

Thermochemistry and Photodissociation Studies of $[\text{CoL}]^+$ and $[\text{CoL}_2]^+$, L = Pyrrole, Furan, Thiophene and Selenophene

Vajira K. Nanayakkara and Ben S. Freiser*

H. C. Brown Laboratory of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

$[\text{CoL}]^+$ and $[\text{CoL}_2]^+$ (L = pyrrole, furan, thiophene and selenophene) were generated in a prototype Nicolet-FTMS 1000 Fourier transform mass spectrometer, where they were irradiated with light from a 2.5 kW Xe arc lamp. Photodissociation thresholds, obtained using energy cut-off filters, yielded the bond energies $D^0(\text{Co}^+ - \text{pyrrole}) = 59 \pm 3 \text{ kcal mol}^{-1}$, $D^0(\text{Co}^+ - \text{furan}) = 57 \pm 3 \text{ kcal mol}^{-1}$, $D^0(\text{Co}^+ - \text{thiophene}) = 61 \pm 3 \text{ kcal mol}^{-1}$ and $D^0(\text{Co}^+ - \text{selenophene}) = 64 \pm 3 \text{ kcal mol}^{-1}$ (1 kcal = 4.184 kJ), as well as $D^0([\text{Co}(\text{pyrrole})]^+ - \text{pyrrole}) \leq 48 \pm 3 \text{ kcal mol}^{-1}$, $D^0([\text{Co}(\text{furan})]^+ - \text{furan}) \leq 46 \pm 3 \text{ kcal mol}^{-1}$, $D^0([\text{Co}(\text{thiophene})]^+ - \text{thiophene}) \leq 49 \pm 3 \text{ kcal mol}^{-1}$ and $D^0([\text{Co}(\text{selenophene})]^+ - \text{selenophene}) \leq 51 \pm 3 \text{ kcal mol}^{-1}$. The photoappearance threshold for $[\text{CoC}_3\text{H}_4]^+$, the CO loss product ion from $[\text{Co}(\text{furan})]^+$, yielded $D^0(\text{Co}^+ - \text{C}_3\text{H}_4) = \text{either } 33 \pm 6 \text{ or } 32 \pm 6 \text{ kcal mol}^{-1}$, depending on whether C_3H_4 was allene or propyne, respectively. Where possible, these bond energy measurements were further corroborated by ligand displacement reactions and competitive collision-induced dissociation experiments.

J. Mass Spectrom. 32, 475–482 (1997)

No. of Figures: 8 No. of Tables: 1 No. of References: 30

KEYWORDS: Fourier transform mass spectrometry; photodissociation; transition metal ions; bond energies; aromatic heterocycles

INTRODUCTION

In recent decades there has been growing interest in the chemistry of heterocycles coordinated to transition metal ion centers such as Ru(I), Os(II) and Mn(I).¹ Among these heterocyclic ligands, pyridine has been the most extensively studied in condensed media.² Pyridine, like benzene, has a high tendency to form stable complexes owing to its good π -donor properties.³ Although the five-membered heterocyclic ligands are poorer π -electron donors than benzene and pyridine, many examples can be found in the literature of such complexes in the condensed phase,² with some examples reported from gas-phase studies.⁴ Among the five-membered heterocycles, pyrroles, furans, thiophenes and selenophenes represent important classes of compounds. The pyrrole ring system, for example, is widely distributed in nature and found as subunits of heme, chlorophylls, vitamin B₁₂, bile pigments, porphyrins, antibiotics and various polymeric systems.^{1c,5}

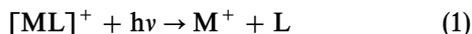
Thiophenes, thiols and cyclic sulfides present in fossil fuels are mainly responsible for the poisoning of heterogeneous catalysts during the hydrogenation process utilized by the petroleum industry.⁶ In crude oil refining, metal ion-promoted degradation of thiophenes is a major process in the removal of organosulfur impurities present in fossil fuels.⁷ Owing to the importance of aromatic heterocycles, especially pyrrole and thiophene, in industrial applications, as well as in the biomedical sci-

ences, extensive studies on the reactivity and binding properties of these heterocycles with different metal centers have been carried out in the condensed phase by several research groups.^{1b,8} Recently, Bakhtiar and Jacobson studied the gas-phase reactions of Fe^+ and $[\text{FeL}]^+$ [(L = O, C_4H_6 , *c*- C_5H_6 , *c*- C_5H_5 , C_6H_6 , $\text{C}_5\text{H}_4(=\text{CH}_2)$] with furan, thiophene and pyrrole.⁴ As part of their study, bond energies were measured including $D^0(\text{Fe}^+ - \text{pyrrole}) \approx D^0(\text{Fe}^+ - \text{thiophene}) \approx D^0(\text{Fe}^+ - \text{C}_4\text{H}_6) \approx 48 \pm 5 \text{ kcal mol}^{-1}$ and $D^0(\text{Fe}^+ - \text{furan}) > 39.9 \pm 1.4 \text{ kcal mol}^{-1}$ (1 kcal = 4.184 kJ). In this work, we examined the binding properties of $[\text{CoL}]^+$ and $[\text{CoL}_2]^+$ (where L = pyrrole, furan, thiophene and selenophene) in the gas phase.

Absolute bond energy measurements are of primary importance in understanding the thermodynamic and mechanistic aspects of various processes which may occur during a reaction. Appearance potential measurements,⁹ thresholds for endothermic ion-molecule reactions,¹⁰ competitive collision-induced dissociation (CID),¹¹ kinetic energy release distribution measurements¹² and photodissociation threshold experiments¹³ are some of the gas-phase techniques that have been widely used for the determination of metal-ligand bond energies. Of these techniques, determining the thresholds of endothermic reactions by using guided ion beams, pioneered by Beauchamp, Armentrout and their co-workers, has been found to be the most useful to date, providing a large number of high-quality absolute bond energy values.¹⁴ Additionally, in the past decade,

theoretical calculations have come a long way towards providing accurate bond energies, as well as detailed descriptions of the bonding.¹⁵

In our laboratory, photodissociation has been found to be an effective tool for obtaining absolute bond energies in metal ion–ligand complexes.¹⁶ Photodissociation thresholds are measured by monitoring the appearance of M^+ in reaction (1) as a function of wavelength.



If the binding energies are in a region where there is a high density of low-lying excited states, then the ions absorb photons at this energy and dissociate to yield the metal ion.^{13,16} In such a situation, the photodissociation threshold provides a good estimate of the absolute thermodynamic bond energy. In contrast, if the low-lying excited states lie in a range above the binding energy, the photodissociation threshold measured is spectroscopic and yields only an upper limit of the bond energy. The only way to know whether a photodissociation threshold is spectroscopic or thermodynamic is to compare the value to the bond energy obtained by at least one other method. In this work, ion–molecule reaction and CID bracketing experiments were used, when possible, to provide corroborating information.

It should also be mentioned that contributions from sequential multiphoton absorption processes¹⁷ may yield erroneously low bond energy values. Based on the generally good agreement of the photodissociation values with those obtained from the bracketing experiments, however, we do not feel that multiphoton dissociation occurs in these experiments to any significant extent.

EXPERIMENTAL

The instrument used in this work was a Nicolet (now Finnigan FT/MS, Madison, WI, USA) prototype FTMS-1000 Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, equipped with a 5.2 cm cubic cell which is placed in between the poles of a Walker 15 in electromagnet maintained at ~ 0.9 T. The principles, theory and performance of FTICR mass spectrometers have been described previously.¹⁸ The two transmitter plates in our instrument are composed of 80% transmittance stainless-steel screens which allow the ions in the cell to be irradiated with light from various sources. Co^+ was generated by focusing the fundamental line ($1.06 \mu m$) of a Quanta Ray Nd:YAG laser on to a high-purity cobalt target which was mounted on one of the transmitter plates.¹⁹ Prior to reaction with the reagent, the Co^+ ions generated were thermalized by collisions with argon for 1–2 s. The argon was introduced into the cell through a leak valve at a background pressure of 3.5×10^{-5} Torr (1 Torr = 133.3 Pa), as measured by an uncalibrated Bayard–Alpert ionization gauge. The $[CoL]^+$ and $[CoL_2]^+$ were also cooled by collisions with argon and the reagent gas during the 5 s irradiation time. All of the

reagents were introduced into the cell through a General Valve Series 9 pulsed solenoid valve.²⁰ The pulsed reagent gas filled the vacuum chamber to a maximum pressure of about 4×10^{-5} Torr with about a 150 ms rise time and was pumped away by a high-speed 6-in diffusion pump in about 300 ms. The $[CoL]^+$ (L = pyrrole, furan, thiophene and selenophene) complex thus formed was then isolated by a swept double-resonance pulse.²¹ In order to make the $[CoL_2]^+$ complex, the pulsed valve opening time was increased from 2 to 20 ms, yielding a maximum chamber pressure of $\sim 8 \times 10^{-5}$ Torr.

An Osram Sylvania XBO model 2.5 kW Xe arc lamp was used in conjunction with different energy cut-off filters to determine thresholds.²² A Spectra-Physics Model 2030-18 argon ion laser was also used in one case for determining $D^0(Co^+ - pyrrole)$, as a further check of the arc lamp results. This ion was chosen since its threshold fell conveniently in the wavelength region of the laser. The beam was focused into the cell through a sapphire window with three optical mirrors. The ions were irradiated for 5 s in all of the experiments and the photoproduct peak intensities were blank subtracted, normalized and plotted against the cut-off energies to determine the thresholds. With the argon ion laser, individual lines in the wavelength range 458–529 nm were selected and operated at 1 W maximum output power, as measured using a Spectra-Physics Model 2030-18 power meter. All chemicals were obtained from commercial sources and used without further purification except for multiple freeze-pump–thaw cycles to remove non-condensable gases.

RESULTS AND DISCUSSION

$[Co(pyrrole)_x]^+$ ($x = 1, 2$)

Photodissociation of $[Co(pyrrole)]^+$ proceeds exclusively by reaction (1) to generate Co^+ . The photoappearance spectrum for Co^+ was obtained by irradiating $[Co(pyrrole)]^+$ with light from the arc lamp. A sharp increase in metal ion abundance was observed in the region from 57–60 kcal mol⁻¹ [Fig. 1(a)]. Photodissociation of $[Co(pyrrole)]^+$ with the individual lines of the argon ion laser is shown in Fig. 1(b) for comparison. The Co^+ abundance remains zero or near zero at 502 nm and, thereafter, a sharp increase in metal ion abundance is observed using the shorter wavelength lines, from which $D^0(Co^+ - pyrrole) = 59 \pm 3$ kcal mol⁻¹ is assigned. Hence there is excellent agreement between the arc lamp and laser results. In addition, the photodissociation results are further corroborated by using ligand displacement reactions and competitive CID experiments, as discussed below.

$[Co(pyrrole)]^+$ reacts readily with benzene by ligand displacement to form $[Co(benzene)]^+$. The reverse reaction of $[Co(benzene)]^+$ with pyrrole, however, yields only the condensation product,

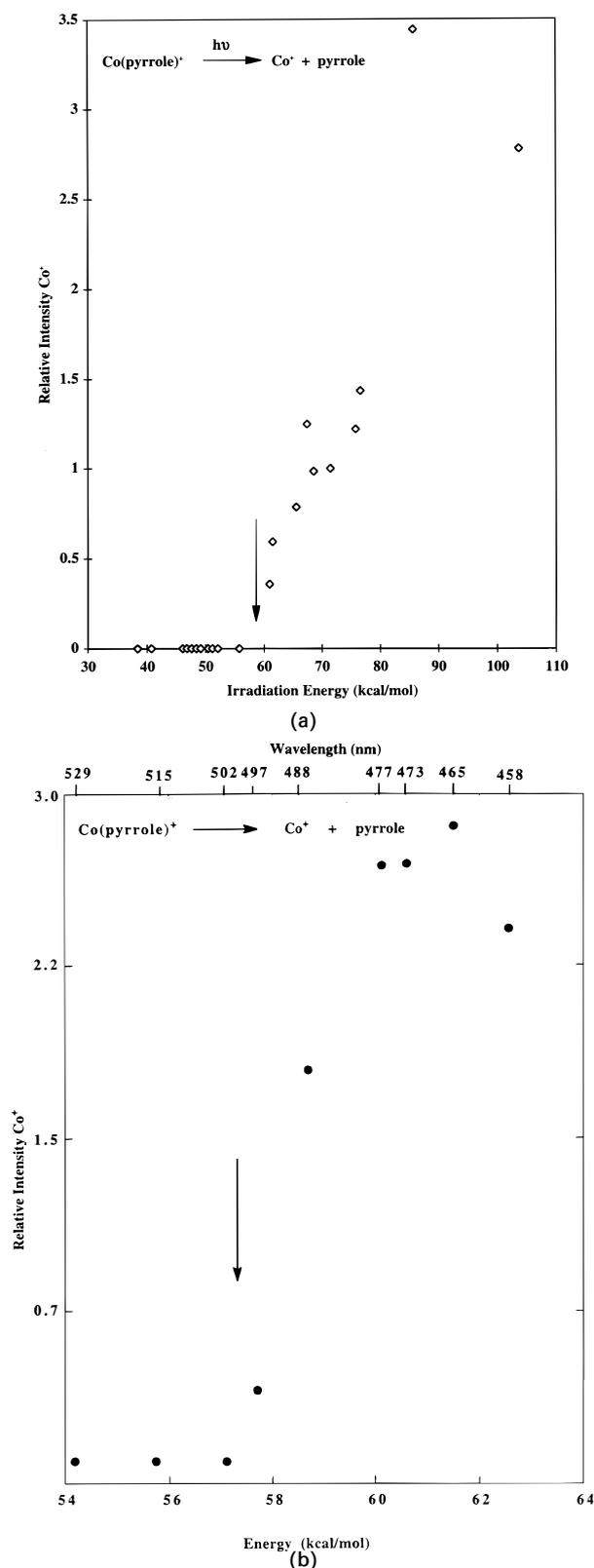


Figure 1. Photoappearance spectrum of Co^+ from photodissociation of $[\text{Co}(\text{pyrrole})]^+$ using (a) the arc lamp and cut-off filters and (b) individual lines of the argon ion laser. The data are normalized per photon at each wavelength.

$[\text{Co}(\text{benzene})(\text{pyrrole})]^+$. Collision-induced dissociation of the condensation product yields $[\text{Co}(\text{benzene})]^+$, exclusively, by loss of pyrrole over the entire energy range studied. These results indicate

that $D^0(\text{Co}^+ - \text{pyrrole}) < D^0(\text{Co}^+ - \text{benzene}) = 61.1 \pm 2.5 \text{ kcal mol}^{-1}$.²³ A lower limit for $D^0(\text{Co}^+ - \text{pyrrole})$ is obtained from the reaction of CoNH_3^+ with pyrrole. CoNH_3^+ , generated from the reaction of Co^+ with pulsed-in NH_3 , reacts readily with pyrrole to yield mainly the ligand displacement product, $[\text{Co}(\text{pyrrole})]^+$, and some of the condensation product. Further, the reverse reaction of $[\text{Co}(\text{pyrrole})]^+$ with NH_3 yields some ligand displacement, but condensation is the major reaction channel observed. Collision-induced dissociation of $[\text{Co}(\text{NH}_3)(\text{pyrrole})]^+$ at low laboratory kinetic energies ($< 26 \text{ eV}$), yields only NH_3 loss. As the laboratory kinetic energy is increased, loss of pyrrole is also observed (Fig. 2). These results indicate that $D^0(\text{Co}^+ - \text{pyrrole}) \geq D^0(\text{Co}^+ - \text{NH}_3) = 58.8 \text{ kcal mol}^{-1}$.²⁴ All of the above results are consistent with the photodissociation threshold value for $D^0(\text{Co}^+ - \text{pyrrole}) = 59 \pm 3 \text{ kcal mol}^{-1}$.

At longer pulsed-valve opening time (30 ms), the secondary product ion $[\text{Co}(\text{pyrrole})_2]^+$ is observed. $[\text{Co}(\text{pyrrole})_2]^+$ was isolated, using frequency sweep double-resonance techniques,²¹ and irradiated with the light from the arc lamp at different energy cut-offs. The sole photoproduct, $[\text{Co}(\text{pyrrole})]^+$, begins to appear using the 48 kcal mol^{-1} energy cut-off filter (Fig. 3). The relative abundance of $[\text{Co}(\text{pyrrole})]^+$ gradually increases from 48–84 kcal mol^{-1} , at which point a sharp increase is observed. From the above photodissociation data, we assign $D^0([\text{Co}(\text{pyrrole})]^+ - \text{pyrrole}) = 48 \pm 3 \text{ kcal mol}^{-1}$. This result is further supplemented by ligand displacement reactions. $[\text{Co}(\text{pyrrole})_2]^+$ reacts with

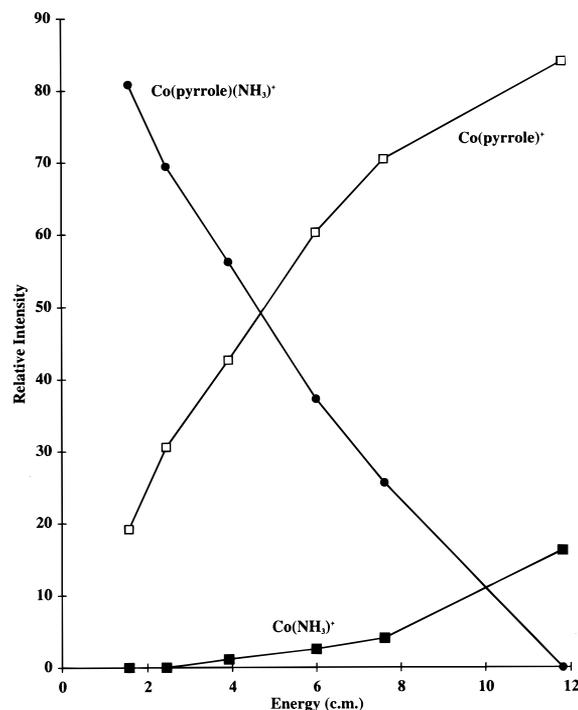


Figure 2. Variation of relative abundance as a function of energy (center of mass frame) for CID of $[\text{Co}(\text{NH}_3)(\text{pyrrole})]^+$ at 3×10^{-5} Torr argon target gas.

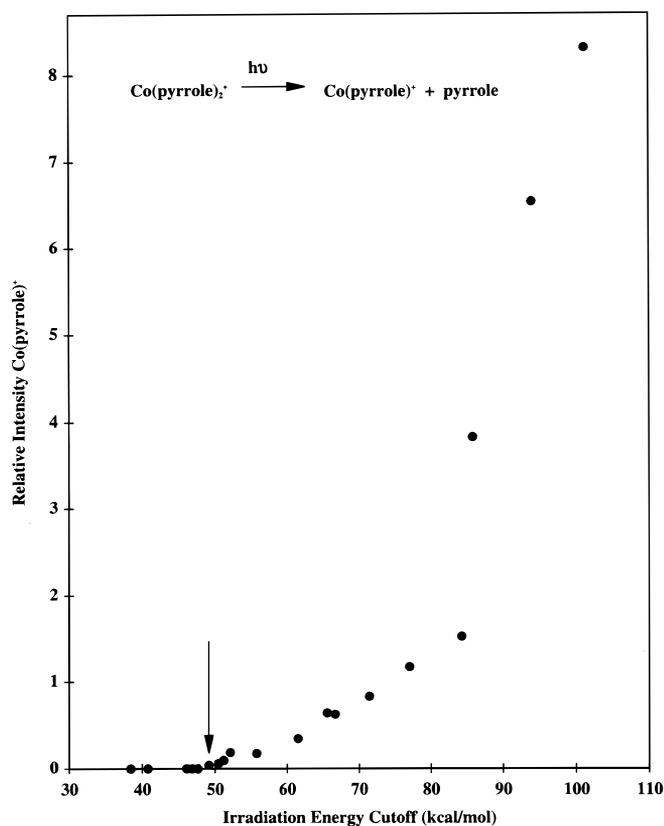


Figure 3. Photoappearance spectrum of $[\text{Co}(\text{pyrrole})]^+$ from photodissociation of $[\text{Co}(\text{pyrrole})_2]^+$ using the arc lamp and cut-off filters.

NH_3 by sequential ligand displacement to yield $[\text{Co}(\text{pyrrole})(\text{NH}_3)]^+$ and $\text{Co}(\text{NH}_3)_2^+$, indicating that $D^0([\text{Co}(\text{pyrrole})]^+ - \text{pyrrole}) < D^0([\text{Co}(\text{pyrrole})]^+ - \text{NH}_3)$ and $D^0(\text{Co}(\text{NH}_3)^+ - \text{pyrrole}) < D^0(\text{Co}(\text{NH}_3)^+ - \text{NH}_3)$. No reaction is observed for the reverse process of $\text{Co}(\text{NH}_3)_2^+$ with pyrrole. These results suggest that $D^0([\text{Co}(\text{pyrrole})]^+ - \text{pyrrole}) < D^0(\text{Co}(\text{NH}_3)^+ - \text{NH}_3) = 61 \pm 2 \text{ kcal mol}^{-1}$.²³ Unfortunately, a lower limit could not be assigned due to the absence of reference bond energy data. Thus, while $D^0([\text{Co}(\text{pyrrole})]^+ - \text{pyrrole}) \leq 48 \pm 3 \text{ kcal mol}^{-1}$ is probably a good estimate of the absolute bond energy, it represents strictly only an upper limit.

$[\text{Co}(\text{furan})_x]^+$ ($x = 1, 2$)

In contrast to pyrrole, where monomer and dimer formation are the only reaction channels observed, with furan, in addition to these channels, CO loss (maximum of 40% under the reaction conditions studied) is also observed. Interestingly, the analogous reaction is not observed with Fe^+ , but is with various $[\text{FeL}]^+$ species ($L = \text{C}_4\text{H}_6$, $\text{c-C}_5\text{H}_6$ and $\text{C}_5\text{H}_4(=\text{CH}_2)$).⁴ The structure of the CO loss product ion, $[\text{CoC}_3\text{H}_4]^+$, was probed by CID and other ion-molecule reactions, some of which are described here. Complete ligand displacement is observed when $[\text{CoC}_3\text{H}_4]^+$ reacts with propene, sug-

gesting that the C_3H_4 moiety bound to Co^+ is intact and that $D^0(\text{Co}^+ - \text{C}_3\text{H}_4) < D^0(\text{Co}^+ - \text{propene}) = 48 \pm 2 \text{ kcal mol}^{-1}$.^{12a} Collision-induced dissociation of $[\text{CoC}_3\text{H}_4]^+$ yields Co^+ as the sole product at all of the energies selected. These results are consistent with a $[\text{Co}(\text{allene})]^+$ and/or $[\text{Co}(\text{propyne})]^+$ structure for $[\text{CoC}_3\text{H}_4]^+$. To date we have been unable to distinguish between these two possibilities.

Photodissociation of $[\text{Co}(\text{furan})]^+$ yields two photoproducts, Co^+ and the CO loss product, $[\text{CoC}_3\text{H}_4]^+$. Co^+ begins to appear at 56 kcal mol^{-1} yielding $D^0(\text{Co}^+ - \text{furan}) = 57 \pm 3 \text{ kcal mol}^{-1}$ (Fig. 4). $[\text{Co}(\text{propene})]^+$, generated from the reaction of Co^+ with pulsed-in propene, reacts with furan to yield the ligand displacement product, $[\text{Co}(\text{furan})]^+$. The reverse reaction of $[\text{Co}(\text{furan})]^+$ with propene yields only the condensation product. Upon CID, $[\text{Co}(\text{furan})(\text{propene})]^+$ yields $[\text{Co}(\text{furan})]^+$, exclusively, over the range of laboratory kinetic energies studied. These results yield a lower limit of $D^0(\text{Co}^+ - \text{furan}) > D^0(\text{Co}^+ - \text{propene}) = 48 \pm 2 \text{ kcal mol}^{-1}$.^{12a} $[\text{Co}(\text{furan})]^+$ reacts with NH_3 by ligand displacement to form $\text{Co}(\text{NH}_3)^+$. In the reverse reaction of $\text{Co}(\text{NH}_3)^+$ with furan, condensation is observed, exclusively. CID on $[\text{Co}(\text{furan})(\text{NH}_3)]^+$ yields the furan loss product, $\text{Co}(\text{NH}_3)^+$. These results yield an upper limit of $D^0(\text{Co}^+ - \text{furan}) < D^0(\text{Co}^+ - \text{NH}_3) = 58.8 \text{ kcal mol}^{-1}$.²⁴ Hence, $D^0(\text{Co}^+ - \text{furan}) = 57 \pm 3 \text{ kcal mol}^{-1}$ is in accordance with the above ion-molecule reactions and CID experiments.

The CO loss photoproduct has a photoappearance threshold at $52 \pm 3 \text{ kcal mol}^{-1}$ [Fig. 4(b)]. This

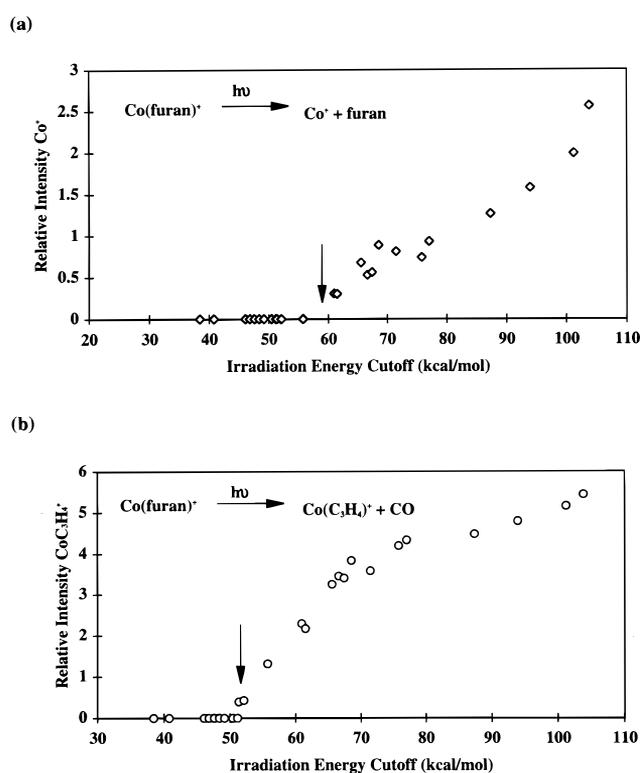


Figure 4. Photoappearance spectrum of (a) Co^+ and (b) $[\text{CoC}_3\text{H}_4]^+$ from photodissociation of $[\text{Co}(\text{furan})]^+$, using cut-off filters.

threshold can be used to calculate $D^0(\text{Co}^+ - \text{C}_3\text{H}_4)$. First, $\Delta H_f([\text{Co}(\text{furan})]^+) = 218 \pm 3 \text{ kcal mol}^{-1}$ is obtained from Eqn (2), using $\Delta H_f(\text{Co}^+) = 283 \text{ kcal mol}^{-1}$,^{25a} $\Delta H_f(\text{furan}) = -8.3 \pm 0.1 \text{ kcal mol}^{-1}$,^{25b} and $D^0(\text{Co}^+ - \text{furan}) = 57 \pm 3 \text{ kcal mol}^{-1}$ obtained in this work. Next, $\Delta H_f([\text{CoC}_3\text{H}_4]^+) = 296 \pm 6 \text{ kcal mol}^{-1}$ is calculated from Eqn (3), using $\Delta H_f(\text{CO}) = -26.42 \text{ kcal mol}^{-1}$,^{25a} and $52 \pm 3 \text{ kcal mol}^{-1}$ from the photoappearance threshold for CO loss from $[\text{Co}(\text{furan})]^+$. Finally, Eqn (4) yields $D^0(\text{Co}^+ - \text{allene}) = 33 \pm 6 \text{ kcal mol}^{-1}$ and/or $D^0(\text{Co}^+ - \text{propyne}) = 32 \pm 6 \text{ kcal mol}^{-1}$ based on either $\Delta H_f(\text{allene})^{26} = 45.6 \pm 0.2 \text{ kcal mol}^{-1}$ or $\Delta H_f(\text{propyne})^{25b} = 44.6 \pm 0.5 \text{ kcal mol}^{-1}$. The values reported above are consistent with the report by Haynes and Armentrout that $D^0(\text{Co}^+ - \text{allene}) > 18.7 \pm 2.1 \text{ kcal mol}^{-1}$ and with our observation above of $D^0(\text{Co}^+ - \text{allene}) < D^0(\text{Co}^+ - \text{propene}) = 48 \pm 2 \text{ kcal mol}^{-1}$.²⁷

$$\Delta H_f([\text{Co}(\text{furan})]^+) = \Delta H_f(\text{Co}^+) + \Delta H_f(\text{furan}) - D^0(\text{Co}^+ - \text{furan}) \quad (2)$$

$$\Delta H_f([\text{CoC}_3\text{H}_4]^+) = \Delta H_f([\text{Co}(\text{furan})]^+) - \Delta H_f(\text{CO}) + 52 \pm 3 \text{ kcal mol}^{-1} \quad (3)$$

$$D^0(\text{Co}^+ - \text{C}_3\text{H}_4) = \Delta H_f([\text{Co}(\text{C}_3\text{H}_4)]^+) - \Delta H_f(\text{Co}^+) - \Delta H_f(\text{C}_3\text{H}_4) \quad (4)$$

The thermochemistry for CX loss (X = NH, O and S) in reaction (5) of Co^+ with pyrrole, furan and thiophene is determined by Eqn (6) and listed in Table 1. All of the heats of formation required to solve Eqn (6) are available except for $\Delta H_f([\text{Co}(\text{C}_3\text{H}_4)]^+)$, which we determined above to be $296 \pm 6 \text{ kcal mol}^{-1}$. As can be seen in Table 1, reaction (5) is only exothermic for furan, which is consistent with the observed reactions of Co^+ with the four heterocyclic compounds. Although $\Delta H_f(\text{CSe})$ is not available for the determination of ΔH_{rxn} for CSe loss, based on the thermochemistry for CS loss, CSe loss is presumably also endothermic. In any event, CSe loss is not observed in the reaction of Co^+ with selenophene.



where X = NH, O, S and Se

$$\Delta H_{\text{rxn}} = \Delta H_f([\text{Co}(\text{C}_3\text{H}_4)]^+) + \Delta H_f(\text{CX}) - \Delta H_f(\text{Co}^+) - \Delta H_f(\text{C}_4\text{H}_4\text{X}) \quad (6)$$

Table 1. Reaction enthalpy (ΔH_{rxn}) for CX loss (X = NH, O and S) in reactions of Co^+ with aromatic heterocycles: $\text{Co}^+ + \text{C}_4\text{H}_4\text{X} \rightarrow [\text{Co}(\text{C}_3\text{H}_4)]^+ + \text{CX}^a$

$\text{C}_4\text{H}_4\text{X}$	X	$\Delta H_f(\text{CX})$ (kcal mol ⁻¹)	$\Delta H_f(\text{C}_4\text{H}_4\text{X})$ (kcal mol ⁻¹)	ΔH_{rxn} (kcal mol ⁻¹)
Pyrrole	NH	+32.3 ^{25a}	25.9 ± 0.1 ²⁶	+19.4 ± 6.1
Furan	O	-26.4 ^{25a}	-8.3 ± 0.1 ^{25b}	-5.1 ± 6.1
Thiophene	S	+64 ²⁶	+27.5 ± 0.1 ²⁶	+49.5 ± 6.1

^a $\Delta H_f([\text{Co}(\text{C}_3\text{H}_4)]^+) = 296 \pm 6 \text{ kcal mol}^{-1}$ as calculated in this work. $\Delta H_f(\text{Co}^+) = 283 \text{ kcal mol}^{-1}$.^{25a}

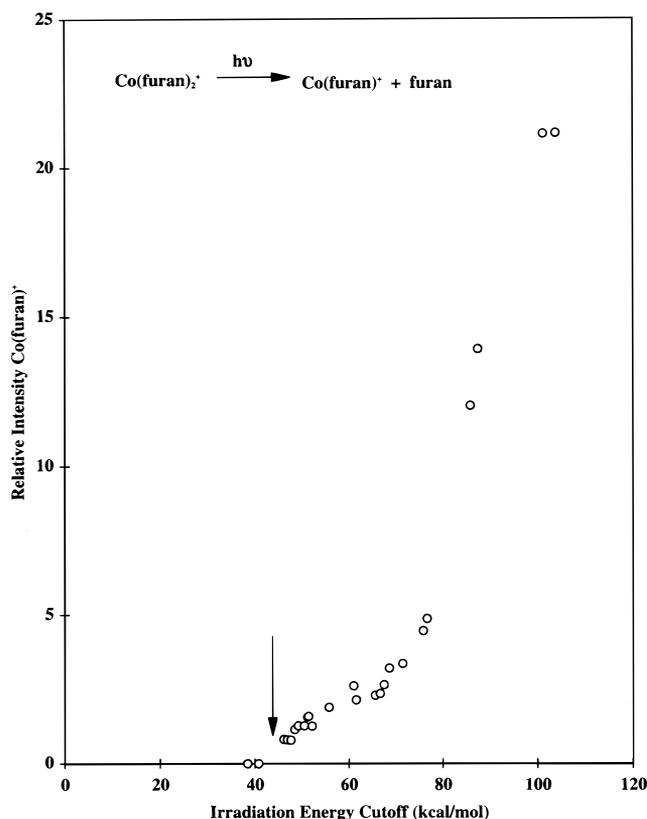


Figure 5. Photoappearance spectrum of $[\text{Co}(\text{furan})]^+$ from photodissociation of $[\text{Co}(\text{furan})_2]^+$ using cut-off filters.

Photodissociation of $[\text{Co}(\text{furan})_2]^+$ yields $[\text{Co}(\text{furan})]^+$ exclusively, as the photoproduct. The onset for the photoappearance of $[\text{Co}(\text{furan})]^+$ is $46 \pm 3 \text{ kcal mol}^{-1}$ (Fig. 5). Owing to a lack of bond energy data for disubstituted Co^+ , the value obtained here for $D^0([\text{Co}(\text{furan})]^+ - \text{furan})$ was not examined by other ion-molecule reactions and CID experiments. Thus, we assign $D^0([\text{Co}(\text{furan})]^+ - \text{furan}) \leq 46 \pm 3 \text{ kcal mol}^{-1}$.

$[\text{Co}(\text{thiophene})_x]^+$ (x = 1, 2)

Based on the photoappearance of Co^+ [Fig. 6(a)], $D^0(\text{Co}^+ - \text{thiophene})$ is measured as $61 \pm 3 \text{ kcal mol}^{-1}$. $[\text{Co}(\text{thiophene})]^+$ is observed to react with NH_3 to yield the condensation product predominantly, with $\text{Co}(\text{NH}_3)_2^+$ formation reaching a maximum of ~47% under the reaction conditions studied. CID of $[\text{Co}(\text{thiophene})(\text{NH}_3)]^+$ resulted in the formation of $[\text{Co}(\text{thiophene})]^+$ from loss of NH_3 . CoNH_3^+ , generated from the reaction of Co^+ with pulsed-in NH_3 , however, reacts with thiophene to yield the ligand displacement product, $[\text{Co}(\text{thiophene})]^+$. At sufficiently longer reaction times (>400 ms), some condensation is also observed. These results indicate that $D^0(\text{Co}^+ - \text{thiophene}) > D^0(\text{Co}^+ - \text{NH}_3) = 58.8 \text{ kcal mol}^{-1}$.²⁴ When $[\text{Co}(\text{benzene})]^+$ is allowed to react with thiophene, condensation is the major reaction channel

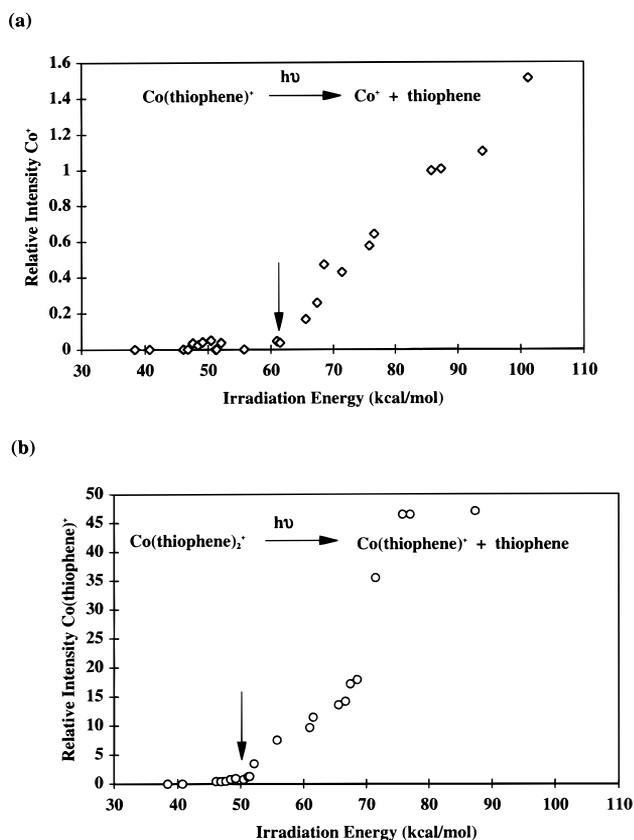


Figure 6. Photoappearance spectrum of (a) Co^+ from photodissociation of $[\text{Co}(\text{thiophene})]^+$ and (b) $[\text{Co}(\text{thiophene})]^+$ from photodissociation of $[\text{Co}(\text{thiophene})_2]^+$, using cut-off filters.

observed. Upon CID, the condensation product ion yields $[\text{Co}(\text{benzene})]^+$ from loss of thiophene. On the other hand, $[\text{Co}(\text{thiophene})]^+$ reacts with benzene to yield the ligand displacement product, $[\text{Co}(\text{benzene})]^+$. Based on these results, $D^0(\text{Co}^+ - \text{thiophene}) < D^0(\text{Co}^+ - \text{benzene}) = 61.1 \pm 2.5 \text{ kcal mol}^{-1}$.^{23a} Thus, $D^0(\text{Co}^+ - \text{thiophene}) = 61 \pm 3 \text{ kcal mol}^{-1}$ measured from arc lamp photodissociation is a reasonable value for the bond energy.

The photoappearance spectrum obtained by monitoring $[\text{Co}(\text{thiophene})]^+$, upon irradiation of $[\text{Co}(\text{thiophene})_2]^+$, is shown in Fig. 6(b). A sharp threshold for the appearance of $[\text{Co}(\text{thiophene})]^+$ begins at $49 \pm 3 \text{ kcal mol}^{-1}$. Similarly to $[\text{Co}(\text{pyrrole})_2]^+$ and $[\text{Co}(\text{furan})_2]^+$, only an upper limit, $D^0([\text{Co}(\text{thiophene})]^+ - \text{thiophene}) \leq 49 \pm 3 \text{ kcal mol}^{-1}$, is assigned.

$[\text{Co}(\text{selenophene})_x]^+$ ($x = 1, 2$)

The photoappearance data of Co^+ from $[\text{Co}(\text{selenophene})]^+$ are shown in Fig. 7(a). From the photodissociation threshold, $D^0(\text{Co}^+ - \text{selenophene}) = 64 \pm 3 \text{ kcal mol}^{-1}$ is assigned. When $\text{Co}(\text{NH}_3)^+$ reacts with selenophene, complete ligand displacement is observed. In contrast, $[\text{Co}(\text{selenophene})]^+$ yields only the condensation product with NH_3 . CID

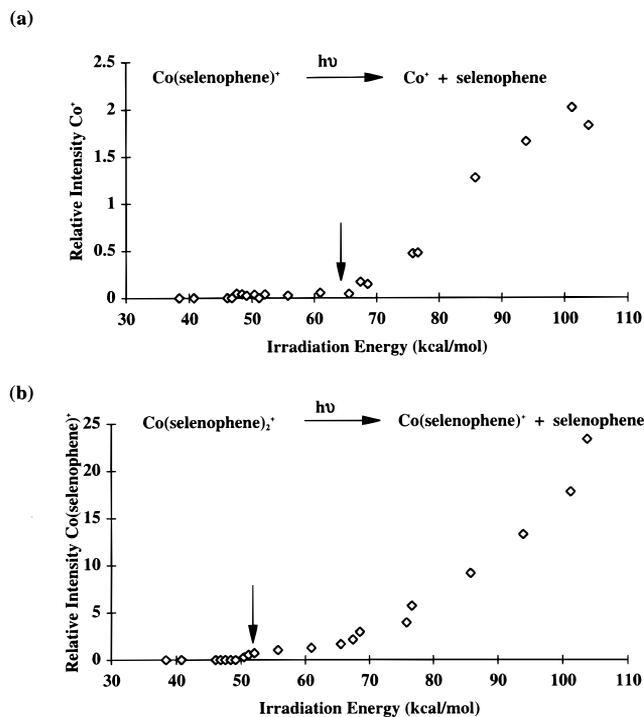


Figure 7. Photoappearance spectrum of (a) Co^+ from the photodissociation of $[\text{Co}(\text{selenophene})]^+$ and (b) $[\text{Co}(\text{selenophene})]^+$ from photodissociation of $[\text{Co}(\text{selenophene})_2]^+$, using cut-off filters.

of $[\text{Co}(\text{selenophene})(\text{NH}_3)]^+$ yields predominantly $[\text{Co}(\text{selenophene})]^+$ from loss of NH_3 . These results indicate that $D^0(\text{Co}^+ - \text{selenophene}) > D^0(\text{Co}^+ - \text{NH}_3) = 58.8 \text{ kcal mol}^{-1}$.²⁴ $[\text{Co}(\text{benzene})]^+$ reacts with selenophene to yield a condensation product which, upon CID, produces $[\text{Co}(\text{benzene})]^+$. Selenophene ligand is displaced in the reverse reaction of $[\text{Co}(\text{selenophene})]^+$ with benzene. These results are consistent with $D^0(\text{Co}^+ - \text{selenophene}) < D^0(\text{Co}^+ - \text{benzene}) = 61.1 \pm 2.5 \text{ kcal mol}^{-1}$.^{22a} Hence the photodissociation threshold is at least nearly thermodynamic and $D^0(\text{Co}^+ - \text{selenophene}) = 64 \pm 3 \text{ kcal mol}^{-1}$, measured from arc lamp photodissociation, is a good estimate of the absolute bond energy.

$[\text{Co}(\text{selenophene})_2]^+$ shows a sharp photodissociation threshold starting at $51 \pm 3 \text{ kcal mol}^{-1}$ [Fig. 7(b)]. As discussed for the other $[\text{CoL}_2]^+$ complexes ($L = \text{pyrrole}$, furan and thiophene), $D^0([\text{Co}(\text{selenophene})]^+ - \text{selenophene}) \leq 51 \pm 3 \text{ kcal mol}^{-1}$ is, in the absence of other corroborating experiments, strictly only an upper limit for the bond energy of $[\text{Co}(\text{selenophene})]^+$ to selenophene.

Competitive collision-induced dissociation on Co^+ -bound heterodimers

Based on the photodissociation threshold measurements, the bond energies of $[\text{CoL}]^+$ vary systematically as follows: $D^0(\text{Co}^+ - \text{furan}) < D^0(\text{Co}^+ - \text{pyrrole}) < D^0(\text{Co}^+ - \text{thiophene}) < D^0(\text{Co}^+ - \text{selenophene})$. Given the error bars and the closeness of the values, however,

additional support for this relative bond energy order was obtained by competitive ligand displacement reactions and CID.

First, $[\text{Co}(\text{pyrrole})]^+$ was allowed to react with furan, yielding only the condensation product. Upon CID, $[\text{Co}(\text{pyrrole})(\text{furan})]^+$ yields mainly $[\text{Co}(\text{pyrrole})]^+$ together with some $[\text{Co}(\text{furan})]^+$ [Fig. 8(a)]. In the reverse process, $[\text{Co}(\text{furan})]^+$ reacts with pyrrole and yields only the ligand displacement product, $[\text{Co}(\text{pyrrole})]^+$. These results suggest that $D^0(\text{Co}^+ - \text{furan}) < D^0(\text{Co}^+ - \text{pyrrole})$, in agreement with the photodissociation threshold measurements.

The reactions of $[\text{Co}(\text{pyrrole})]^+$ with thiophene and $[\text{Co}(\text{thiophene})]^+$ with pyrrole were examined next. $[\text{Co}(\text{pyrrole})]^+$ reacts with thiophene to generate predominantly the ligand displacement product, $[\text{Co}(\text{thiophene})]^+$. At longer reaction times (>400 ms), the condensation product ion ($\sim 18\%$ maximum under the reaction conditions studied) is also observed. The reaction of $[\text{Co}(\text{thiophene})]^+$ with pyrrole yields $[\text{Co}(\text{thiophene})(\text{pyrrole})]^+$ as the major product and $[\text{Co}(\text{pyrrole})]^+$ as the minor product ion at all of the reaction times studied. CID on the condensation product, $[\text{Co}(\text{pyrrole})(\text{thiophene})]^+$, yields $[\text{Co}(\text{thiophene})]^+$ as the major product with some $[\text{Co}(\text{pyrrole})]^+$ formation [Fig. 8(b)]. Similarly, $[\text{Co}(\text{selenophene})]^+$ reacts with thiophene to yield the condensation product, $[\text{Co}(\text{selenophene})(\text{thiophene})]^+$.

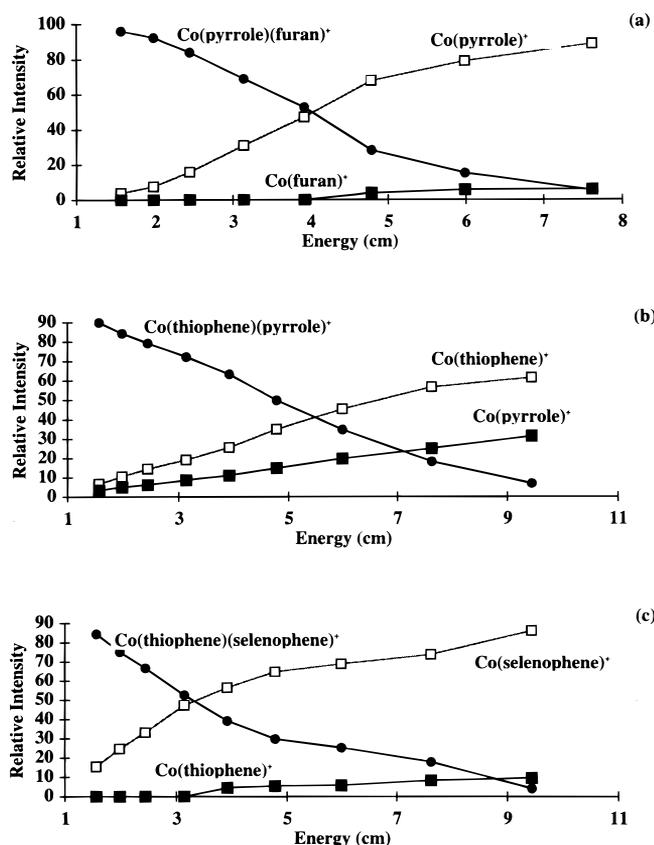


Figure 8. Variation of relative abundance as a function of energy (center of mass frame) for CID of Co^+ -bound heterodimers (a) $[\text{Co}(\text{pyrrole})(\text{furan})]^+$, (b) $[\text{Co}(\text{pyrrole})(\text{thiophene})]^+$ and (c) $[\text{Co}(\text{thiophene})(\text{selenophene})]^+$ at 3.5×10^{-6} Torr argon target gas.

CID of $[\text{Co}(\text{thiophene})(\text{selenophene})]^+$ yields predominantly $[\text{Co}(\text{selenophene})]^+$, with $[\text{Co}(\text{thiophene})]^+$ observed as a minor product ion above ~ 3 eV center of mass energy [Fig. 8(c)]. In accordance with the photodissociation threshold measurements, these results indicate that $D^0(\text{Co}^+ - \text{furan}) < D^0(\text{Co}^+ - \text{pyrrole}) < D^0(\text{Co}^+ - \text{thiophene}) < D^0(\text{Co}^+ - \text{selenophene})$.

CONCLUSION

The bond energies obtained from photodissociation, $D^0(\text{Co}^+ - \text{pyrrole}) = 59 \pm 3$ kcal mol $^{-1}$, $D^0(\text{Co}^+ - \text{furan}) = 57 \pm 3$ kcal mol $^{-1}$, $D^0(\text{Co}^+ - \text{thiophene}) = 61 \pm 3$ kcal mol $^{-1}$ and $D^0(\text{Co}^+ - \text{selenophene}) = 64 \pm 3$ kcal mol $^{-1}$, are in accordance with the upper and lower limits assigned by ligand displacement reactions and CID experiments and, therefore, represent thermodynamic thresholds. Previous studies carried out in condensed phases by several research groups have shown that pyrrole π -bonds to metal centers.¹ With thiophene, however, several π -bonding modes, as well as σ -bonding via the S atom, have been suggested.²⁸ The experimental data and bond energies obtained in this study do not allow us to distinguish the mode of bonding present in these $[\text{ML}]^+$ complexes. The similarities of the bond energies, especially to pyrrole, however, prompt us to suggest that the most likely bonding mode is π -bond formation instead of heteroatom bound σ -bond formation. These results are also consistent with those obtained by Bakhtiar and Jacobson⁴ indicating that $D^0(\text{Fe}^+ - \text{pyrrole}) \approx D^0(\text{Fe}^+ - \text{thiophene}) \approx 48 \pm 5$ kcal mol $^{-1}$. Considering that $D^0(\text{Co}^+ - \text{benzene})^{23a} - D^0(\text{Fe}^+ - \text{benzene})^{23c} \approx 11$ kcal mol $^{-1}$, the higher values we obtained for the cobalt complexes are certainly reasonable.

For the $[\text{CoL}_2]^+$ species, photodissociation yielded the bond energy limits $D^0([\text{Co}(\text{pyrrole})]^+ - \text{pyrrole}) \leq 48 \pm 3$ kcal mol $^{-1}$, $D^0([\text{Co}(\text{furan})]^+ - \text{furan}) \leq 46 \pm 3$ kcal mol $^{-1}$, $D^0([\text{Co}(\text{thiophene})]^+ - \text{thiophene}) \leq 49 \pm 3$ kcal mol $^{-1}$ and $D^0([\text{Co}(\text{selenophene})]^+ - \text{selenophene}) \leq 51 \pm 3$ kcal mol $^{-1}$. The observation that the second ligand is more weakly bound to the Co metal center in these species is in accordance with previous experiments carried out on systems such as $[\text{M}(\text{C}_6\text{H}_6)_x]^+$ (M = Fe, Co, Ni and Cu) where $x = 1, 2$.²⁷ In order to satisfy the 18-electron rule, the formation of stable $[\text{Co}(\text{pyrrole})_2]^+$, $[\text{Co}(\text{furan})_2]^+$, $[\text{Co}(\text{thiophene})_2]^+$ and $[\text{Co}(\text{selenophene})_2]^+$ complexes suggests that, assuming the bonding mode of the first ligand is η^6 , then that of the second ligand is η^x ($x \leq 5$) or heteroatom bound and, thus, more weakly bonded. This is reasonable considering that a variety of different binding modes for these heterocycles have been characterized.²⁹ There are also other reasons for reduced $D^0([\text{ML}]^+ - \text{L})$ in $[\text{ML}_2]^+$ species, including steric and electronic factors. Ion-dipole and ion-induced dipole interactions decrease as the charge is delocalized to any extent on the ligand in the monomer, $[\text{ML}]^+$.^{15a,30} Second, the steric effects caused by the ligand already present increases the ligand-ligand repulsions. Hence,

the reduced electrostatic interactions and crowding effects are two other important factors which may cause $D^0([ML]^+ - L) < D^0(M^+ - L)$.

Energy (under grant DE-FG02-87ER13766) for supporting this research.

Acknowledgements

Acknowledgement is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of

REFERENCES

- (a) K. M. K. Dailey, T. B. Rauchfuss, A. L. Rheingold and G. P. A. Yap, *J. Am. Chem. Soc.* **117**, 6396 (1995); (b) L. M. Hodges, J. Gonzalez, J. I. Koontz, W. H. Myers and W. D. Harman, *J. Org. Chem.* **58**, 4788 (1993); (c) R. Cordone, W. D. Harman and H. Taube, *J. Am. Chem. Soc.* **111**, 5969 (1989); (d) B. Chaudret and F. A. Jalon, *J. Chem. Soc., Chem. Commun.* 711 (1988).
- P. George, *Chem. Rev.* **75**, 85 (1975), and references cited therein.
- (a) M. J. Cook, A. R. Katritzky and P. Linda, *Adv. Heterocycl. Chem.* **17**, 255 (1974); (b) B. J. Deelman, W. M. Stevels, J. H. Teuben, M. T. Lakin and A. L. Spek, *Organometallics* **13**, 3881 (1994).
- R. Bakhtiar and D. B. Jacobson, *J. Am. Soc. Mass Spectrom.* **7**, 938 (1996).
- (a) A. Jones, *Chemistry of Heterocyclic Compounds*, Vol. 48. Wiley, New York (1990); (b) W. H. Myers, J. I. Koontz and W. D. Harman, *J. Am. Chem. Soc.* **114**, 5684 (1992); (c) W. T. Brockmann and J. M. Tour, *J. Am. Chem. Soc.* **117**, 4437 (1995).
- T. Inul and Y. Tanabe, *J. Catal.* **52**, 375 (1978).
- T. B. Rauchfuss, *Prog. Inorg. Chem.* **39**, 259 (1991).
- (a) E. W. Abel and C. J. Towers, *J. Chem. Soc., Dalton Trans.* 814 (1979); (b) C. Segard, C. Pommier, B. P. Roques and G. Guiochon, *J. Organomet. Chem.* **77**, 49 (1974); (c) R. B. King and J. Efraty, *J. Organomet. Chem.* **20**, 264 (1969).
- E. Murad, *J. Chem. Phys.* **73**, 1381 (1980).
- (a) P. B. Armentrout and J. L. Beauchamp, *J. Am. Chem. Soc.* **103**, 784 (1981); (b) P. B. Armentrout, L. F. Halle and J. L. Beauchamp, *J. Am. Chem. Soc.* **103**, 6501 (1981).
- S. A. McLuckey, A. E. Schoen and R. G. Cooks, *J. Am. Chem. Soc.* **104**, 848 (1982).
- (a) M. A. Hanratty, J. L. Beauchamp, A. J. Illies, P. van Koppen and M. T. Bowers, *J. Am. Chem. Soc.* **110**, 1 (1988); (b) P. A. M. van Koppen, D. B. Jacobson, A. J. Illies, M. T. Bowers, M. A. Hanratty and J. L. Beauchamp, *J. Am. Chem. Soc.* **111**, 1991 (1989).
- (a) S. W. Buckner and B. S. Freiser, *Polyhedron* **7**, 1583 (1988); (b) W. J. van der Hart, *Mass Spectrom. Rev.* **8**, 237 (1989).
- (a) P. B. Armentrout, R. V. Hodges and J. L. Beauchamp, *Chem. Phys.* **66**, 4683 (1977); (b) P. B. Armentrout and R. Georgiadis, *Polyhedron* **7**, 1573 (1988); (c) P. B. Armentrout, in *Gas Phase Inorganic Chemistry*, edited by D. H. Russell, p. 1. Plenum Press, New York (1989); (d) P. B. Armentrout and B. Kickel, in *Organometallic Ion Chemistry*, edited by B. S. Freiser, p. 1, Kluwer, Dordrecht (1995); (e) E. R. Fisher, B. L. Kickel and P. B. Armentrout, *J. Phys. Chem.* **97**, 10204 (1993).
- (a) C. W. Bauschlicher, Jr, S. R. Langhoff and H. Partridge, in *Organometallic Ion Chemistry*, edited by B. S. Freiser, Kluwer, Dordrecht (1995); (b) G. B. McGaughey, E. L. Stewart and J. P. Bowen, *J. Comput. Chem.* **17**, 1395 (1996); (c) F. Chan and J. Baker, *J. Comput. Chem.* **17**, 888 (1996); (d) M. W. Schmidt, T. L. Windus and M. S. Gordon, *J. Am. Chem. Soc.* **117**, 7480 (1995); (e) C. W. Bauschlicher, Jr, H. Partridge and S. R. Langhoff, *J. Phys. Chem.* **96**, 3273 (1992).
- (a) S. Afzaal and B. S. Freiser, *Chem. Phys. Lett.* **218**, 254 (1994); (b) B. S. Freiser and J. L. Beauchamp, *J. Am. Chem. Soc.* **98**, 3136 (1976); (c) L. M. Roth, B. S. Freiser, C. W. Bauschlicher, Jr, H. Partridge and S. R. Langhoff, *J. Am. Chem. Soc.* **113**, 3274 (1991); (d) Y. A. Ranasinghe, I. B. Surjasmita and B. S. Freiser, in *Organometallic Ion Chemistry*, edited by B. S. Freiser, p. 229, Kluwer, Dordrecht (1995).
- (a) L. R. Thorne and J. L. Beauchamp, in *Gas Phase Ion Chemistry*, edited by M. I. Bowers, Vol. 3, p. 42. Academic Press, New York (1984); (b) R. C. Dunbar, in *Gas Phase Ion Chemistry*, edited by M. I. Bowers, Vol. 3, p. 130. Academic Press, New York (1984).
- (a) P. B. Grosshans and A. G. Marshall, *Int. J. Mass Spectrom. Ion Process.* **100**, 347 (1990); (b) A. G. Marshall, *Acc. Chem. Res.* **18**, 316 (1985); (c) A. G. Marshall and P. B. Grosshans, *Anal. Chem.* **63**, 215A (1991).
- (a) R. B. Cody, R. C. Burnier, W. D. Reents, Jr, T. J. Carlin, D. A. McCreary, R. K. Lengel and B. S. Freiser, *Int. J. Mass Spectrom. Ion Phys.* **33**, 37 (1980); (b) B. S. Freiser, *Talanta* **32**, 697 (1985).
- T. J. Carlin and B. S. Freiser, *Anal. Chem.* **55**, 571 (1983).
- (a) A. G. Marshall and D. C. Roe, *J. Chem. Phys.* **73**, 1581 (1980); (b) A. G. Marshall, T. C. L. Wang and T. L. Ricca, *Chem. Phys. Lett.* **108**, 63 (1984).
- (a) D. R. A. Ranatunga and B. S. Freiser, *Chem. Phys. Lett.* **233**, 319 (1995); (b) C. J. Cassady, S. Afzaal and B. S. Freiser, *Org. Mass Spectrom.* **29**, 30 (1994); (c) Y. A. Ranasinghe and B. S. Freiser, *Chem. Phys. Lett.* **200**, 135 (1992).
- (a) F. Meyer, F. A. Khan and P. B. Armentrout, *J. Am. Chem. Soc.* **117**, 9740 (1995); (b) C. W. Bauschlicher, H. Partridge and R. Langhoff, *J. Chem. Phys.* **96**, 3273 (1992); (c) R. L. Hettich, T. C. Jackson, E. M. Stanko and B. S. Freiser, *J. Am. Chem. Soc.* **108**, 5086 (1986).
- R. R. Squires, *J. Am. Chem. Soc.* **111**, 4101 (1989).
- (a) D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11**, Suppl. 1 (1982); (b) J. B. Pedley and J. Rylance, *Sussex-NPL Computer Analysed Thermochemical Data: Organic and Organometallic Compounds*. University of Sussex, Brighton (1977).
- S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, **17**, Suppl. 1, 1988.
- C. L. Haynes and P. B. Armentrout, *Organometallics* **13**, 3480 (1994).
- (a) R. J. Angelici, *Coord. Chem. Rev.* **105**, 61 (1990), and references cited therein; (b) Y. S. Nekrasov and N. I. Vasyukova, *J. Organomet. Chem.* **122**, 227 (1976).
- (a) A. E. Ogilvy, A. E. Skaugset and T. B. Rauchfuss, *Organometallics* **8**, 2739 (1989); (b) A. E. Skaugset, T. B. Rauchfuss and C. L. Stern, *J. Am. Chem. Soc.* **112**, 2432 (1990); (c) J. Chen and R. J. Angleici, *Organometallics* **9**, 849 (1990).
- M. L. Mandich, L. F. Halle and J. L. Beauchamp, *J. Am. Chem. Soc.* **106**, 4403 (1984).