$) (4)

Figure 2. Temporal plot for the ligand-exchange ion–molecule reaction of (a) $\text{Cr}_2(\text{CO})_x^+$ and (b) $\text{Cr}_2(\text{CO})_y^+$ with oxygen.

$\text{Cr}(\text{CO})_2\text{O}_x^+$, which arises by addition of $\text{O}_2$ to $\text{Cr}(\text{CO})_2\text{O}_x^+$ followed by cleavage of the metal–metal bond is formed as the major ion–molecule product. Note that the $\text{Cr}(\text{CO})_2\text{O}_x^+$ ion–molecule reaction product is not observed for $\text{Cr}_2(\text{CO})_x^+$ and $\text{Cr}_2(\text{CO})_y^+$.

The product ions of the ligand-exchange reactions of $\text{Cr}_2(\text{CO})_x^+$ with $\text{O}_2$, specifically the $\text{Cr}_2(\text{CO})_x(\text{O}_2)_y^+$ ion formed by metal–metal bond cleavage, were verified by $^{18}\text{O}_2$ isotopic labeling experiments; $\text{Cr}_2(\text{CO})_x(\text{O}_2)_y^+$ and $\text{Cr}_2(\text{O}_2)_y^+$ have the same nominal mass, e.g., $m/z$ 168. All of the $\text{O}_2$ ligand-exchange reaction products from $\text{Cr}_2(\text{CO})_x^+$ and $\text{Cr}_2(\text{CO})_y^+$, e.g., $\text{Cr}_2(\text{O}_2)_y^+$ and $\text{Cr}_2(\text{O}_2)_y^+$ increased in mass by 2$n$, where $n$ is the number of oxygen atoms contained in the product ions. For the $\text{Cr}_2(\text{CO})_x^+$ ligand-exchange reaction products, reactions with $^{18}\text{O}_2$ gave products which also increased in mass by 2$n$; however, the product ion observed at $m/z$ 168 using unlabeled $\text{O}_2$ is shifted to $m/z$ 176 ($\text{Cr}_2^{18}\text{O}_4^+$), and a signal at $m/z$ 172 ($\text{Cr}_2(\text{O}_2)^{18}\text{O}_2^+$) is also observed (reactions 4 and 5).

$$\text{Cr}_2(\text{CO})_y^+ + \gamma(\text{O}_2) \rightarrow \text{Cr}_2(\text{O}_2)_y^+$$

(5)

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(23) Similar reactions have been observed for dimer and trimer ions of Fe and Co ions; see: Jacobson, D. B.; Freiser, B. S. J. Am. Chem. Soc. 1986, 108, 27.

It is of interest to note that the Cr(CO)_{5}O^{+} product ion is not observed as an ion-molecule product at short reaction times, but at reaction times of greater than ~300–400 ms the Cr(CO)_{5}^{+} and Cr(CO)_{6}^{18}O^{+} product ions are of comparable abundances. This result suggests that the Cr(CO)_{5}^{+} ion must undergo some relaxation process (either collisional or radiative) before the Cr(CO)_{5}^{18}O^{+} reaction channel becomes competitive. Also, the efficiency of the ion–molecule reaction is low (exp/calc reaction rate = 60%), which also suggest that not all ion-molecule collisions yield product ions. The details of this process are being studied further.

The rate constants for the disappearance of the Cr(CO)_{5}^{+} ionic cluster fragments with oxygen are shown in Table 1. Note that the rate of Cr(CO)_{5}^{+} (k = 1.1 \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) reacting with oxygen is approximately 25% faster than that for Cr(CO)_{5}^{+} (k = 9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) and ca. 40% faster than that for Cr(CO)_{5}^{+} (k = 7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}).

Ligand-Exchange Reactions with Methanol. Cr(CO)_{5}^{+} reacts with CH_{3}OH to displace one or two CO ligands (reactions 6 and 7). The ligand-exchange product ions react to displace two additional CO ligands, yielding Cr(CO)(CH_{3}OH)_{2}^{+} or Cr(CO)(CH_{3}OH)_{3}^{+}.

The Cr(CO)_{5}^{+} ionic cluster fragment undergoes ligand-exchange reactions with CH_{3}OH by displacement of one CO ligand to form Cr(CO)(CH_{3}OH)_{2}^{+} (reaction 8). The Cr(CO)_{5}^{+}(CH_{3}OH)_{2}^{+} product ion reacts with CH_{3}OH to displace another CO ligand, yielding Cr(CO)(CH_{3}OH)_{3}^{+}, but this ion does not react further. In addition, the Cr(CO)_{5}^{+} ionic cluster fragment reacts with CH_{3}OH to yield metal–metal bond cleavage products, e.g., Cr(=CH_{3}OH)^{+} (reaction 9), and the Cr(=CH_{3}OH)^{+} ion reacts with CH_{3}OH to yield Cr(=CH_{3}OH)_{2}^{+}. Presumably the neutral formed in reaction 9 is Cr(CO)_{5}.

Cr(CO)_{5}^{+} + CH_{3}OH →

[Cr(CO)_{5}(CH_{3}OH)]^{+} + CO

additional CO ligands, yielding Cr(CO)(CH_{3}OH)_{2}^{+} or Cr(CO)(CH_{3}OH)_{3}^{+}.

The Cr(CO)_{5}^{+} ionic cluster fragment reacts with CH_{3}OH to displace one CO ligand, but this ligand-exchange product does not react further with methanol. The dominant ion–molecule products observed for Cr(CO)_{5}^{+} with CH_{3}OH correspond to metal–metal cleavage products, e.g., Cr(=CH_{3}OH)^{+}, and this ion reacts with CH_{3}OH to form Cr(=CH_{3}OH)_{2}^{+}.

The rate constants for reaction of the Cr(CO)_{5}^{+} ionic cluster fragments with methanol are given in Table 1. The rate of Cr(CO)_{5}^{+} (k = 7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) reacting with methanol is approximately 15% faster than those observed for Cr(CO)_{5}^{+} (k = 6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) and Cr(CO)_{5}^{+} (k = 6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}).

Ligand-Exchange Reactions with Ammonia. Cr(CO)_{5}^{+} reacts with NH_{3} to displace one or two CO ligands (reactions 10 and 11).

Cr(CO)_{5}^{+} + NH_{3} →

[Cr(CO)_{5}(NH_{3})]^{+} + CO

or two CO ligands, and these product ions react to displace the remaining CO ligands to yield Cr(NH_{3})_{2}^{+}. The ligand-exchange reaction between Cr(CO)_{5}^{+} and NH_{3} also yields products which correspond to metal–metal cleavage of the ionic cluster fragment to form CrNH_{3}^{+} and Cr(NH_{3})_{2}^{+}. The temporal distribution for the ligand-exchange reaction products for Cr(CO)_{5}^{+} with NH_{3} is shown in Figure 3a.
The rate constants for the disappearance of the Cr\(_2\)(CO)\(_6^+\) ionic cluster fragments for ligand-exchange reactions with benzene and 1,3-butadiene are shown in Table I. The rate of Cr\(_2\)(CO)\(_6^+\) (\(k = 3 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) reacting with benzene is approximately 25% faster than those for Cr\(_2\)(CO)\(_5^+\) (\(k = 2 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) and Cr\(_2\)(CO)\(_4^+\) (\(k = 3 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) reacting with 1,3-butadiene. The rate of Cr\(_2\)(CO)\(_5^+\) (\(k = 3 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) reacting with 1,3-butadiene is approximately 10% faster than that for Cr\(_2\)(CO)\(_6^+\) (\(k = 2 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) and that for Cr\(_2\)(CO)\(_4^+\) (\(k = 2 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)).

Discussion

In order for an ionic transition metal cluster fragment to undergo a ligand-exchange reaction, an open coordination site must be available to the incoming ligand, i.e., formation of an associative collision complex (reaction 1). The ion–molecule collision complex \([M(CO)\(_x\)X\(_y\)]^+\) contains excess internal energy, and some fraction of the excess energy can be dissipated by expulsion of other ligands. Therefore, the exothermicity of the reaction and the number of CO ligands displaced by the incoming ligand (L) depends upon the relative binding energies of the ligands to the metal cluster. Steric effects may influence the overall rate of reaction, but it is unlikely that such effects (where L is a small molecule) will play a very important role for the \(M(CO)\(_x\)\)\(^+\) species. Conversely, geometric relaxation (e.g., structural rearrangement and/or changes in the metal–metal–ligand bond order) of the ion–molecule collision complex may be important. That is, formation of a ligand (L) to metal\(_2\) complex significantly alters the nature of the metal–metal bond or even the metal–CO bonding. The photodissociation data for the \(M(CO)\(_x\)\)\(^+\) ionic species clearly show that metal–CO bond energies are sensitive to the metal-to-ligand ratio, a result consistent with studies of metal–CO bond energies of mono-metal species.

The thermoneutral ligand-exchange reactions with \(^{13}\)CO provide an indication of the ligand lability for the Cr\(_2\)(CO)\(_x^+\) ions. The ligands of Cr\(_2\)(CO)\(_x^+\) and Cr\(_2\)(CO)\(_y^+\) ions are very labile and readily exchange with the \(^{13}\)CO; conversely, the Cr\(_2\)(CO)\(_x^+\) ions do not undergo ligand exchange with \(^{13}\)CO. There are several factors which may influence the thermoneutral ligand-exchange reaction between \(^{13}\)CO and Cr\(_2\)(CO)\(_x^+\) ions: (i) the ligands of the Cr\(_2\)(CO)\(_y^+\) are very strongly bound and the geometric relaxation required to accommodate the incoming ligand is associated with a high activation (either kinetic or thermodynamic) barrier; (ii) the Cr\(_2\)(CO)\(_y^+\) ion does not have an open coordination site to accept bonding electrons from the incoming CO ligand. In our original work on Cr\(_2\)(CO)\(_x^+\) ionic cluster fragments, we suggested that the electron deficiency of Cr\(_2\)(CO)\(_x^+\) is low (e.g., 3.5); an electron deficiency of 3.5 suggests that there are open (1.75 per Cr atom) coordination sites for attachment of the incoming ligand. Therefore, it seems unlikely that the reactivity of Cr\(_2\)(CO)\(_x^+\) with CO can be attributed to the lack of an open coordination site.

It is interesting to compare the reaction rates of Cr\(_2\)(CO)\(_x^+\) with \(^{13}\)CO and the electron deficiencies for the ionic cluster fragments. For example, the rate of the ion–molecule reactions with \(^{13}\)CO (ligand lability) increases as the nature of the metal–metal bond or even the metal–CO bonding.

The rate constants for the disappearance of the Cr\(_2\)(CO)\(_x^+\) ionic cluster fragments for ligand-exchange reactions with benzene and 1,3-butadiene are given in Table I. The rate of Cr\(_2\)(CO)\(_x^+\) (\(k = 3 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) reacting with benzene is approximately 25% faster than those for Cr\(_2\)(CO)\(_5^+\) (\(k = 2 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) and Cr\(_2\)(CO)\(_4^+\) (\(k = 3 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) reacting with 1,3-butadiene. The rate of Cr\(_2\)(CO)\(_5^+\) (\(k = 3 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) reacting with 1,3-butadiene is approximately 10% faster than that for Cr\(_2\)(CO)\(_6^+\) (\(k = 2 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) and that for Cr\(_2\)(CO)\(_4^+\) (\(k = 2 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)).
entation theories show that ligand exchange does not occur for every ion–neutral collision, e.g., 70% and 80% for Cr(CO)₆ and Cr₂(CO)₁₀, respectively. Thus, the reaction efficiency may result from a strong orientation dependence on the reaction. But the reaction efficiency may also be due to a preference for loss of the incoming ¹³CO ligand upon dissociation of the collision complex, e.g., Cr₂(CO)₆⁺→Cr₂(CO)₅⁺ + ¹³CO. That is, at early stages in the reaction the ligands are nonfluctuous and the ligand identity is preserved.

Issues related to ligand fluxionality were examined in separate experiments. Kerley and Russell examined the extent of ¹³CO retention by Fe₃(CO)₁₂⁺ formed by reaction of Fe(CO)₉ with Fe(CO)₃⁺.27 The results of these studies suggest that geometric relaxation of the [Fe₃(CO)₁₂⁺Fe(CO)₃⁺] collision complex occurs by rearrangement within the neutral moiety. That is, the extent of label retention in the Fe₃(CO)₁₂⁺ and Fe₃(CO)₁₀ product ions is low, less than a few percent, which suggests preferential elimination of ¹³CO from the collision complex. There may, however, be fundamental differences in the dynamics of addition of L to M₃(CO)₁₀⁺ and addition of (¹³CO)Fe⁺ to Fe(CO)₅.

For example, the initial interaction between (¹³CO)Fe⁺ and Fe(CO)₅ occurs via the Fe⁺ and the CO ligands of Fe(CO)₅, whereas, the initial interaction between L and M₃(CO)₁₀⁺ probably involves addition of L to the metal center.

Beauchamp recently suggested that variations in the rates for ligand-exchange reactions of mono-metal ionic species arise due to the spin-forbidden nature of the ligand addition reaction. We interpreted data from photodissociation reactions in mono-metallic ionic species in a similar fashion; however, we have not observed such effects for metal dimer or trimer ions. Presumably, the metal dimer and trimer ions promote spin–orbit coupling through a heavy atom effect; this interpretation is consistent with the photochemistry of Fe(CO)₅X species, X = Br, Cl.28 Fe(CO)₅⁺ (v = 1–3, 5) ions do not photodissociate between 514.5 and 458 nm, presumably because Fe(CO)₅⁺ → Fe(CO)₄⁺ is spin-forbidden, but the Fe(CO)₅X⁺ ions readily photodissociate to Fe(CO)₅X and Fe(CO)₄⁺X⁻.

In our original work on the formation of ionic cluster fragments by ion–molecule reactions, we explained the clustering sequence in terms of the addition of a 14-electron metal carbonyl fragment (L') to M₃(CO)₁₀⁺ to form [M₃(CO)₁₀⁺L']⁻ which subsequently rearranges to a stable M₃X₄(CO)⁺ ion.19 The transformation [M₃(CO)₁₀⁺L']⁻ → M₃X₄(CO)⁺ corresponds to a complete rearrangement of the electronic structure, or, in terms of Lauher's model of the cluster bonding, a complete restructuring of the cluster valence molecular orbital (CVMO).29 An important factor which emerges from this model is that the reactivity (as measured by the disappearance of the reactant ion or the appearance of the ion–molecule product ion) of the ionic cluster fragment will be strongly dependent upon the (relative) strength of the interaction between the reacting ion and the neutral. For example, if the interaction between the reacting ion and the neutral is weak, relative to the metal–metal and metal–ligand binding energy of the reacting species, the collision complex will simply dissociate to re-form the reactants. However, a strong interaction between the ionic and neutral reactants will lead to displacement of ligands of the ionic or neutral reactants and formation of a new product ion.

Formation of an associative ligand-exchange collision complex can be viewed in a similar manner. That is, L (CO, O₂, etc.) reacts with M₃(CO)₁₀⁺ to form [M₃(CO)₁₀⁺L−]⁻, and CO ligands are expelled to form M₃(CO)₉⁺L⁻. If formation of M₃(CO)₉⁺L⁻ is strongly exothermic, several CO ligands may be displaced from [M₃(CO)₁₀⁺L−]⁻ upon addition of L. Because the exothermicity of the reaction may be due to geometric relaxation or rearrangement of the [M₃(CO)₁₀⁺L−]⁻ collision complex as well as differences in the bond energies of the in-coming and out-going ligands, bracketing of ligand bond energies is not a straightforward problem. For example, such rearrangements are suggested when competitive reaction channels are involved, e.g., CH₃OH reacts with Cr₂(CO)₁₀⁺ to yield Cr₂(CO)₅(CH₃OH)⁺ and Cr₂(CO)₅⁺-(CH₃OH)⁺. Clearly, there must be relaxation channels available to the collision complex in addition to simple ligand expulsion.

The occurrence of metal–metal cleavage ion–molecule reactions follows a general trend which can be explained in terms of metal–metal and metal–ligand bond energies. For example, the fraction of ions which react by Cr–Cr cleavage increases with decreasing electron deficiencies, (e.g., Cr₂(CO)₁₀⁺ > Cr₂(CO)₉⁺ > Cr₂(CO)₈⁺). Also, Cr–Cr cleavage product ions follow the general trend, NH₃ > CH₃OH > CH₃OH > H₂O. Although accurate metal–ligand bond energies for Cr₂⁺–L species (L = CO, O₂, CH₃OH, etc.) are not known, preliminary studies suggest that Cr₂⁺–L bond energies roughly parallel those reported for mono-metallic ions.31 That is, the metal–ligand bond energies for the ligands examined approximate the trend observed for metal–metal bond cleavage reactions of the Cr₂(CO)₅⁺ ions: D*(Cr₂⁺–L) values are NH₃ > CH₃OH > CH₃OH > O₂. On the basis of the observed reactivity, for example, Cr₂(CO)₅⁺ undergoes metal–metal bond cleavage only with NH₃, whereas, Cr₂(CO)₅⁺ undergoes metal–metal bond cleavage with ligands having bond energies greater than that of O₂. On the basis of preliminary estimates of metal–ligand bond energies,32 we estimate that the metal–metal bond of Cr₂(CO)₅⁺ is ca. 15–20 kcal/mol stronger than that for Cr₂(CO)₆⁺.

Questions concerning the metal–metal bond of the Cr₂ dimer are of importance to the general area of metal clusters and cluster chemistry. Smalley et al. reported a Cr–Cr bond length of 1.68 Å.33 Such a short bond length is consistent with the view that Cr₂ involves a sextuple bond. Although chromium carbonyl species do not generally bond together to form clusters, the stability of small Cr₂(CO)₆⁺ ionic species suggests that such species are not intrinsically unstable. In fact, collision-induced dissociation of Cr₂(CO)₆⁺ ions suggest that the Cr–Cr bond in dimers, trimers, and tetramers is quite substantial. For example, collisionally activated Cr₂(CO)₆⁺ ions favor dissociation by loss of CO over cleavage of the Cr–Cr bond, and the collision-induced dissociation spectra can be used to estimate the relative Cr–Cr bond strengths for the ions. The branching ratios for formation of M⁺ and M₂⁺ product ions from collisionally activated Cr₂(CO)₆⁺ ions should be sensitive to the metal–metal bond energy. Figure 5 contains a plot of the ratio of M⁺/M₂⁺ versus the number of CO ligands contained in the Cr₂(CO)₆⁺ ionic cluster fragment. Note that for y = 4 the M⁺/M₂⁺ ratio is 0.25; whereas for y = 6 the


Figure 5. Plot of the M⁺/M₂⁺ branching ratio from collision-induced dissociation reactions versus the number of CO ligands (y) of the Cr₂(CO)₆⁺ (y = 4–7) ionic cluster fragment.
Ligand Fluxionality and the Formation of Cationic Iron Carbonyl Clusters

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Abstract: The clustering gas-phase reactions of Fe(13CO)+ with Fe(CO)S to form Fe3(13CO),(CO): are studied by Fourier transform ion cyclotron resonance mass spectrometry. It was found that the binary cluster cations formed by these reactions have a strong tendency to lose the 13CO ligand during cluster formation. Label preference ratios varied only slightly from 0.56 ± 0.06 to 0.7 ± 0.1, indicating a clear preference for loss of the labeled carbonyl ligand. This preferential loss is indicative of the nonfluxional nature of these systems. Nonfluxionality in the cationic iron carbonyl clusters results from a decrease in back-bonding to the 2π orbital of the carbonyl ligands.

Introduction

Ligand fluxionality is commonly observed for coordinatively and electronically saturated iron carbonyl compounds. For example, Fe5(CO)12 exists in solution as a continuum of structures ranging from the symmetrically bridged C5 to the nonbridged D5h structure. The activation energy for going from one structure to the other is estimated at <5 kcal mol⁻¹, giving rise to the observation of only a single 13C NMR resonance at -150 °C.² The concept of ligand fluxionality has been successfully employed for prediction of structures of binary carbonyl clusters.³ In this procedure, carbonyl ligands are assumed to be equivalent such that the repulsions between ligands ultimately determine their arrangement around a bare metal cluster. The solid-state C2v structure of Fe5(CO)12 can be rationalized by this method if one considers the 12 carbonyl ligands to form an icosahedron with an Fe₃ triangle placed inside. Further, the D₃h structure of the isovalent Ru₅(CO)₁₂ and Os₅(CO)₁₂ species can be explained by realizing that the interstice of the icosahedral carbonyl arrangement cannot support these larger homologues, causing the icosahedron to expand to an anticuboctahedron. The amphoteric nature of the carbonyl ligand gives rise to the fluxional behavior observed for iron carbonyl compounds. Ligands with occupied σ orbitals and unoccupied π orbitals can act as both Lewis bases (σ donors) and Lewis acids (π acids). A number of transition metal atoms (especially those in groups 6–8) display the σ- and π-bonding components remains constant as a carbonyl ligand moves from terminal to bridging for a given cluster nucleus, then CO fluxionality should occur. As the coordinative saturation or electronic charge (electronic saturation) of a cluster is changed, the tendency for

M⁺/M₂⁺ ratio is 3.7. The collision-induced dissociation data are interpreted as evidence that the Cr-Cr bond strength is directly influenced by the M/L ratio. That is, the metal-metal bond strength follows the order Cr₃(CO)₆⁺ < Cr₃(CO)₅⁺ < Cr₃(CO)₄⁺. The CID data have also been obtained for the Cr₃(CO)₆⁺ (y = 6, 7) ionic cluster fragments and the M⁺/M₂⁺ ratio is 1/12 for y = 6 and 1/10 for y = 7; whereas the M₂⁺/M₃⁺ ratio is 1/6 for y = 6 and 1/5 for y = 7, suggesting a very strong metal-metal interaction for the chromium trimer center. The general utility of the collision-induced dissociation experiment for probing the metal-metal bond order is now being examined on larger Cr-containing clusters as well as clusters containing Fe, Co, and Ni.

Conclusions

The reactivities of Cr₂(CO)₆⁺ (y = 4, 5, 6) with small neutral molecules do not parallel that observed for reactions with Cr₃(CO)₆⁺. That is, reaction rates for Cr₂(CO)₆⁺ with Cr(CO)₅ differ considerably and the reactivity can be explained by an electron deficiency argument, but the variations in reaction rate for the Cr₂(CO)₆⁺ ions with the small neutral molecules are rather small, e.g., 10-40%. In each case the ion-molecule reaction efficiency (determined by comparing theoretical collision frequency with the experimental reaction) is quite high and approaches unity.

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