Gas-Phase Photofragmentation of $Co_3(CO)_9CCH_3$

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The gas-phase photodissociation of $Co_3(CO)_9CCH_3$ in the visible and near-ultraviolet spectral regions is investigated by using laser photodissociation/multiphoton ionization techniques. The fragments observed upon photolysis are cobalt–carbon clusters free of terminal carbonyl ligands. Significant changes in the distribution of photofragments are observed as a function of photolysis wavelength with the trend likely correlated with the nature of the initially excited electronic state of $Co_3(CO)_9CCH_3$.

Introduction

The study of metal–cluster complexes has yielded extensive information on the nature of metal–metal bonds.[1] Some metal–cluster carbonyls, such as those containing the triangular tricobalt cluster, involve non-metal atoms forming symmetric bridges across metal atoms of the cluster. A notable example is the class of methinyltricobalt enneacarbonyls ($Co_3(CO)_9CY$) which is built on a tetrahedral Co_3C unit. The bonding of a carbon atom to three cobalt atoms forming a pyramidal core gives these compounds unique properties and unusual stability. Interest in $Co_3(CO)_9CY$ complexes is linked to the expectation that they, as well as their fragments, could have important catalytic properties.[2,3] In addition, the bonding pattern in these complexes has been proposed as a model for chemical adsorption of a molecule CY attached to a surface.[4]

The nature of bonding in such a molecule can, in principle, be investigated by spectroscopic methods. However, like many transition-metal–carbonyl complexes where excited-state lifetimes are shortened by chemical processes, the methinyltricobalt enneacarbonyls display diffuse and congested spectra from which very little direct structural information can be obtained. Photoelectron experiments and molecular-orbital calculations have yielded some insight about the nature of several filled molecular orbitals.[4-7] In contrast, little is known about the chemically important first several excited states which govern the photochemistry in the visible and near-ultraviolet regions. The first excited state is, however, thought to be Co–Co antibonding in character.[5] When in the presence of CO and/or H_2 in solution, complexes of $Co_3(CO)_9CY$ (Y = H or CH_3) are photolyzed to yield $Co_4(CO)_{12}$ and $Co_2(CO)_8$ for photolytic wavelengths under 500 nm.[8] This fact was interpreted as indicating that the predominant photochemical pathway in solution is the breaking of the Co_3C core framework, in keeping with the assumed antibonding nature of the excited state involved in the first electronic absorption.[5]

We report here the results of studies we have undertaken on the photodissociation in the gas phase of a representative member of this class, $Co_3(CO)_9CCH_3$ (nonacarbonyl-μ_3-ethylidynetri, -*triangulato* cobalt, registry no. 13682-04-7). The technique employed uses photofragmentation of the parent compound followed by multiphoton-ionization (MPI) detection of the photofragments.[9] This technique is notable for its high sensitivity. Metal carbonyls generally have high absorption cross sections in the near-ultraviolet and blue regions of the spectrum. In addition, these metal-containing compounds generally photofragment with near unit efficiency. When coupled with highly sensitive ion-counting techniques, a compound with even a very low vapor pressure such as this one may be studied.

Experimental Section

The apparatus employed here is similar to that described previously.[10] The output of a focused excimer laser (Lambda Physik EMG101) was used either directly on the 337 nm N_2 line or at 308 nm to pump a dye laser (Lambda Physik FL2000) operated at 450 nm. The laser output was directed into the middle of the ionization region of a time-of-flight mass spectrometer. Laser-power densities were on the order of 10^6–10^8 W/cm^2 and were varied by adjusting the position of a focusing lens. Ions were detected by a channel-electron multiplier (De Tech 400). The signal was amplified 100-fold (Pacific Instruments 2A50), digitized (LeCroy WD8256), and stored in a microcomputer. The sample was introduced passively into the vacuum chamber through a pinhole near the time-of-flight region. Typical operating conditions had a compound pressure in the chamber of about 10^{-5} Torr. Mild heating of up to 100 °C was used for improvement of signal intensities. The electronic absorption spectrum of $Co_3(CO)_9CCH_3$ at 77 K in an EPA solution consists of two broad, structureless bands with peaks centered at 360 and 475 nm.[8] In the experiments described here, the molecule is excited into one or the other of these electronic bands in a one-photon step and, in a multiphoton step, fragmented and ionized to produce the observed ions.

Results and Discussion

The fragments observed upon excitation of $Co_3(CO)_9CCH_3$ at 337 nm are Co_3CCH^+, Co_2CCH^+, $CoCCH^+$, Co_3C^+, Co_2C^+, CoC^+, Co_3^+, Co_2^+, and Co^+. At 450 nm, only three ions are observed: CoC^+, Co_2^+, and Co^+. Additional results at 308 nm were obscured by significant background ionization at that wavelength; however, the basic trends observed at 308 nm closely matched the fragmentation pattern at 337 nm. As with other metal compounds, no fragments retaining carbonyl ligands were observed, presumably because such unsaturated carbonyls are themselves very labile and decarbonylation competes efficiently with MPI. These basic ionization patterns persisted throughout the range of photon fluxes that were used.

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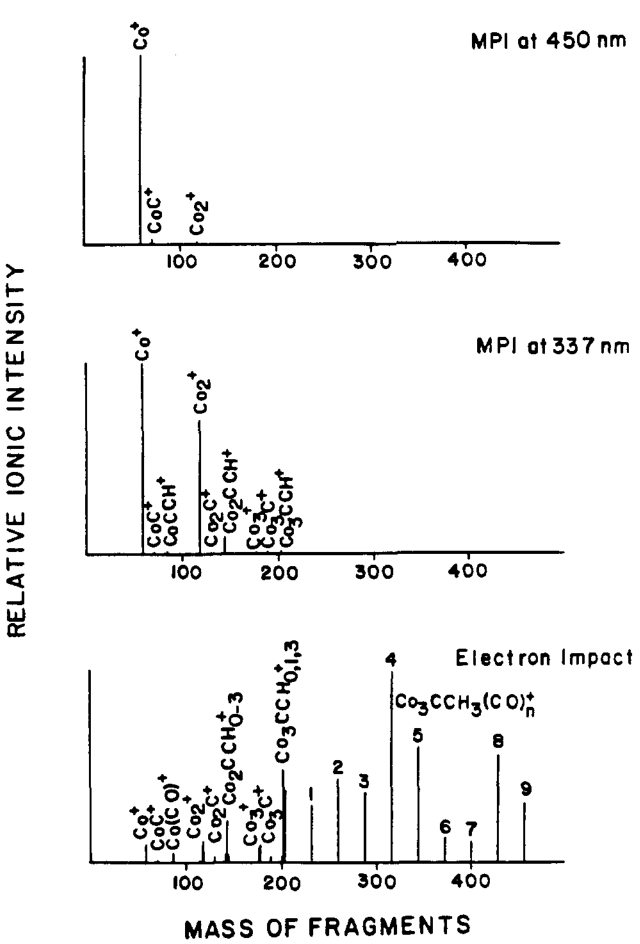

Figure 1. The fragmentation patterns for $Co_3(CO)_9CCH_3$ from multiphoton ionization at 450 and 337 nm are compared to that from electron impact at 70 eV.[11]

There were small changes in the relative intensities of the ions observed as the flux was changed, but the ionic patterns obtained in photolyzing at 337 and 450 nm were quite distinct with the results of photolyzing at 337 nm favoring a greater degree of retention of the Co_3 core compared to photolysis at 450 nm. Typical fragmentation patterns are shown in Figure 1 compared with a typical electron-impact (EI) mass spectrum at 70 eV.[11]

MPI studies of transition-metal carbonyls[9,10] have indicated that, following excitation, neutral fragments are generated. In the case of $Co_3(CO)_9CCH_3$, this fragmentation pathway is supported by the differences between the MPI and EI spectra as shown in Figure 1. Hence the neutral fragments that are produced following the initial absorption into the electronic state of the parent are ionized only in later steps in the multiphoton process. Primary fragments cannot be identified in the MPI technique since further fragmentation among transition-metal neutral fragments as well as among ions[12] is possible as more photons are absorbed. The ionic fragments that are ultimately observed merely identify the major branching patterns followed in the photofragmentation by identifying which bonds within the core structure have been preserved.

The range of ions produced in the electron-impact fragmentation[11] is much greater than that obtained by MPI in that nearly all possible CO fragments are observed. While MPI generally produces ions of low mass only, electron impact yields ions throughout the possible range and is dominated by the loss of carbonyl ligands from the parent. Using electrons with a much greater energy than any molecular electronic state leads to a process that favors parent ionization followed by fragmentation. In contrast, MPI processes in metal carbonyls lead to a rapid dissociation into neutral fragments after the first photon accesses a molecular energy level.

For the photolytic wavelength of 450 nm, we observe extensive destruction of the Co_3 core with only the smallest cobalt fragments CoC^+, Co_2^+, and Co^+ being observed. This is consistent with the antibonding description for the electronic state involved and the interpretation of the solution-photochemistry experiment.[8] However, when the photolysis wavelength is changed to 337 nm, fragments such as Co_2^+ and Co_2CCH^+ in addition to Co^+ predominate in the mass spectrum, with other fragments also retaining the Co_3C core unit being present at lower intensities; this distinction persists throughout a wide range of photon densities investigated. The higher degree of retention of the Co_3C central core in this case suggests a photolytic event destabilizing the ligand-core structure, indicating that the character of the state that is accessed at 337 nm is not predominantly antibonding in character between the cobalt atoms.

An important driving force for understanding the photofragmentation of these molecules is aimed at the design of photochemical synthesis of novel and reactive materials through the control of wavelength and molecular precursors. The gas-phase photofragmentation of $Co_3(CO)_9CCH_3$ shows a marked wavelength dependence giving the experimentalist access to a range of unique and very interesting unsaturated metal–metal and metal–non-metal fragments such as the bare pyramid Co_3C^+ and most likely the neutral analogue as well. Thus, with the selection of the proper precursor and laser wavelength, it is possible to produce a wide range of interesting gas-phase species such as Co_n^+, Co_nC^+, and Co_nCCH^+ (n = 1–3). Their production may be exploited in future studies of the photochemistry, reactivity, and spectroscopy of small metal clusters.

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