Negative-Ion Photoelectron Spectrum of Tricarbonyl(η^5-methylcyclopentadienyl)manganate(0)

A. A. Martel and I. M. Waller*

Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada

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Fixed-frequency negative-ion photoelectron spectra of tricarbonyl(η^5-methylcyclopentadienyl)manganate(0), $Cp^*Mn(CO)_3^-$, are obtained at 355 and 532 nm. The adiabatic electron affinity of tricarbonyl(η^5-methylcyclopentadienyl)manganese(I), $Cp^*Mn(CO)_3$, as obtained from the experiments, is 0.5 ± 0.1 eV, and the vertical ionization potential of the anion is 1.0 ± 0.1 eV. By combining our electron affinity results with literature gas-phase acidity estimates for $Cp^*Mn(CO)_3$ we determine that the C−H bond dissociation energy, D[$H-CH_2C_5H_4Mn(CO)_3^-$], in the anion is 2.2 ± 0.8 eV.

Introduction

Organotransition-metal complexes that contain a cyclopentadienyl ligand have been the subjects of a vast amount of research, primarily due to the synthetic and catalytic versatility[1] of such species and the rich bonding modes that are available to the cyclopentadienyl ligand. Tricarbonyl(η^5-methylcyclopentadienyl)manganese(I), $Cp^*Mn(CO)_3$, has been used as an antiknock agent in gasoline since 1976 in Canada[2] and more recently in the U.S.A.[3] In addition, $Cp^*Mn(CO)_3$ is known to be a very effective octane-enhancing agent.[4] Because of its widespread use, it is important to obtain more information about $Cp^*Mn(CO)_3$, including its atmospheric lifetime, combustion properties, decomposition mechanism in aqueous and atmospheric environments, and other thermodynamic properties.

In this paper, we report the fixed-frequency negative-ion photoelectron spectra of $Cp^*Mn(CO)_3^-$ as a means to determine the electron affinity of $Cp^*Mn(CO)_3$.

Experimental Section

The negative-ion photoelectron spectrometer has been described in detail previously.[5,6] A carrier gas (either argon or helium) at 1 atm backing pressure is passed over room-temperature liquid $Cp^*Mn(CO)_3$. The resulting dilute mixture ($Cp^*Mn(CO)_3$ has a vapor pressure of 9.3 mm at 100 °C) is expanded through a pulsed molecular beam nozzle and crossed with a 1 keV electron beam.[7] The negative ions produced in the process are cooled to approximately 100 K as the expansion progresses.[8]

The resulting anions are accelerated to 1 keV and then mass selected using a 1.5 m beam-modulated time-of-flight mass spectrometer.[9,10] The mass spectrometer is also equipped with an einzel lens and a temporal focusing lens. For these experiments, the mass spectrometer is calibrated using oxygen anion clusters.

The mass-selected anion bunch of interest is intersected at 90° with the doubled or tripled output from a pulsed Nd:YAG laser. A small fraction of the detached electrons is energy analyzed in a 1 m time-of-flight spectrometer, located mutually perpendicular to both the ion flight path and the laser beam path. The electron spectrometer is calibrated using the known photoelectron spectra of O^-, O_2^-, and NO^- and has a resolution of 80 meV at 1.6 eV.

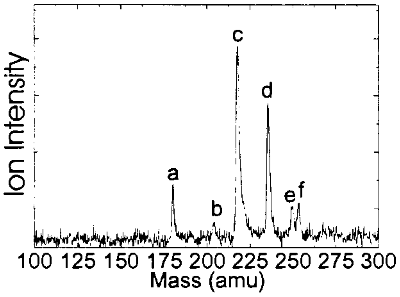

Figure 1. Mass spectrum of negative ions produced from a dilute mixture of room-temperature $Cp^*Mn(CO)_3$ expanded with 1 atm backing pressure of helium carrier gas: (a) $CpCo(CO)_2^-$; (b) $CpMn(CO)_3^-$; (c) $Cp^*Mn(CO)_3^-$; (d) $Cp^*Mn(CO)_3^-\cdot H_2O$; (e) $[Cp^*Mn(CO)_3\cdot O_2]^-$; (f) $Cp^*Mn(CO)_3^-\cdot 2H_2O$.

Results

A mass spectrum of a helium expansion of $Cp^*Mn(CO)_3$ is displayed in Figure 1. The two major peaks in the spectrum occur at *m*/*e* values of 218 and 236. The third largest peak has an *m*/*e* of 180, while a "doublet" of peaks occurs at *m*/*e* = 250 and 254. A trace amount of an anion corresponding to an *m*/*e* of 204 is also detected.

The electron time-of-flight spectrum for electrons photodetached from $Cp^*Mn(CO)_3^-$ using the third harmonic (355 nm, 3.49 eV) of the Nd:YAG laser is shown in Figure 2. Two broad peaks are observed in this spectrum, one at a flight time of 1000 ns with a width of 120 ns and a second feature centered at a flight time of 1250 ns. This spectrum is converted in the usual manner into an electron kinetic energy spectrum and displayed in Figure 3. From this figure, a high electron kinetic-energy threshold of 3.0 ± 0.1 eV is revealed with a maximum in the signal occurring at an electron kinetic energy of 2.5 ± 0.1 eV. The second threshold occurs at 2.0 ± 0.2 eV.

The electron kinetic-energy spectrum for electrons photodetached from $Cp^*Mn(CO)_3^-$ using the second harmonic (532 nm, 2.33 eV) of the Nd:YAG laser is shown in Figure 4. Only one

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* Corresponding author. E-mail: *waller@chem.ubc.ca*. Fax: (604) 822-2847.

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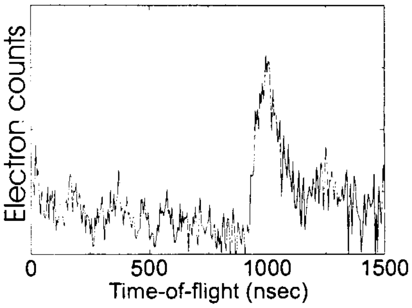

Figure 2. The electron time-of-flight spectrum for electrons photodetached from $Cp^*Mn(CO)_3^-$ using 355 nm (3.49 eV) photons (30 mJ/pulse).

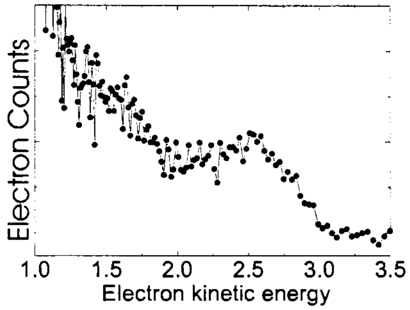

Figure 3. The electron kinetic-energy spectrum of electrons photodetached from $Cp^*Mn(CO)_3^-$ using 355 nm (3.49 eV) light (30 mJ/pulse).

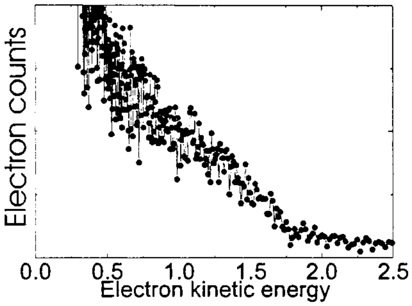

Figure 4. The electron kinetic energy spectrum for electrons photodetached from $Cp^*Mn(CO)_3^-$ using the second harmonic (532 nm, 2.33 eV) of the Nd:YAG laser (40 mJ/pulse).

broad peak is observed in this spectrum. From Figure 4, a high electron kinetic-energy threshold of 1.8 ± 0.1 eV is apparent.

Discussion

Mass Spectrum. The dominant peak in the mass spectrum of Figure 1 is due to the parent anion $Cp^*Mn(CO)_3^-$ at 218 amu. It is very typical of the anion source used (crossed molecular beam/electron beam) that very little fragmentation of the parent molecule is observed. In the mass spectrometry work on the related complex, tricarbonyl(η^5-cyclopentadienyl)manganese(I), $CpMn(CO)_3$, by Winters and Kiser,[11] the dominant negative ion that they observed, using 70 eV electron energy, was the parent ion $CpMn(CO)_3^-$. (Note that $Cp^* \equiv CH_3C_5H_4$, the methylcylopentadienyl ligand, and $Cp \equiv C_5H_5$, the cyclopentadienyl ligand.)

The anions detected at *m*/*e* values of 236, 250, and 254 may be assigned to $Cp^*Mn(CO)_3^-{\cdot}H_2O$, $[Cp^*Mn(CO)_3{\cdot}O_2]^-$, and $Cp^*Mn(CO)_3^-{\cdot}2H_2O$, respectively. This clustering of the organometallic compound with residual water and oxygen in the source gas lines has been observed in our previous studies.

The signal at *m*/*e* = 204 may be due to an anion from which a methyl group has been lost from the methylcyclopentadienyl ligand resulting in an anion of mass 203 amu. Alternatively, it may be due to the $CpMn(CO)_3^-$ anion (mass of 204 amu) possibly produced by a 1,2-hydrogen shift and elimination of a methylene unit from the methylcyclopentadienyl ligand. The resolution of the mass spectrometer is insufficient to distinguish between these two possibilities. The driving force for the formation of either of these anions may be the desire to reduce the electron density on the manganese atom. In neutral complexes, methyl groups on a cyclopentadienyl ring are known to be electron donating, and this ligand in turn increases the electron density on the metal center.[12,13] The methylated ligand thus directs increased electron density toward the manganese center in a complex. In $Cp^*Mn(CO)_3^-$, the extra electron represents a strain on the manganese center that can be relieved by elimination of the methyl or methylene group on the Cp* ligand.

The peak at 180 amu is $CpCo(CO)_2^-$, which arises due to contamination of the source by $CpCo(CO)_2$ which was studied in the spectrometer just prior to the running of the present experiments.

Electron Spectra. The adiabatic electron affinity, EA_{ad}, is the minimum energy required to remove an electron from the ground electronic, vibrational, and rotational state of an anion, thus producing the corresponding ground-state neutral molecule and an electron with zero kinetic energy.

$$EA_{ad} = [E(R_e) - E^-(R_e^-)]$$

$E(R_e)$ is the energy of the neutral molecule at its ground-state equilibrium geometry, R_e, and $E^-(R_e^-)$ is the energy of the anion determined at the equilibrium geometry of the anion, R_e^-. The threshold at high electron kinetic energy in the negative-ion photoelectron spectrum can give an upper bound to EA_{ad} by subtracting the observed threshold from the photon energy.

The 355 nm (3.49 eV) photoelectron spectrum of $Cp^*Mn(CO)_3^-$ is displayed in Figure 3. From the observed high-energy electron kinetic-energy threshold of 3.0 ± 0.1 eV, the adiabatic electron affinity of $Cp^*Mn(CO)_3$ is estimated to be 0.5 ± 0.1 eV.

The vertical ionization potential, FIP_{vert}, of the anion is the difference between the energy of the neutral molecule determined at the equilibrium geometry of the anion, $E(R_e^-)$, and the energy of the anion determined at the ground-state equilibrium geometry of the anion, $E^-(R_e^-)$,

$$FIP_{vert} = E(R_e^-) - E^-(R_e^-)$$

This can be obtained from the experimental data by subtracting the position of the maximum intensity in the electron kinetic-energy spectrum from the photon energy. In Figure 3, the maximum occurs at an electron kinetic energy of 2.5 ± 0.1 eV corresponding to a $FIP_{vert}[Cp^*Mn(CO)_3^-]$ of 1.0 ± 0.1 eV.

The second threshold at a 2.0 ± 0.2 eV electron kinetic energy in Figure 3 corresponds to transitions to an excited state of $Cp^*Mn(CO)_3$, which lies 1.0 eV above the ground state.

The high-energy threshold of 1.8 ± 0.1 eV electron kinetic energy observed when the photon energy of 532 nm (2.33 eV) is used for photodetachment, as displayed in Figure 4, confirms that $EA_{ad}[Cp^*Mn(CO)_3]$ is 0.5 ± 0.1 eV.

Comparison with Related Complexes. The low electron affinity that we observe, $EA_{ad}[Cp^*Mn(CO)_3] = 0.5 \pm 0.1$ eV, is consistent with $Cp^*Mn(CO)_3^-$ being a 19-electron complex.[14,15] An ESR study[16] of the related complex $CpMn(CO)_3^-$, which contains the unmethylated cyclopentadienyl ligand, indicated that the singly occupied molecular orbital was

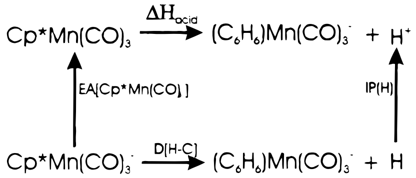

Figure 5. Thermodynamic cycle used for calculating the C−H bond dissociation energy, $D[\mathrm{H{-}CH_2C_5H_4Mn(CO)_3^-}]$, in tricarbonyl($\eta^5$-methylcyclopentadienyl)manganate(0), indicated as D[H−C] in the figure. ΔH_{acid} is the gas-phase acidity of Cp*Mn(CO)$_3$, and IP(H) is the ionization potential of hydrogen.

primarily manganese d_{z^2} with the population in this orbital increasing to approximately 69%. The neutral complex Cp*Mn(CO)$_2$(NO), which is isoelectronic with Cp*Mn(CO)$_3^-$, undergoes ligand substitution by a dissociative mechanism consistent with Cp*Mn(CO)$_2$(NO) being viewed as a 19-electron complex.[17] ESR studies of CpCr(CO)$_2$NO$^-$ and CpMo(CO)$_2$NO$^-$, both of which are isoelectronic to Cp*Mn(CO)$_3^-$, showed that a large amount of the electron density is localized on the metal center and that these anions can be viewed as 19-electron complexes.[18]

The 17-electron manganese complex, Mn(CO)$_5$, has been assigned an electron affinity of 2.43 ± 0.21 eV from values of the proton affinity of Mn(CO)$_5^-$ and the Mn−H bond dissociation energy in HMn(CO)$_5$.[19] If the Cp* ring distorted so as to reduce the electron density on the Mn center in the Cp*Mn(CO)$_3^-$ anion, we would expect a much high electron affinity for Cp*Mn(CO)$_3$ than we have measured.

Carbon−Hydrogen Bond Dissociation Energy. VanOrden and Buckner[20] were able to bracket the gas-phase acidity of Cp*Mn(CO)$_3$ between that of HCl [$\Delta H_{\mathrm{acid}}(\mathrm{HCl}) = 333$ kcal mol^{-1}] and HF [$\Delta H_{\mathrm{acid}}(\mathrm{HF}) = 371.5$ kcal mol^{-1}] by studying the reactions of Cl$^-$ and F$^-$ with Cp*Mn(CO)$_3$. By using a thermodynamic cycle, as depicted in Figure 5, to couple our results for the electron affinity of Cp*Mn(CO)$_3$ with these gas-phase acidity results we can calculate the carbon−hydrogen bond dissociation energy in the Cp*Mn(CO)$_3^-$ anion.

$$D[\mathrm{H{-}CH_2C_5H_4Mn(CO)_3^-}] = \mathrm{EA[Cp^*Mn(CO)_3]} + \Delta H_{\mathrm{acid}}[\mathrm{Cp^*Mn(CO)_3}] - \mathrm{IP[H]}$$

$D[\mathrm{H{-}CH_2C_5H_4Mn(CO)_3^-}]$ is the C−H bond strength in the methyl group on the cyclopentadienyl ligand on the anion, and IP[H] = 313.6 kcal mol^{-1} is the ionization potential of the hydrogen atom. Using our electron affinity, we estimate that the C−H bond dissociation energy is between 30.9 and 69.9 kcal mol^{-1} (2.2 ± 0.8 eV).

This range for the C−H bond strength in the methyl group of the Cp* ligand is consistent with the notion that the methylated ligand is electron donating with respect to the manganese center. As electron density is moved toward the metal, the C−H bond on the methyl group will weaken. This is seen in a comparison of the C−H bond strengths[21] in methane ($D[\mathrm{H_3C{-}H}] = 104.1$ kcal mol^{-1}]) and toluene ($D[\mathrm{C_6H_5CH_2{-}H}] = 85$ kcal mol^{-1}]) with our value of 50.5 ± 19.5 kcal mol^{-1} for removal of a hydrogen from the methyl group of the Cp* ligand in Cp*Mn(CO)$_3^-$.

Conclusion

The 355 and 532 nm fixed-frequency negative-ion photoelectron spectra of the tricarbonyl(η^5-methylcyclopentadienyl)manganate(0) anion, Cp*Mn(CO)$_3^-$ are discussed in this paper. From the high electron kinetic-energy threshold in these spectra, we are able to infer that the adiabatic electron affinity of tricarbonyl(η^5-methylcyclopentadienyl)manganese(I), Cp*Mn(CO)$_3$, is 0.5 ± 0.1 eV and that the vertical ionization potential of the corresponding anion is 1.0 ± 0.1 eV. The low electron affinity measured for Cp*Mn(CO)$_3$ is consistent with a 19-electron formulation for Cp*Mn(CO)$_3^-$. By combining our electron affinity results with literature gas-phase acidity estimates for Cp*Mn(CO)$_3$, we determine that the C−H bond dissociation energy, $D[\mathrm{H{-}CH_2C_5H_4Mn(CO)_3^-}]$, in the anion may be bracketed between 2.2 ± 0.8 eV.

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