that benzene is much more likely to decompose than to desorb as the temperature is raised (only about 2% desorb intact):[8] this indicates that the tightly bound benzene will more likely distort and break its π-ring stabilization than remain intact. Also, coadsorption of potassium, a net electron donor, decreases the likelihood of decomposition, at least on Pt(111).[35] Therefore, we may tentatively propose that coadsorption of CO, a net electron acceptor, would enhance the decomposition of benzene by favoring distortion. Furthermore, a detailed analysis[36] of the benzene decomposition products upon heating on Rh(111) (namely –CH and –CCH species) favors acetylene as an intermediate product, even if short-lived.

Rh, unlike Pd, does not catalyze the conversion of acetylene to benzene. Whereas such a reaction has been observed on Pd(111),[3] it was not seen on the Rh(111) single-crystal surface. It is, however, most encouraging that the benzene-to-acetylene conversion appears to have been observed recently for the first time:[4] indeed, Raman spectroscopy detected acetylene formation after benzene adsorption on supported Rh particles in the presence of coadsorbed CO in an ultra-high vacuum cell.

Hopefully, structural results such as ours for benzene on Rh(111) and others in preparation on Pt(111) and Pd(111) will help clarify the mechanisms of this reaction.

5. Conclusions

We have made the first structural analysis of a molecular coadsorbate system. It is characterized by mutual ordering and site shifting of the coadsorbate species, benzene and CO. We have found the first confirmed hollow-site adsorption of CO on a single-crystal surface, with bond lengths that are quite consistent with comparable bond lengths in metal–carbonyl clusters.

The benzene is also hcp-hollow-sited and its carbon ring exhibits a strong Kekulé-type distortion and an expansion. This result may be connected with the mechanisms of acetylene–benzene interconversion reactions on metal catalysts.

We have recently also analyzed[37] the Rh(111)–(3 × 3)–C_6H_6 + 2CO system with LEED intensities. It differs from the Rh(111)–$\left(\begin{smallmatrix}3&1\\1&3\end{smallmatrix}\right)$–$C_6H_6$ + CO system described here mainly in the presence of two rather than one CO molecules per unit cell. The structural results are essentially identical: hcp hollow sites for benzene and CO and the same Kekulé distortion for benzene. The optimal numerical values for the bond lengths are somewhat different: short and long C–C bond lengths of 1.48 ± 0.15 and 1.58 ± 0.15 Å, respectively. This agreement, using totally independent LEED data bases, gives additional confidence in our results.

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Registry No. C_6H_6, 71-43-2; CO, 630-08-0; Rh, 7440-16-6.

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(34) Dubois, L. H.; Castner, D. G.; Somorjai, G. A. *J. Chem. Phys.* **1980**, *72*, 5234.

(35) Garfunkel, E. L.; Maj, J. J.; Frost, J. C.; Farias, M. H.; Somorjai, G. A. *J. Phys. Chem.* **1983**, *87*, 3629. Crowell, J. E., Ph.D. Thesis, University of California, 1984.

(36) Koel, B. E.; Crowell, J. E.; Bent, B. E.; Mate, C. M.; Somorjai, G. A., unpublished results.

(37) Koestner, R. J.; Lin, R. F.; Blackman, G. S.; Kao, C. T.; Van Hove, M. A.; Somorjai, G. A., unpublished results.

Gas-Phase Photodissociation of $FeCH_2^+$ and $CoCH_2^+$: Determination of the Carbide, Carbyne, and Carbene Bond Energies

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Abstract: Photodissociation of MCH_2^+ (M = Fe, Co) is observed to yield three products M^+, MC^+, and MCH^+. This result is in contrast to the low-energy collision-induced dissociation of MCH_2^+, which yields M^+ exclusively. From the photoappearance thresholds of the products, the following bond energies are assigned: $D°(Co^+{-}CH_2) = 84 \pm 5$ kcal/mol, $D°(Co^+{-}CH) = 100 \pm 7$ kcal/mol, $D°(Co^+{-}C) = 90 \pm 7$ kcal/mol, $D°(Fe^+{-}CH_2) = 82 \pm 5$ kcal/mol, $D°(Fe^+{-}CH) = 101 \pm 7$ kcal/mol, and $D°(Fe^+{-}C) = 94 \pm 7$ kcal/mol. Compared to the results of an earlier ion-beam study, the $Co^+{-}CH_2$ bond energy reported here is in excellent agreement while the $Fe^+{-}CH_2$ value is significantly lower.

The transition metal–ligand chemical bond has been described as being the key to linking organometallic chemistry, surface chemistry, and catalysis.[1] In particular, metal–ligand bond energies provide a means of assessing whether a proposed reaction pathway is energetically feasible. We recently reported that photodissociation shows promise as a method for obtaining this information,[2] complementing the growing number of theoretical[3] and experimental[4] techniques.

In order for an ion to photodissociate, process 1, first the ion

$$AB^+ + h\nu \rightarrow A^+ + B \qquad (1)$$

must absorb a photon, second the photon energy must exceed the enthalpy for the reaction, and third the quantum yield for photodissociation must be non-zero.[5,6] Because of these requirements, thresholds observed in the photodissociation spectrum are governed

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(1) Schaefer, H. F., III *Acc. Chem. Res.* **1977**, *10*, 287.

(2) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176.

(3) (a) Alvarado-Swaisgood, A. E.; Allison, J.; Harrison, J. F. *J. Phys. Chem.* **1985**, *89*, 2517. (b) Shim, I.; Gingerich, K. A. *J. Chem. Phys.* **1982**, *77*, 2490. (c) Harris, J.; Jones, R. O. *J. Chem. Phys.* **1979**, *70*, 830.

(4) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Ervin, K.; Loh, S. K.; Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1983**, *87*, 3593. (c) Morse, M. D.; Smalley, R. E. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 228. (d) Murad, E. *J. Chem. Phys.* **1983**, *78*, 6611.

(5) Freiser, B. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3136.

(6) Orth, R. G.; Dunbar, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 5617.

0002-7863/86/1508-2537$01.50/0

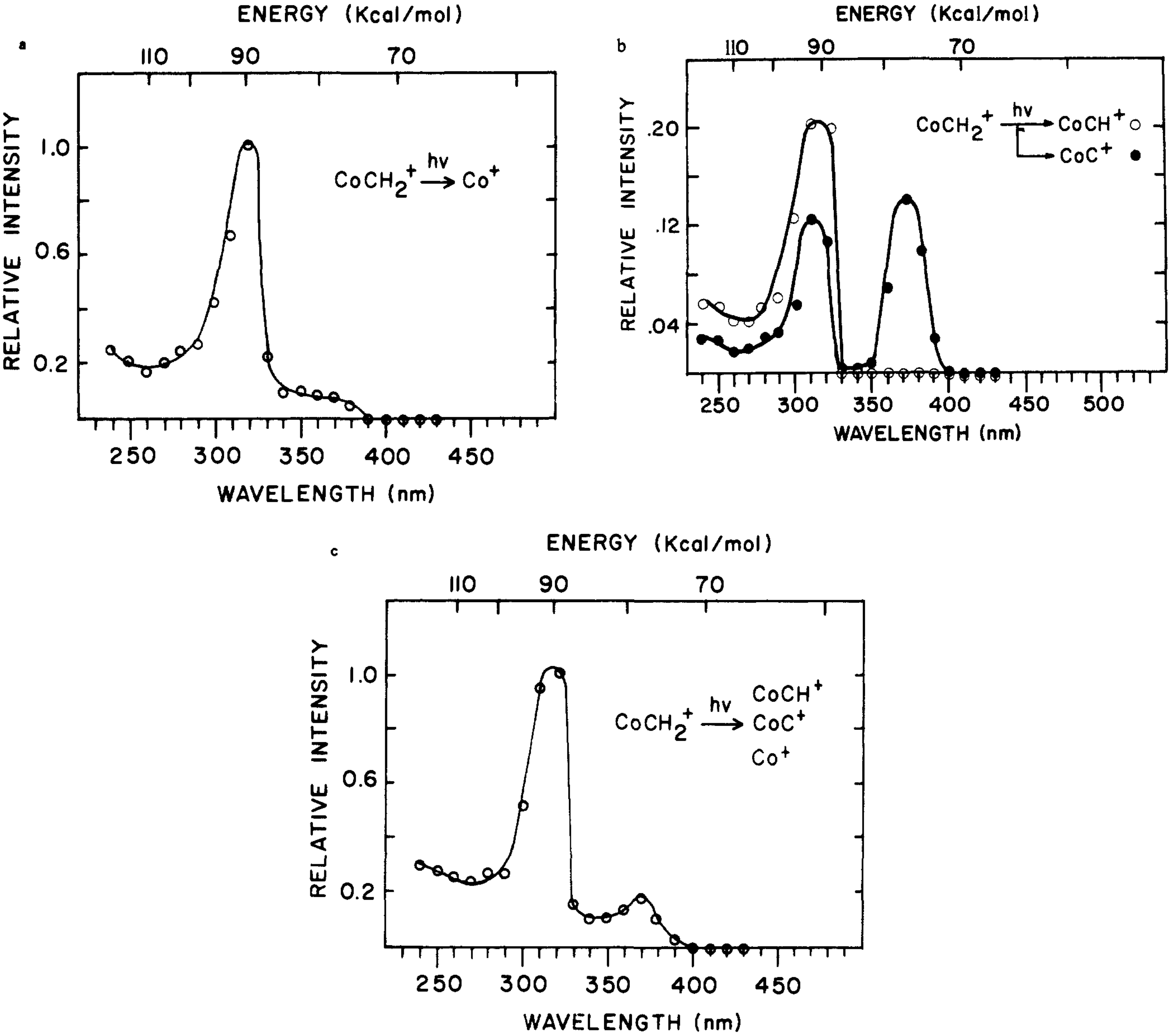

Figure 1. (a) The photoappearance spectrum of Co^+ obtained by monitoring reaction 3 as a function of wavelength at a pressure of 1×10^{-6} torr of argon. All spectra shown here are averages of four separate trials to verify peak positions and peak heights. (b) The photoappearance spectra of $CoCH^+$ (open circles) and CoC^+ (closed circles) obtained by monitoring reactions 4 and 5, respectively, as a function of wavelength at 1×10^{-6} torr of argon. The relative intensity of these photoproducts has been scaled relative to the photoappearance of Co^+ in spectrum a, which was assigned to be 1.0 at 320 nm. (c) The photodissociation spectrum of $CoCH_2^+$ obtained by monitoring the appearance of all three photoproducts (reactions 3–5) as a function of wavelength at 1×10^{-6} torr of argon.

either by thermodynamic or by spectroscopic factors. A spectroscopically determined threshold (determined by ion absorption) yields an upper limit to the reaction enthalpy, whereas a thermodynamically determined threshold (determined by bond strength(s)) by definition can provide an absolute reaction enthalpy. Preliminary studies on a variety of simple metal ion–ligand complexes[2,7] and metal dimer ions[8] suggest that these species absorb over a broad wavelength region, yielding thermodynamically determined thresholds from which absolute bond energies can be obtained.

Transition metal–carbene ions have been the focus of several recent gas-phase studies[9-12] and are of interest due to the role that metal–carbenes play as intermediates in a number of important catalytic transformations. In particular, experimental values of $D°(Fe^+–CH_2) = 96 \pm 5$ kcal/mol and $D°(Co^+–CH_2) = 85 \pm 7$ kcal/mol, determined with an ion beam instrument, have been reported.[10] More recently, ion-molecule reaction studies have suggested that $D°(Fe^+–CH_2)$ may be between 77 and 87 kcal/mol.[11] The photodissociation of MCH_2^+ (M = Fe, Co) was, therefore, examined in an effort to obtain values for the bond energies as well as spectral information about the metal–carbene ions.

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer[13] equipped with laser ionization for generating metal ions.[14] The 5.2 cm cubic cell, which is situated between the poles of a Varian 15-in. electromagnet maintained at 0.85 T, utilizes

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(7) Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.*, in press.

(8) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 6222.

(9) (a) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2584. (b) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449.

(10) $D°(Fe^+–CH_2)$ from: Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501. $D°(Co^+–CH_2)$ from: Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.

(11) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 2605.

(12) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4373.

(13) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

(14) Burnier, R. C.; Byrd, G. D.; Carlin, T. J.; Wise, M. B.; Cody, R. B.; Freiser, B. S. *Lecture Notes in Chemistry*; Wanczek, K. P., Ed.; Springer-Verlag: West Germany, 1982.

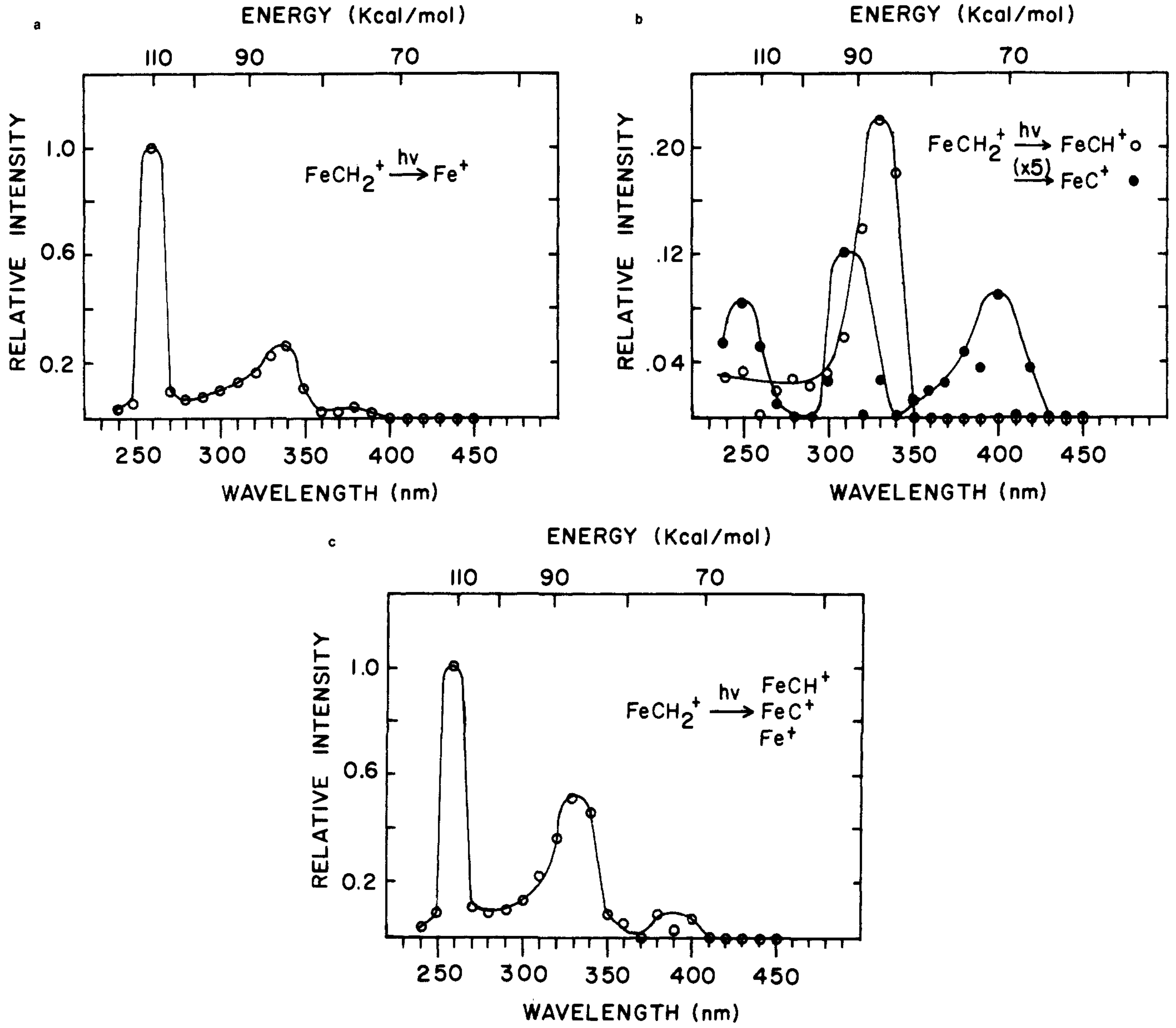
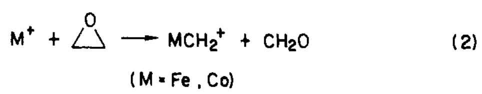


Figure 2. (a) The photoappearance spectrum of Fe^+ obtained by monitoring reaction 3 as a function of wavelength at a pressure of 1×10^{-6} torr of argon. (b) The photoappearance spectra of $FeCH^+$ (open circles) and FeC^+ (closed circles) obtained by monitoring reactions 4 and 5, respectively, as a function of wavelength at 1×10^{-6} torr of argon. The FeC^+ spectrum has been multiplied by a factor of 5. The relative intensity of these photoproducts has been scaled relative to the photoappearance of Fe^+ in spectrum a, which was assigned to be 1.0 at 260 nm. (c) The photodissociation spectrum of $FeCH_2^+$ obtained by monitoring the appearance of all three photoproducts (reactions 3–5) as a function of wavelength at 1×10^{-6} torr of argon.

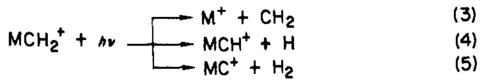
two 80% transmittance stainless steel screens as the transmitter plates in order to permit irradiation of the trapped ions.[2] $FeCH_2^+$ and $CoCH_2^+$ were synthesized, as shown in reaction 2 by pulsing in ethylene oxide,[15,16] and then trapped for 4–5 s. During this time they were irradiated with


$$M^+ + C_2H_4O \longrightarrow MCH_2^+ + CH_2O \quad (2)$$
(M = Fe, Co)

a 2.5 kW Hg-Xe arc lamp used in conjunction with a 0.25-m Schoeffel monochromator set for 10-nm resolution. The concentration of the ions in the cell at $\sim 10^{-18}$ M precludes monitoring the absorption spectrum directly. The photodissociation spectrum is obtained by monitoring the fragmentation of the MCH_2^+ ions as a function of wavelength. Poor reproducibility of the laser (shot-to-shot variation) made monitoring the disappearance of the parent ion impractical. Because of this, the ratio of ion photoproduct intensities to parent ion intensity is monitored as a function of wavelength.[7] To obtain absolute values for the cross sections of the ions being examined, the photodissociation of $C_7H_8^+$ (from toluene at 20 eV) at 410 nm (σ(410 nm) = 0.05 A^2)[17] was compared to the photodissociation of a given ion at its λ_{max}, both taken under similar experimental conditions. All cross sections determined in this manner have an estimated uncertainty of ±50% due to instrumental variables.

Results and Discussion

Photodissociation of MCH_2^+ yields three products, reactions 3–5, in direct contrast to low-energy (0–100 eV) collision-induced


$$MCH_2^+ + h\nu \longrightarrow \begin{cases} M^+ + CH_2 & (3) \\ MCH^+ + H & (4) \\ MC^+ + H_2 & (5) \end{cases}$$

dissociation which results in exclusive cleavage of CH_2 to form M^+.[18] This interesting difference, which is being further investigated, may arise due to the kinetics of the dissociation processes or due to the difference of adding vibrational vs. electronic excitation. Figure 1a shows the photoappearance spectrum of Co^+

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[15] Ethylene oxide was pulsed into the cell to provide a lower background pressure during the trapping time. For details of the pulsed valve operation, see: Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

[16] Photodissociation of MCH_2^+ produced by reaction of M^+ with cycloheptatriene (Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 67) gave identical spectra to the MCH_2^+ produced by reaction 2.

[17] Dunbar, R. C. *Chem. Phys. Lett.* **1975**, *32*, 508.

[18] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 5870.

(process 3);[19] Figure 1b shows the photoappearance spectra of $CoCH^+$ and CoC^+ (processes 4 and 5); and Figure 1c shows the overall photoappearance spectrum combining all three photoproducts. Figure 1c indicates that $CoCH_2^+$ has photodissociation maxima at 320 ± 10 nm ($\sigma = 0.05$ A^2) and 370 ± 10 nm with a threshold at 400 ± 10 nm.

The threshold at 390 nm in Figure 1a for the photoappearance of Co^+ implies $D°(Co^+-CH_2) = 73 \pm 5$ kcal/mol. This value is unreasonably low, however, since observation of reaction 2 requires $D°(Co^+-CH_2) > 78$ kcal/mol.[20,21] Adding argon and raising the pressure from 1×10^{-8} to 1×10^{-6} torr decreases dissociation in the tail region (340–390 nm) while slightly enhancing dissociation from 240–330 nm. The significant pressure quenching of the tail region might indicate the presence of internally or kinetically excited $CoCH_2^+$ ions. Alternatively, a multiple photon process is believed to be less likely but cannot be completely ruled out.[22] Presumably, a sufficiently high pressure of Ar would, in any event, completely quench the tail, but reduced trapping efficiency precluded doing this experiment. The wavelength at which Ar begins to reduce the photoappearance of Co^+ and which corresponds to the extrapolated onset of the absorption band ($\lambda_{max} = 320$ nm) is about 340 nm. Assuming this to be the cutoff for the ground-state ions (or single photon process) yields $D°(Co^+-CH_2) = 84 \pm 5$ kcal/mol, consistent with a previously reported value $D°(Co^+-CH_2) = 85 \pm 7$ kcal/mol,[10] and $\Delta H_f°(CoCH_2^+) = 292 \pm 7$ kcal/mol.[20]

Figure 1b shows the photoappearance spectra of $CoCH^+$ and CoC^+, both taken at a pressure of 1×10^{-6} torr of argon.[23] The sharp cutoff for the appearance of $CoCH^+$ at 340 nm yields $D°(CoCH^+-H) = 84 \pm 5$ kcal/mol from which $\Delta H_f°(CoCH^+) = 324 \pm 7$ kcal/mol and $D°(Co^+-CH) = 100 \pm 7$ kcal/mol are derived. The threshold for the appearance of CoC^+ at 400 nm yields $D°(CoC^+-H_2) = 71 \pm 5$ kcal/mol from which $\Delta H_f°(CoC^+) = 363 \pm 7$ kcal/mol, $D°(CoC^+-H) = 91 \pm 10$ kcal/mol, and $D°(Co^+-C) = 90 \pm 7$ kcal/mol are derived.

Figure 2 shows the photoappearance spectra derived from $FeCH_2^+$ in analogy to those from $CoCH_2^+$. The cross section for photodissociation of $FeCH_2^+$ at 260 nm in Figure 2c is 0.12 Å^2. Once again the photoappearance spectrum of Fe^+ (Figure 2a) displays a pressure-dependent tail. Adding Ar decreases the photoappearance of Fe^+ in the tail region from 350 to 430 nm while enhancing the Fe^+ signal in the region from 240 to 340 nm. The latter result indicates that ground-state ions do photodissociate in the 240–340-nm region and therefore we assign a cutoff of 350 nm, yielding $D°(Fe^+-CH_2) = 82 \pm 5$ kcal/mol and $\Delta H_f°(FeCH_2^+) = 292 \pm 5$ kcal/mol. The earlier reported value of $D°(Fe^+-CH_2) = 96 \pm 5$ kcal/mol seems high on the basis of the intense photoappearance of Fe^+ at 340 nm even in the presence of argon, which requires $D°(Fe^+-CH_2) < 84$ kcal/mol.[24] The photodissociation result, however, is consistent with the 77–87-kcal/mol range suggested from ion–molecule studies.[11]

The photoappearance threshold for $FeCH^+$ at 350 nm (Figure 2b) implies $D°(FeCH^+-H) = 82 \pm 5$ kcal/mol from which $\Delta H_f°(FeCH^+) = 322 \pm 7$ kcal/mol and $D°(Fe^+-CH) = 101 \pm 7$ kcal/mol are derived. Similarly, the photoappearance threshold for FeC^+ (Figure 2b) at 430 nm gives $D°(FeC^+-H_2) = 66 \pm 5$ kcal/mol from which $\Delta H_f°(FeC^+) = 358 \pm 7$ kcal/mol, $D°(FeC^+-H) = 88 \pm 10$ kcal/mol, and $D°(Fe^+-C) = 94 \pm 7$ kcal/mol are derived.

The values determined in this study compare favorably with $D°(V^+-CH) = 115 \pm 5$ kcal/mol and $D°(V^+-C) = 88 \pm 5$ kcal/mol obtained from a separate study.[25]

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) for supporting this research and to the National Science Foundation (CHE-8310039) for continued support of the FTMS. R.L.H. would like to thank the American Cyanamid Co. for providing fellowship support.

Registry No. Fe^+, 14067-02-8; Co^+, 16610-75-6; $FeCH_2^+$, 90143-30-9; $CoCH_2^+$, 76792-07-9; ethylene oxide, 75-21-8.

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(19) Co^+ is the predominant photoproduct from $CoCH_2^+$, as is evident in the intensity axes for Figure 1 (a–c). Similar results are observed for the photodissociation of $FeCH_2^+$.

(20) All heats of formation (and other supplementary values) are taken from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6*.

(21) Reaction 2 for Co^+ was first reported by: Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819. Reaction 2 is observed for both Fe^+ and Co^+ even when a pulse of argon is admitted into the cell to collisionally cool the laser desorbed metal ions prior to reaction.

(22) For two-photon processes, see: (a) Freiser, B. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1975**, *35*, 35. (b) Orlowski, T. E.; Freiser, B. S.; Beauchamp, J. L. *Chem. Phys.* **1976**, *16*, 439.

(23) Increased argon pressure did not affect peak positions but did quench the tail in each case by 10–30 nm.

(24) A possible explanation for the high ion-beam value is poor sensitivity in the threshold region. Lower values for $D°(M^+-H)$, for example, have recently been reported with use of a new beam apparatus with improved sensitivity: Elkind, J. L.; Armentrout, P. B. *J. Chem. Phys.*, in press. Alternatively, excited state Fe^+, which is estimated to be 24% of the population under the conditions used in the ion-beam experiment, could lead to the erroneously high bond energy determination: Armentrout, P. B., private communication.

(25) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065.