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Electron Transfer in Gas-Phase Ligand-Switching Reactions

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Bimolecular rate constants for the gas-phase ion-molecule reactions of $V(CO)_5^-$ with a variety of molecules have been obtained at thermal energies by using Fourier transform ion cyclotron resonance spectroscopy. Three distinct reaction mechanisms are observed. For the first type, ligand displacement of CO by various neutrals is observed. For a variety of ligands a correlation is observed between the reaction efficiency and the ligand electron affinity. For all reactive ligands, extensive loss of carbonyls is observed. A mechanism is proposed which involves a 1-e$^-$ transfer from $V(CO)_5^-$ to the incoming ligand, facilitated by the initial ion-dipole complexation energy. Simple ligand field orbital diagrams indicate the acceptor orbital for $V(CO)_5^-$ is half-filled. Thus, 2-e$^-$ donors cannot coordinate to the metal center without electron transfer. The radicals $NO^•$ and $(\textit{tert}\text{-butyl})_2NO^•$, which can act as 1-e$^-$ donors to the half-filled acceptor orbitals, react rapidly to displace multiple CO from $V(CO)_5^-$. $NO^•$ displaces CO at ~16% of the collision frequency, while $(t\text{-}C_4H_9)_2NO^•$ reacts at <1% of the collision frequency. The difference in reaction efficiency for the radicals is most likely due to a steric effect introduced by the large *tert*-butyl groups. The ligand displacement results suggest $V(CO)_5^-$ is a triplet in the ground state. Most molecules that undergo primary reaction with $V(CO)_5^-$ also undergo secondary reaction via further displacement of carbonyl ligands. The second type of reaction studied was chlorine transfer from chloromethanes to generate predominantly $VCl(CO)_x^-$ (x = 3-5). The rate constants correlate with the C-Cl bond dissociation energies, suggesting initial insertion into the C-Cl bond or a direct chlorine atom transfer mechanism. HCl addition to the metal center becomes competitive as the rate for chlorine transfer decreases. The third type of reaction studied involved oxidative addition/reductive elimination. $V(CO)_5^-$ reacts with CH_3NH_2 to generate $V(CO)_4(CH_2NH)^-$. Dehydrogenation is only observed with monomethyl-substituted organic molecules (i.e. CH_3OH and CH_3NH_2) suggesting a steric effect in one of the intermediates.

Introduction

Gas-phase ion-molecule reactions exhibit many features that contrast with condensed-phase reactions. Some of the unusual aspects of gaseous ion-molecule reactions can be traced to the long-range electrostatic forces that occur in the initial stages of the reaction.[1] In condensed phases the charge on the reactant ion is shielded by the surrounding environment so neutral reactants do not feel a significant electric field outside of the solvation shell. However, gaseous molecules experience significant electrostatic forces at long range, especially highly polarizable neutrals or molecules with permanent dipoles. These ion-induced dipole and ion-dipole forces are the source of the very high collision cross sections for gas-phase ion-molecule reactions.[2] These forces also result in the elimination of activation barriers for many gaseous ion reactions where barriers are present for their neutral counterparts.[1] Finally, these ion-molecule complexes can have very long lifetimes which allow sampling of a large number of reaction pathways.[3]

Ligand-switching reactions of gas-phase metal ion complexes have been the focus of a number of recent studies.[4] As has previously been discussed, gas-phase ligand-switching reactions must proceed by an associative rather than a dissociative mechanism, reaction 1.[5] The simple

$$ML_1^{\pm} + L_2 \rightleftharpoons [ML_1L_2^{\pm}]^* \rightleftharpoons ML_2^{\pm} + L_1 \qquad (1)$$

ligand-switching process has been used to determine ladders of relative metal ion-ligand binding strengths by assuming the absence of activation barriers and entropic effects for the gas-phase reactions. A few recent studies, however, have probed some of the dynamic aspects of ligand switching reactions. These observations have indicated that ligand displacement is not always driven by relative ligand binding strengths. In particular, McDonald and Schell have proposed that ligand displacement reactions for some 17-e$^-$ metal complex anions might proceed by electron transfer within the initially formed ion-dipole complex, reaction 2.[6] Pan and Ridge subsequently studied

$$ML_1^- + L_2 \rightleftharpoons [ML_1^-\cdots L_2]^* \rightleftharpoons [ML_1\cdots L_2^-]^* \rightleftharpoons [ML_1L_2^-]^* \rightleftharpoons ML_2^- + L_1 \qquad (2)$$

the ligand-switching reactions of $Cr(CO)_5^{•-}$ with a variety of ligands.[7] They noted that direct electron transfer from $Cr(CO)_5^{•-}$ to most of the ligands was endothermic, but formation of an ion-dipole complex in the initial stages of the reaction could energetically facilitate an electron-transfer step to generate $[Cr(CO)_5\cdots L^-]$ as an intermediate. The anionic ligand L^- then binds to the nascent 16-e$^-$ complex, $Cr(CO)_5$. This intermediate then decomposes by loss of carbonyl groups. Their proposal was based on the observation of rapid CO displacement by ligands with high electron affinities and the absence of reaction for ligands with low electron affinities. Both of these studies involved reactions of 17-e$^-$ metal anion complexes. It has been suggested that singlet 16-e$^-$ complexes and 18-e$^-$ systems may not exhibit this type of behavior.

Another type of reaction that has been observed to proceed via electron transfer after formation of an ion-dipole complex is the halogen atom transfer reactions of 17-e$^-$ metal anion complexes.[8] A correlation was observed between the rate of halogen atom transfer, reaction 3, and

$$ML(CO)_x^{•-} + RX \rightleftharpoons XML(CO)_{x-1}^- + R^• \qquad (3)$$

the rate for thermal electron attachment by a series of halomethanes and haloethanes. A harpoon mechanism was proposed in which electron transfer from the metal com-

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plex to the haloalkane resulted in dissociation of the haloalkane anion to form X^- and the alkyl radical. X^- then binds to the metal to generate M^-–X. All of this chemistry occurs within a long-lived ion–molecule complex. McElvaney and Allison have also observed a number of gas-phase reactions of metal anion complexes that implicate intermediate electron-transfer steps.[9]

We report here on the reactions of $V(CO)_5^-$ with a variety of molecules in the gas phase. These reactions include ligand displacement, chlorine atom transfer, and oxidative addition/reductive elimination. The oxidative addition studies are a continuation of our recent work in which $V(CO)_5^-$ is observed to exhibit steric effects in its reactions with small alcohols.[10] In the present study we observe similar effects with amines. The results from the ligand displacement reactions for this 16-e complex suggest an initial electron transfer within the incipient ion-dipole complex that is driven by energy from the electrostatic complexation step. Comparison of the rates for $V(CO)_5^-$/chloromethane reactions with various thermochemical properties indicates breaking of the C–Cl bond is the rate-determining step, suggesting a direct chlorine atom transfer mechanism or oxidative addition of the C–Cl bond to the metal center.

Experimental Section

All experiments were performed on a Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS).[11] The ion cyclotron resonance spectrometer was recently constructed in our laboratory and has previously been described in detail.[10] Briefly, a rectangular trapping cell (1.375 in. × 1.375 in. × 2.75 in. (between trap plates)) is contained in a UHV chamber that is pumped by an Alcatel Crystal 100 UHV diffusion pump. The base pressure in the chamber is $\sim 1 \times 10^{-9}$ Torr. Reagents are admitted into the chamber via Varian variable leak valves. The system is contained in a 0.7-T magnetic field generated by a 10-in. Varian electromagnet. Pressures within the chamber are monitored by a Granville-Phillips 271 ionization gauge. The system is controlled by a Nicolet FTMS 2000 computer.

$V(CO)_5^-$ was generated by dissociative electron capture as in reaction 4.[12] The electron energy was nominally set at 0.1 eV

$$V(CO)_6 + e^- \rightarrow V(CO)_5^- + CO \qquad (4)$$

with a beam duration of 1–2 ms and an electron beam intensity of 1 μA. Trapping voltages were maintained at −1 V throughout the experiment. $V(CO)_6$ was obtained from Alfa products and used as supplied. All other reagents were obtained commercially and used as supplied with the inclusion of multiple freeze–pump–thaw cycles to remove noncondensible gases from liquid samples.

In order to determine accurate rate constants it was necessary to determine the number densities for the neutral reagents in the ICR cell. For these experiments, $V(CO)_6$ was maintained at a nominal pressure of 1×10^{-6} Torr (nitrogen equivalent pressure). The ligand or hydrocarbon pressure was maintained at 2×10^{-6} Torr (nitrogen equivalent pressure). The uncalibrated pressure of any system gas is then the ratio of the nitrogen equivalent gauge reading to the sensitivity factor, r_x, acquired from standard tables.[13] To determine the correct absolute pressure within the ICR cell, the gauge was calibrated by using the well-studied reaction of $O^{\bullet -}$ with N_2O, reaction 5, which has a low-pressure rate constant (previously determined by ICR) of 1.5×10^{-11} cm^3/(molecule s).[14]

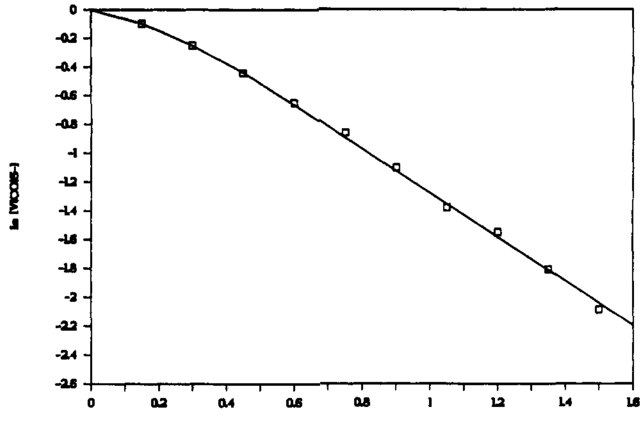

Figure 1. Logarithm of parent ion intensity as a function of time for the reaction of $V(CO)_5^-$ with SO_2.

$$O^{\bullet -} + N_2O \rightarrow NO^- + NO^{\bullet} \qquad (5)$$

Bimolecular rate constants for $V(CO)_5^-$ reactions were obtained from plots of ln [$V(CO)_5^-$ intensity/total ion intensity] vs time using the above gauge corrections. Some of the plots of decay kinetics for the parent showed a slight negative second derivative for the first 1–30 ms of the reaction period. This is due to stray electrons remaining in the trapping cell after the initial electron beam pulse. After this short period, the plots were linear for 3 half-lives of the parent ion intensity. Rate constants were obtained from the linear portions of the kinetic plots. Branching ratios for primary reactions were based on product distributions at early reaction times in order to minimize effects from secondary reactions. Product distributions for secondary reactions were based on the longest reaction times studied.

Results and Discussion

Ligand Displacement. Many recent studies of ligand switching in metal complexes indicate the relative binding energies of the ligands determines the product branching ratios and kinetic behavior. Work by McDonald and Schell[6] and Pan and Ridge,[7] however, suggests that $17\text{-}e^-$ metal complexes must undergo an intermediate electron-transfer step prior to ligand displacement. Presumably, the electron-transfer step creates an empty orbital for coordination by $2\text{-}e^-$ donors. For $17\text{-}e^-$ systems the HOMO is half-filled and cannot accept electron density from $2\text{-}e^-$ donors. For $16\text{-}e^-$ systems, if the ground state is a singlet, the metal complex should readily react with all $2\text{-}e^-$ donors (for which the incoming ligand binding energy is greater than the leaving group) without the need for an intermediate electron-transfer step.

We have reacted $V(CO)_5^-$, which formally has a $16\text{-}e^-$ metal center, with a variety of ligands. Figure 1 shows a plot of the decay of the parent ion as a function of time for the reaction of $V(CO)_5^-$ with SO_2. Table I shows the reaction rates, product branching ratios, efficiencies, and associated electron affinities (EA) for the ligands.[15] H_2O, CH_3CN, and benzene, ligands which have previously been observed to readily displace CO in a variety of gas-phase metal ion complexes, are unreactive with $V(CO)_5^-$. Benzaldehyde and benzophenone are also unreactive, while similar ligands maleic and phthalic anhydride and benzoquinone react efficiently to displace multiple CO ligands.

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(13) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149. The following sensitivity factors were used for compounds not listed in standard tables: $(C_4H_9)_2NO$ = 10.0, maleic anhydride = 5, phthalic anhydride = 6, benzoquinone = 6.5.

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Table I. Summary of Kinetic and Product Data for the Reaction of $V(CO)_5^-$ with Neutral Molecules[15]

neutral	EA, eV	product ion [assumed neutral(s)]	branching fraction	k_{EXP}, cm^3 molecule^{-1} s^{-1}	k_{ADO}, cm^3 molecule^{-1} s^{-1}	reaction efficiency	secondary products
H_2O		no reaction		$<10^{-13}$			
CH_3CN		no reaction		$<10^{-13}$			
$P(CH_3)_3$		no reaction		$<10^{-13}$			
benzene	<0	no reaction		$<10^{-13}$			
benzaldehyde	0.43	no reaction		$<10^{-13}$			
anthracene	0.57	no reaction		$<10^{-13}$			
benzophenone	0.62	no reaction		$<10^{-13}$			
o-nitrotoluene	0.90	no reaction		$<10^{-13}$			
nitrobenzene	1.01	no reaction		$<10^{-13}$			
SO_2	1.1	$V(CO)_4SO_2^-$ [CO]	0.22	9.9 (±2.5) × 10^{-12}	1.4 × 10^{-9}	0.0071	$V(CO)_2(SO_2)_2^-$ (86%)
		$V(CO)_3SO_2^-$ [2CO]	0.68				$V(CO)_3(SO_2)_2^-$ (14%)
		$V(CO)_2SO_2^-$ [3CO]	0.03				
		VSO_2^- [5CO]	0.07				
phthalic anhydride	1.21	$V(CO)_4(PHTH)^-$ [CO]	0.01	1.0 (±0.3) × 10^{-10}	2.9 × 10^{-9}	0.035	$V(CO)(PHTH)_2^-$ (100%)
		$V(CO)_3(PHTH)^-$ [2CO]	0.27				
		$V(CO)_2(PHTH)^-$ [3CO]	0.67				
		$V(CO)(PHTH)^-$ [4CO]	0.05				
maleic anhydride	1.44	$V(CO)_4(MAH)^-$ [CO]	0.01	6.0 (±0.2) × 10^{-10}	2.4 × 10^{-9}	0.25	$V(MAH)_2^-$ (57%)
		$V(CO)_3(MAH)^-$ [2CO]	0.47				$V(CO)(MAH)_2^-$ (43%)
		$V(CO)_2(MAH)^-$ [3CO]	0.49				
		$V(CO)(MAH)^-$ [4CO]	0.03				
p-benzoquinone	1.91	$V(CO)_3(BZQ)^-$ [2CO]	0.97	2.7 (±0.7) × 10^{-10}	9.2 × 10^{-10}	0.29	$V(BZQ)_2^-$ (35%)
		$V(CO)_2(BZQ)^-$ [3CO]	0.03				$V(CO)(BZQ)_2^-$ (65%)
NO	0.02	$V(CO)_4NO^-$ [CO]	0.03	5.4 (±1.4) × 10^{-11}	3.5 × 10^{-10}	0.16	$V(CO)(NO)_2^-$ (60%)
		$V(CO)_3NO^-$ [2CO]	0.86				$V(CO)_2(NO)_2^-$ (40%)
		$V(CO)_2NO^-$ [3CO]	0.11				
$(t\text{-}C_4H_9)_2NO$	~0.5	$V(CO)_3NO(C_4H_9)_2^-$ [2CO]	0.30	5.5 (±2.2) × 10^{-12}	2.4 × 10^{-9}	0.0023	
		$V(CO)_4NO(C_4H_9)^-$ [CO, C_4H_9]	0.01				
		$V(CO)_4NO^-$ [CO, $2C_4H_9$]	0.56				
		$V(CO)_3NO(C_4H_9)^-$ [2CO, C_4H_9]	0.13				

Additionally, $P(CH_3)_3$, which can act as a π-acceptor, does not displace CO, while SO_2, which also acts as a π-acceptor, displaces multiple CO ligands. It is expected that the $(CO)_4V^-$–CO bond will be relatively weak and that many of the unreactive ligands listed in Table I should have a stronger binding energy to V^- than CO, with the lack of reactivity due to mechanistic factors.

The reactivity results shown in Table I reveal a correlation between reaction efficiency and ligand EA, with the exception of NO• and di-*tert*-butyl nitroxide, which will be discussed later. This correlation suggests electron transfer is involved for these ligand displacement reactions. If electron transfer is playing an important role in these ligand displacement reactions, it may indicate that the ground state of $V(CO)_5^-$ is not a singlet.

Figure 2 shows approximate energy level diagrams for the two structures of $V(CO)_5^-$ that are most reasonable, trigonal bipyramidal (TBP) and square pyramidal (SPY). On the basis of the ligand field splitting in $Cr(CO)_6$ and $V(CO)_6$, CO is expected to be a strong field ligand. For the case of TBP it is expected that there will be two unpaired electrons; one in $d_{x^2-y^2}$ and one in d_{xy}. For the SPY structure a singlet would be expected. It is possible, but unlikely, that the axial V–CO bond is sufficiently elongated to reduce the energy of the d_{z^2} orbital such that the triplet configuration is lowest in energy. Initial matrix isolation EPR studies by Kundig and Ozin suggested 16-e$^-$ pentacarbonyl complexes have a TBP structure.[16] Additional matrix isolation EPR and infrared spectroscopic studies of $V(CO)_5$ indicate it has a slightly distorted trigonal-bipyramidal structure.[17,18] Gas-phase studies of $V(CO)_5$ generated by photolysis of $V(CO)_6$ are not conclusive as to structure.[19] Theoretical results are not in agreement as to the structure of $V(CO)_5$, with distorted TBP and SPY structures both proposed. However, theoretical results indicate both are low-lying structures.[20] The experimental results generally suggest $V(CO)_5$ has a D_{3h} structure or is

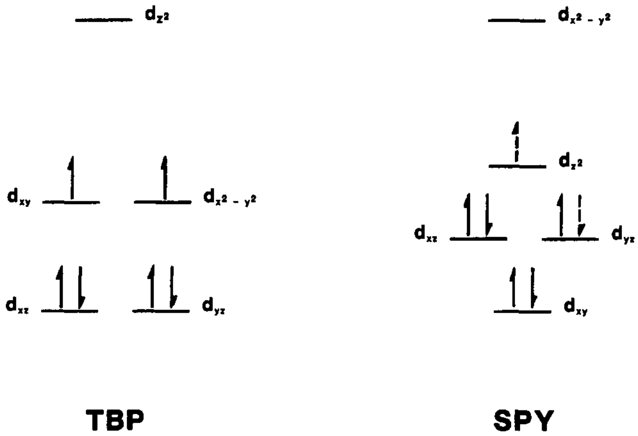

Figure 2. Orbital diagrams for two possible structures of $V(CO)_5^-$, trigonal bipyramidal (TBP) and square pyramidal (SPY). The dotted arrow for the SPY structure indicates possible locations for the electron.

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(21) No literature values are available for the electron affinity of (*tert*-butyl)$_2$NO. However, a value for the ethyl analogue, EA($(C_2H_5)_2NO$) = 0.54 ± 0.2 eV has been obtained: Bartmess, J. E.; Basso, T.; Georgiadis, R. M. *J. Phys. Chem.* **1983**, *87*, 912. The *tert*-butyl compound should have an electron affinity slightly larger than the ethyl compound, but it will clearly be significantly less than 1.0 eV.

slightly distorted toward C_{2v}.[16-19] A TBP structure for $V(CO)_5^-$ would indicate the ground state is a triplet.

For the TBP structure the relevant acceptor orbital for a ligand displacement reaction will be either the d_{xy} or the $d_{x^2-y^2}$, as binding to these orbitals will result in an octahedral complex. The diagrams in Figure 2 indicate both of these orbitals are half-filled and cannot accept electron density from a 2-e donor. For the SPY structure an incoming ligand will bind along the z axis. The appropriate orbital for metal–ligand bond formation, d_{z^2}, may be low in energy and singly occupied or high in energy and unoccupied (singlet configuration), depending on the splitting of the d_{xz} and d_{z^2} orbitals. Neither the singlet or the triplet configurations of the SPY structure can directly bind to a $2\text{-}e^-$ donor. An electron transfer from a singlet configuration would result in a half-filled orbital that still could not bind a $2\text{-}e^-$ donor. Thus, the above data, along with the reactions of NO and $(t\text{-}C_4H_9)_2NO$, suggest $V(CO)_5^-$ is a triplet. The reaction rates in Table I are consistent with an intermediate electron-transfer step from the metal complex to the ligand. For a singly occupied acceptor orbital, electron transfer results in a vacant orbital for bonding with a $2\text{-}e^-$ donor ligand. Thus, the results indicate $V(CO)_5^-$ is a triplet with the possibility of a TBP structure or an SPY structure with the d_{z^2} and d_{xz} orbitals lying close in energy.

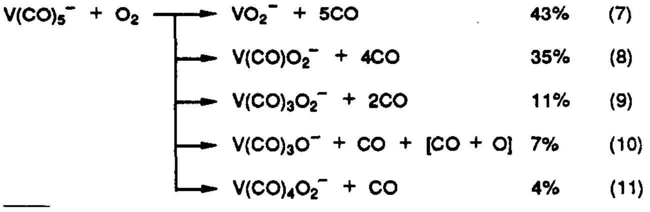
Two exceptions to the correlation of reaction efficiency with ligand electron affinity are $NO^\bullet$ and $(t\text{-}C_4H_9)_2NO^\bullet$, which have low EA's but react to displace CO. Since both of these molecules are radicals they can function as 1- or $3\text{-}e^-$ donors. Thus, they can directly bond to a half-filled orbital without an electron-transfer step by acting as a $1\text{-}e^-$ donor. The reaction with $(t\text{-}C_4H_9)_2NO^\bullet$ also results in a loss of *tert*-butyl groups from the ligand. The loss of *tert*-butyl groups presumably occurs by activation of a C–N bond by the unsaturated metal center after displacement of CO. $NO^\bullet$ displaces CO from $V(CO)_5^-$ with much higher efficiency than $(t\text{-}C_4H_9)NO^\bullet$. This is due to a steric effect introduced by the bulky *tert*-butyl groups which significantly reduces the ability of the ligand to enter the coordination sphere.

Interestingly, $Cr(CO)_5^{\bullet-}$, which is a doublet, also reacts readily with $NO^\bullet$ to displace a carbonyl group, reaction 6.

$$Cr(CO)_5^{\bullet-} + NO^\bullet \rightarrow Cr(CO)_4NO^- + CO \qquad (6)$$

This was initially observed by McDonald and co-workers in the high-pressure flowing afterglow reactor. We have also observed this reaction to be facile at low pressures in the FT-ICR spectrometer. This is the only direct ligand displacement reaction that has been observed for $Cr(CO)_5^{\bullet-}$ and a ligand with low electron affinity.

One other reaction recently reported which has a bearing on the present results is the oxidation of $V(CO)_5^-$ by O_2, reactions 7–11. Triplet O_2 has been observed by Squires and co-workers to react with a variety of $17\text{-}e^-$ metal complexes.[22] The reaction is proposed to proceed via a homolytic bond formation process coupling the two radicals. However, for $V(CO)_5^-$ the mechanism was not previously clear. The reaction could proceed via a radical coupling mechanism, or if $V(CO)_5^-$ is a singlet, an initial π-coordination by O_2. The present results suggest a radical mechanism may also be involved in reactions 7–11.



$$V(CO)_5^- + O_2 \rightarrow VO_2^- + 5CO \qquad 43\% \qquad (7)$$
$$\rightarrow V(CO)O_2^- + 4CO \qquad 35\% \qquad (8)$$
$$\rightarrow V(CO)_3O_2^- + 2CO \qquad 11\% \qquad (9)$$
$$\rightarrow V(CO)_3O^- + CO + [CO + O] \qquad 7\% \qquad (10)$$
$$\rightarrow V(CO)_4O_2^- + CO \qquad 4\% \qquad (11)$$

The overall mechanism for ligand displacement in $V(CO)_5^-$ is shown in reaction 12, based on the initial mechanism suggested by Pan and Ridge.[7] Initially, the formation of an ion-dipole complex supplies ~15 kcal/mol for the intermediate to use in overcoming the energetic barrier to a $1\text{-}e^-$ transfer from the metal complex to the ligand. After electron transfer, the empty orbital on the metal center can accept $2\text{-}e^-$ donation from the negatively charged ligand. The formation of a strong metal–ligand bond results in subsequent decomposition of the metal complex via loss of carbonyl groups.

$$V(CO)_5^- + L \rightleftharpoons [V(CO)_5^-\cdots L]^* \rightleftharpoons [V(CO)_5\cdots L^-]^* \rightleftharpoons [LV(CO)_5^-]^* \rightleftharpoons LV(CO)_{5-x}^- + xCO \qquad (12)$$

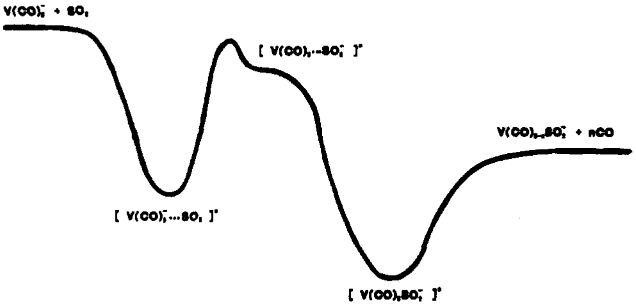


Figure 3. Reaction coordinate showing relative potential energy as a function of extent of reaction for $V(CO)_5^-$ with SO_2.

Figure III illustrates system potential energy as a function of extent of reaction for the displacement of CO from $V(CO)_5^-$ by SO_2.[23] The intermediate barrier in the reaction arises due to the electron transfer from $V(CO)_5^-$ to the ligand. This electron-transfer step requires energy due to two factors, including the lower electron affinity of the ligand relative to $V(CO)_5$ and any associated geometry change during the electron-transfer process.[24] As the ligand electron affinity decreases, the intermediate barrier height increases. From the data in Table I it is clear that the reaction efficiency (K_{exp}/K_{coll}) for ligand displacement increases as the electron affinity of the ligand increases above 1.1 eV. Each of the observed reactions is highly exothermic, as exemplified by the extensive loss of carbonyls for all reactive ligands. All reactive ligands studied displace at least three carbonyl groups, indicating the ligand-switching process is highly exothermic for all reactive ligands. However, the reaction rates are relatively slow, and SO_2 displaces CO with very low efficiency. The

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[23] An ion-dipole complexation energy was calculated for the $V(CO)_5^-/SO_2$ complex by using the equation

$$V(r) = -\alpha e^2/2r^4 - e\mu_D/r^2$$

with $\alpha = 5.12$ Å^3, $\mu = 1.63$ D, and r estimated at 3.25 Å. This results in a complexation energy of ~13 kcal/mol. The intermediate barrier height is estimated as $EA(V(CO)_5) - EA(SO_2)$. Since SO_2 is the two-electron donor with the lowest electron affinity that is observed to react, the sum of the ion-dipole complexation energy and $EA(SO_2)$ gives a lower limit for $EA(V(CO)_5)$ of 1.6 eV.

[24] The barrier to electron transfer within the ion-dipole complex can be related to the inner-sphere reorganization energy term in Marcus electron-transfer theory; see: Richardson, D. E. *J. Phys. Chem.* **1986**, *90*, 3697.

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Table II. Summary of Kinetic and Product Data for the Reaction of $V(CO)_5^-$ with Alkyl Chlorides[15]

R–Cl	$D°$[R–Cl], kcal mol^{-1}	k_{TEA}, cm^3 molecule^{-1} s^{-1}	product ion [assumed neutral(s)]	branching fraction	k_{EXP}, cm^3 molecule^{-1} s^{-1}	k_{ADO}, cm^3 molecule^{-1} s^{-1}	reaction efficiency	secondary products
CCl_4	70.3	3.9×10^{-7}	$V(CO)_5Cl^-$ [$^\bullet CCl_3$]	0.01	$2.4\ (\pm 0.6) \times 10^{-10}$	8.2×10^{-10}	0.30	$V(CO)_3Cl_2^-$ (100%)
			$V(CO)_4Cl^-$ [CO, $^\bullet CCl_3$]	0.63				
			$V(CO)_3Cl^-$ [2CO, $^\bullet CCl_3$]	0.36				
$CHCl_3$	79.2	4.4×10^{-9}	$V(CO)_5Cl^-$ [$^\bullet CHCl_2$]	0.07	$2.6\ (\pm 0.7) \times 10^{-10}$	1.0×10^{-9}	0.26	$V(CO)_3Cl_2^-$ (100%)
			$V(CO)_4Cl^-$ [CO, $^\bullet CHCl_2$]	0.77				
			$V(CO)_3HCl^-$ [2CO, CCl_2]	0.05				
			$V(CO)_3Cl^-$ [2CO, $^\bullet CHCl_2$]	0.11				
CH_2Cl_2	82.8	4.8×10^{-12}	$V(CO)_5Cl^-$ [$^\bullet CH_2Cl$]	0.26	$4.9\ (\pm 2.0) \times 10^{-11}$	1.3×10^{-9}	0.0038	
			$V(CO)_4Cl^-$ [CO, $^\bullet CH_2Cl$]	0.07				
			$V(CO)_3HCl^-$ [2CO, CHCl]	0.54				
			$V(CO)_3Cl^-$ [2CO, $^\bullet CH_2Cl$]	0.13				
CH_3Cl	83.6	$<2 \times 10^{-15}$	$V(CO)_4Cl^-$ [CO, $^\bullet CH_3$]	0.10	$8.9\ (\pm 2.2) \times 10^{-13}$	1.6×10^{-9}	0.0005	
			$V(CO)_3HCl^-$ [2CO, CH_2]	0.75				
			$V(CO)_3Cl^-$ [2CO, $^\bullet CH_3$]	0.15				
CF_3Cl	86.2	1.8×10^{-13}	no reaction		$<10^{-13}$			

high exothermicity coupled with observation of low reaction efficiency is consistent with an intermediate bottleneck to reaction.

Though $Cr(CO)_5^-$ does not undergo secondary reaction with NO and most of the other reports on ligand displacements with 17-e$^-$ metal complexes that implicate electron transfer as an intermediate step do not indicate the presence of secondary reactions, $V(CO)_5^-$ is observed to undergo secondary reactions with all of the ligands that have a primary displacement pathway. Additionally, there are no tertiary or higher order reactions observed. The secondary reactions do not appear to be limited due to steric effects since $V(CO)_5^-$ reacts with NO and SO_2 only twice. The secondary reactions of $V(CO)_5^-$ may be due to its second unpaired electron. This reaction would require the same intermediate electron-transfer step that is operative in the primary reactions. For the larger ligands, maleic anhydride, phthalic anhydride, and *p*-benzoquinone, and final products are, most likely, sandwich complexes or sandwich compounds with one carbonyl group on the metal center.

Chlorine Atom Transfer. Table II shows the reaction rates, reaction efficiencies, branching ratios, and associated thermochemical data for the reaction of $V(CO)_5^-$ with the chlorine substituted methanes. The chloromethanes react via pathways 13–16.

$$V(CO)_5^- + CH_xCl_{4-x} \longrightarrow V(CO)_5Cl^- + CH_xCl_{3-x} \quad (13)$$

$$\longrightarrow V(CO)_4Cl^- + CO + CH_xCl_{3-x} \quad (14)$$

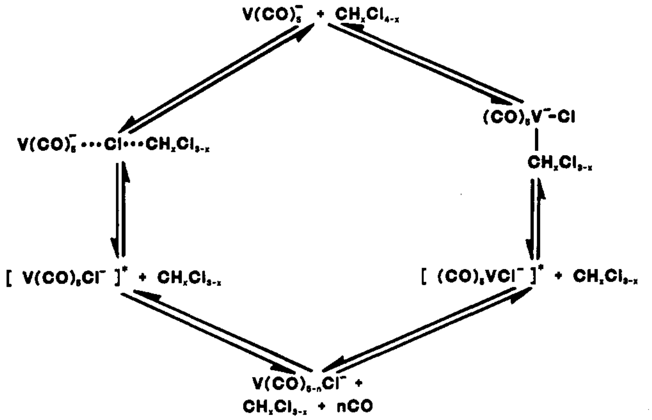
$$\longrightarrow V(CO)_3Cl^- + 2CO + CH_xCl_{3-x} \quad (15)$$

$$\longrightarrow V(CO)_3HCl^- + 2CO + CH_{x-1}Cl_{3-x} \quad (16)$$

In a study of the reactions of 11 17-e$^-$ anionic metal complexes with 14 C_1 and C_2 halogen-substituted compounds, McDonald and co-workers noted a correlation between the rate of thermal electron attachment and the rate for the halogen atom transfer reaction.[8] They attributed this to the presence of an initial electron-transfer step for the halogen atom transfer process. Addition of the halocarbon with loss of the carbonyl was observed in only two cases ($Fe(CO)_4^{\bullet -}$ with CF_3X (Br and I) accounting for 27% and 12% of the products, respectively). Another salient feature of their results was that none of the 17-e$^-$ metal ion complexes were observed to react with CH_3Cl and only $Re(CO)_3(C_3H_5)^-$ was observed to react with CH_2Cl_2.

For the present reactions shown in Table II it is clear there is not a correlation between the rate for thermal electron attachment and the rate of $V(CO)_5^-$ reaction. Additionally, there is no correlation between the reaction rate and the electron affinity of the corresponding chloromethane. CH_3Cl, which has not previously been observed to attach electrons at thermal energies, reacts via Cl$^\bullet$ transfer and HCl transfer. CF_3Cl, which attaches thermal energy electrons at a rate comparable to that of CH_2Cl_2, is unreactive with $V(CO)_5^-$. The data in Table II, however, reveal a correlation between the C–Cl bond dissociation energy and the rate of reaction. This may suggest a direct chlorine atom transfer mechanism, as in Scheme I, is occurring. The data are also consistent with initial insertion of V into the C–Cl bond.

Scheme I



McElvaney and Allison have studied the reactions of $Fe(CO)_{3,4}^-$, $Cr(CO)_{3-5}^-$, $Co(CO)_{2,3}^-$, and $CoNO(CO)_{1,2}^-$ with the C_1 to C_6 chloroalkanes and observed a variety of products corresponding to Cl atom transfer, addition of the chloroalkane with loss of carbonyls, and addition of HCl with loss of carbonyls.[26] Many of these reactions were proposed to involve intermediate electron-transfer steps. Other reactions were suggested to proceed via initial insertion into the C–Cl bond. For $V(CO)_5^-$, reactions with CH_3Cl and CH_2Cl_2 result in significant amounts of HCl addition to $V(CO)_5^-$, consistent with an initial oxidative addition of the C–Cl bond to the metal center followed by an α-hydrogen migration.

An unusual aspect of the chlorine-transfer reactions is that though the rate constants decrease from CCl_4 to CH_3Cl by more than 2 orders of magnitude, the number

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(26) McElvaney, S. W.; Allison, J. *Organometallics* **1986**, *5*, 416.

(27) (a) Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 3. (b) Polarizabilities used to calculate collision frequencies and ion-dipole complexation energies were calculated by using the method found in: Miller, K. A.; Savchick, K. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206.

of carbonyls lost in the final products remains similar. Though the reaction of CH_3Cl is highly exothermic, as exemplified by the loss of two carbonyl ligands in the product, the efficiency is quite low. This suggests the reaction has an activation barrier. The obvious correlation between the reaction efficiency and the bond dissociation energy for the corresponding chloroalkane indicates that C–Cl bond cleavage is associated with the height of this activation barrier.

The four reactive chlorocarbons generate a secondary product corresponding to $V(CO)_3Cl_2^-$, which grows into the mass spectrum slowly at long reaction times. No other higher order reaction products were observed up to reaction times of ~200 ms with halocarbon pressures of 1×10^{-6} Torr (corrected pressure).

Oxidative Addition. Oxidative addition reactions of many gas-phase metal ions and metal ion complexes have been observed to be quite facile.[28-31] The broad spectrum of oxidative addition/reductive elimination reactions that have been reported has in large part been due to the ease of generation of highly unsaturated transition-metal systems in the gas phase. These highly unsaturated systems can efficiently precoordinate reactant molecules prior to dehydrogenation and dealkylation reactions. The requirement for a 16-e⁻ (or fewer) metal center has directed most of the gas-phase metal chemistry toward these highly unsaturated systems. We recently reported the reactions of $V(CO)_5^-$ with small alcohols.[10] Though $V(CO)_5^-$ has a 16-e⁻ metal center, the large number of carbonyls groups modify its chemistry relative to that observed for highly unsaturated metal complexes. Reaction 17 is observed

$$V(CO)_5^- + CH_3OH \rightarrow V(CO)_4CH_2O^- + CO + H_2 \quad (17)$$

with methanol, while larger alcohols are not observed to react with $V(CO)_5^-$. Labeling studies indicate a 1,2-dehydrogenation mechanism with retention of the incoming C–O in the final product. The lack of reactivity with larger alcohols was attributed to steric as opposed to energetic constraints, as dehydrogenation of methanol requires more energy than dehydrogenation of the larger alcohols.

We have studied the reactions of $V(CO)_5^-$ with small amines in order to test the proposal of the steric effect in the reaction intermediate. As expected, $V(CO)_5^-$ reacts with CH_3NH_2 via dehydrogenation with loss of a carbonyl group, reaction 18. Other amines, including dimethylamine, ethylamine, and diethylamine are unreactive with $V(CO)_5^-$. The dehydrogenation of methylamine to methylimine requires 37.5 kcal/mol whereas 1,2-dehydrogenation of ethylamine requires only 13 kcal/mol, dehydrogenation of the N–C bond in dimethylamine requires 21 kcal/mol, and dehydrogenation of the N–C bond in diethylamine requires 21 kcal/mol.[15] Thus, the reactivity trend for the amines is not likely due to differences in reaction exothermicity. This further supports the proposal of a steric effect in the reaction intermediate initially suggested for the case of the alcohols. A rate constant could not be obtained for reaction 18 because the decay of the reactant ion signal was nonlinear and the parent signal never decreased below ~85% of the total ion current, which is similar to the result observed in the reaction with CH_3OH. The initial oxidative addition of CH_3NH_2 or CH_3OH to $V(CO)_5^-$ results in the formation of a heptavalent complex. An observed positive second derivative in the decay kinetics for reactions 17 and 18 may be due to a barrier along the reaction coordinate that is associated with formation of a heptavalent complex.

$$V(CO)_5^- + CH_3NH_2 \rightarrow V(CO)_4CH_2NH^- + (H_2, CO) \quad (18)$$

Conclusion

Three general mechanisms have been observed for the gas-phase reactions of $V(CO)_5^-$. Correlations of bimolecular rate constants with thermochemical properties of many of the neutrals studied indicates that electron transfer may be occurring within the initially formed ion-dipole complex. Electron transfer facilitates ligand switching due to the triplet ground state of $V(CO)_5^-$ where the acceptor orbital is half-occupied. After electron transfer a 2-e⁻ donation into the previously half-filled orbital occurs. Though NO and $(t\text{-}C_4H_9)_2NO$ have low EA's, they react to displace multiple CO ligands. Both of these molecules are radicals and can act as 1-e⁻ donors, which eliminates the requirement for electron transfer prior to metal–ligand bond formation. Reaction rates for chlorine atom transfer reactions do not correlate with the rate for thermal electron attachment by the associated chloromethane, suggesting electron transfer is not involved in the chlorine-transfer mechanism. However, the rates do show a rough correlation with the C–Cl bond dissociation energy, supporting a direct chlorine atom transfer mechanism or an initial C–Cl bond insertion mechanism. Finally, $V(CO)_5^-$ is observed to dehydrogenate methylamine to form $V(CO)_4CH_2NH^-$. $V(CO)_5^-$ is unreactive with larger amines.

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