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Determination of the Fe^+–OH and Co^+–OH Bond Energies by Deprotonation Reactions and by Photodissociation

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Abstract: Two complementary approaches were used to determine $D(Fe^+–OH)$ and $D(Co^+–OH)$. The first method involved obtaining the proton affinities of FeO and CoO by monitoring the deprotonation reactions of the corresponding hydroxides with a variety of bases. The proton affinities provided the only missing pieces of information necessary in a thermochemical cycle to determine the bond energies. The second, more direct, method involved determining the threshold energies at which photodissociation of MOH^+ to M^+ and OH was observed. Reasonable agreement is observed for the two methods with values of $D(Fe^+–OH) = 77 \pm 6$ kcal/mol and $D(Co^+–OH) = 71 \pm 6$ kcal/mol obtained by proton transfer and $D(Fe^+–OH) = 73 \pm 3$ kcal/mol and $D(Co^+–OH) = 71 \pm 3$ kcal/mol obtained by photodissociation. The advantages and disadvantages of the two methods are discussed together with the possible origin of the photodissociation spectra of the two hydroxides.

In recent years several research groups have been actively involved in the study of the gas-phase reactions of atomic metal ions with organic compounds.[1] One of the important aims of this work has been to obtain information pertaining to metal–ligand bond strengths. This provides an aid, for example, in assessing whether a proposed reaction pathway is energetically feasible. In addition, these bond strengths also have relevance to organometallic chemistry, surface chemistry, catalysis, and atmospheric chemistry. Four methods which are commonly employed in determining metal–ligand bond strengths in the gas phase involve measurements of (i) ionization thresholds,[2,3] (ii) endothermic reaction thresholds,[4] (iii) ligand equilibrium,[5,6] and (iv) proton affinities.[7] In this paper, we present photodissociation[8] as an alternative approach for obtaining absolute metal–ligand bond energies.

In order to observe the photodissociation process 1, the energy of the photon absorbed must be greater than the bond dissociation energy $D(A^+–B)$. A photodissociation threshold which is spectroscopically determined (i.e., determined by where the ion absorbs) yields an upper limit to the bond dissociation energy while a photodissociation threshold which is thermodynamically determined (i.e., determined by the bond strength of the ion) may yield an absolute bond energy.[9] This method has been previously used in our laboratory, for example, to determine upper limits of $D(CpNi^+–NO) \leqslant 43 \pm 3$ kcal/mol[10] and $D(Fe^+–CO) \leqslant 43 \pm 3$ kcal/mol.[11] The $CpNi^+$–NO bond energy had been previously reported to be 41.9 ± 1 kcal/mol,[12] while our result for the Fe^+–CO bond energy supports a literature value of 37.6 kcal/mol[13] as opposed to 60.5 kcal/mol.[3] It is evident from these examples that photodissociation can provide a valuable complementary method for determining metal–ligand bond energies.

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

The species of particular interest in this study are $FeOH^+$ and $CoOH^+$, which were generated by the reaction of M^+ with nitromethane, reaction 2.[14] (The other first-row group 8 transition-metal ion, Ni^+, does not react with nitromethane.) In addition to being of interest in gas-phase metal ion reactivity studies, these bond energies are also important since metal hydroxides are believed to play roles in the atmospheric[15] and surface[16] chemistries of metals. A value of $D(Fe^+–OH) = 76 \pm 5$ kcal/mol has been previously determined by Murad[2] from electron impact threshold measurements made on FeOH generated by passing $H_2(g)$ and $H_2O(g)$ over $Fe_2O_3(s)$ in a Knudsen cell. This value serves as a check of the accuracy of the Fe^+–OH bond energy obtained in this study.

$$M^+ + CH_3NO_2 \rightarrow MOH^+ + CH_2NO \qquad (2)$$

As an additional comparison for the bond energies obtained by photodissociation, proton affinity bracketing[7] was also used to determine the M^+–OH bond energies. The proton affinity of MO can be obtained by monitoring the deprotonation reactions of MOH^+ with a series of bases. From this value, and by using other known thermodynamic values, the heat of formation of MOH^+ and thus the M^+–OH bond dissociation energy can be calculated readily by using eq 3 and 4.

$$\begin{gathered} MOH^+ \rightarrow MO + H^+ \qquad PA(MO) = \Delta H_{rxn} \\ \Delta H_f(MOH^+) = \Delta H_f(MO) + \Delta H_f(H^+) - PA(MO) \end{gathered} \qquad (3)$$

$$\begin{gathered} MOH^+ \rightarrow M^+ + OH \qquad D(M^+–OH) = \Delta H_{rxn} \\ D(M^+–OH) = \Delta H_f(M^+) + \Delta H_f(OH) - \Delta H_f(MOH^+) \end{gathered} \qquad (4)$$

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[1] Papers representative of groups active in the area include the following: (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7487. (b) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67. (c) Huang, S. K.; Allison, J. *Organometallics* **1983**, *2*, 883. (d) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794. (e) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.

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[11] Cassady, C. J.; Jacobson, D. B.; Wise, M. B.; Freiser, B. S., unpublished results.

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Table I. Deprotonation Reaction Data

base	proton affinity,[a] kcal/mol	direct protonation of base obsd
aniline	211.5	no
2-chloropyridine	214.8	no
3-chloropyridine	215.7	no
1-propylamine	218.5	no
pyridine	220.4	yes
3-methylpyridine	222.8	yes
4-vinylpyridine	223.2	yes
piperazine	224	yes
diethylamine	225.1	yes
2,4-dimethylpyridine	226.9	yes
triethylamine	231.2	yes

[a] All proton affinities are for 298 K and are referenced to PA(NH_3) = 205.0 kcal/mol. These values were obtained from Aue and Bowers (Aue, D. H.; Bowers, M. T. "Gas Phase Ion Chemistry;" Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9).

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 which has been previously described in detail.[17] The mass spectrometer is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell has been modified by replacing the transmitter plates with 80% transmittance screens to facilitate the photodissociation experiments. Metal ions are generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) onto a metal foil which is mounted onto one of the metal screens. Details of the laser ionization technique have been described elsewhere.[18]

The MOH^+ ions were formed by the reaction of Fe^+ and Co^+ with nitromethane (reaction 2). The nitromethane reagent gas was introduced into the vacuum chamber through a General Valve Corp. series 9 pulsed solenoid valve.[19] The pulse of reagent gas, which was concurrent with a laser pulse to generate the metal ions, filled the vacuum chamber to a maximum of approximately 10^{-5} torr and was pumped away by a high-speed 5-in. diffusion pump in approximately 250 ms. Swept double-resonance pulses[20] were then used to isolate the MOH^+. For the proton transfer reactions, the MOH^+ was then allowed to react with a static pressure (roughly 2×10^{-7} torr) of a selected base in the absence of complicating reactions with nitromethane.

For the photodissociation studies, MOH^+ was isolated and trapped for 8 s in the absence of reagent gas. During this time, the ions were irradiated with light from a 2.5-kW mercury–xenon arc lamp. Wavelength selection was made with a Schoeffel 0.25-m monochromator set for 10-nm resolution. Photodissocation curves were obtained by plotting the log of the ratio of ion intensity with light on and with light off vs. wavelength, normalizing for light intensity. Photoappearance curves were obtained by plotting the log of 1 minus the ratio of the product ion intensity to the intensity of MOH^+ with light off vs. wavelength, again after normalizing for light intensity. The photoappearance and photodissociation curves gave excellent agreement. Photodissociation thresholds were also confirmed by using cutoff filters.

All chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases.

Results and Discussion

Deprotonation Reactions. The proton affinities of FeO and CoO were determined by monitoring reaction 5 for $FeOH^+$ and $CoOH^+$ with a series of compounds of known basicity (Table I). Unfortunately, these experiments were hampered not only by competing reactions of the $FeOH^+$ and $CoOH^+$ with the bases but, in several cases, by the further reactions of the products of these competing reactions to form protonated base. Ion ejection experiments were used to determine whether MOH^+ underwent direct proton transfer to the base or indirect proton transfer through a reaction product. Even in cases where direct proton transfer occurred, however, it was never the dominant pathway. Thus, while a reasonable value for PA(MO) could be obtained (±5 kcal/mol) a highly precise assignment of the proton affinities of FeO and CoO was impossible.

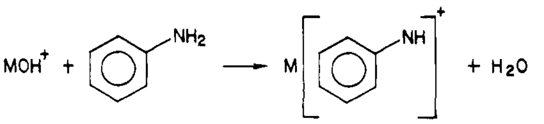
$$MOH^+ + B \rightarrow MO + BH^+ \quad (5)$$

Table II. Thermochemical Data

species	ΔH_f,[a] kcal/mol
Fe^+	280.4[b]
Co^+	282[b]
FeO	66[c,d]
CoO	74[c,e]
Fe	98.94[b]
Co	101.119[b]
O	58.983[b]
OH	9.25[b]
H^+	365.2[b]
H_2O	−57.102[b]
$CH_3CH_2NH_2$	−11.27[b,f]
$CH_3CHNH_2^+$	157[g]
$(CH_3)_2CHNH_2$	−20.02[b,f]
$(CH_3)_2CNH_2^+$	141[g]

[a] Except as noted, all values referenced to 0 K. [b] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6*. [c] Derived from $\Delta H_f(MO) = \Delta H_f(M) + \Delta H_f(O) - D(MO)$. [d] Derived by using $D(FeO) = 93 \pm 3$ kcal/mol from Murad and Hildenbrand: Murad, E. *J. Chem. Phys.* **1980**, *73*, 1381. Hildenbrand, D. L. *Chem. Phys. Lett.* **1975**, *34*, 352. [e] Derived by using $D(CoO) = 87 \pm 4$ kcal/mol from Grimley and Smoes: Grimley, R. T.; Burns, R. P.; Ingrhram, M. G. *J. Chem. Phys.* **1966**, *45*, 4158. Smoes, S.; Mandy, F.; Auwera-Mahieu, A.; Drowart, J. *Bull. Soc. Chim. Belg.* **1972**, *81*, 45. [f] Referenced to 298 K. [g] Lossing, F. P.; Lam, Y.-T.; MacColl, A.; *Can. J. Chem.* **1981**, *59*, 2228.

The pyridines and amines used in this study were found to react in a similar manner with both $FeOH^+$ and $CoOH^+$. No deprotonation was observed for aniline (PA = 211.5 kcal/mol[21]), but rather dehydration reaction 6 dominated. For the other amines, however, the major reaction pathway observed was hydride abstraction to form $(R-H)R_2N^+$, reaction 7. Thermodynamic information (Table II) suggests that formation of M and H_2O as the neutral products in reaction 7 would be exothermic, but an MH_2O complex is also possible. Thermodynamic arguments, for example, have been made for the formation of FeH_2[22] and $CoCH_4$.[23] The organic product ion, $(R-H)R_2N^+$, subsequently reacts with the amine to form protonated amine. Since the product of the secondary reaction is the same as that being monitored in reaction 5, it was difficult to bracket the proton affinity of MO by using amines. Ion ejection experiments on $(R-H)R_2N^+$ indicated that in the case of *n*-propylamine (PA = 218.5 kcal/mol[21]) direct protonation was not occurring. However, for piperazine (PA = 224 kcal/mol[21]) and diethylamine (PA = 225.1 kcal/mol[21]) it appeared that a small percentage of the MOH^+ ions (approximately 10%) was undergoing reaction 5. For triethylamine, the base with the highest proton affinity studied (PA = 231.2 kcal/mol[21]), direct deprotonation of MOH^+ could clearly be observed. Nevertheless, this pathway was still minor (approxi-



(6)

$$MOH^+ + R_3N \rightarrow (R-H)R_2N^+ + M + H_2O \text{ or } MH_2O \quad (7)$$
$$R = H, \text{alkyl}$$

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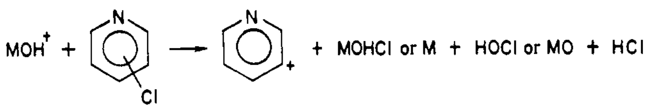
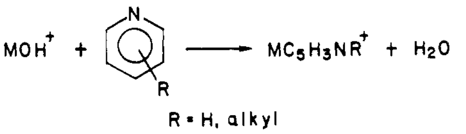
mately 30%) compared to hydride abstraction (reaction 7).

For the reactions of pyridine and substituted pyridines with $FeOH^+$ and $CoOH^+$, deprotonation was only observed with pyridine (PA = 220.4 kcal/mol[21]) and bases of greater proton affinity than pyridine. Again, even with the most basic compounds, direct proton transfer was only a minor pathway. For 2-chloropyridine (PA = 214.8 kcal/mol[21]) and 3-chloropyridine (PA = 215.7 kcal/mol[21]) no proton transfer was observed. Instead, the major process was chloride abstraction, reaction 8. None of the



(8)

other substituted pyridines were observed to undergo reactions analogous to reaction 8. Instead, pyridine and the substituted pyridines of greater basicity predominantly underwent the dehydration reaction 9. Some direct protonation was also observed.



(9)

In summary, since proton transfer only occurred for bases with proton affinities of 220 kcal/mol and greater, we assign a proton affinity of 219 ± 5 kcal/mol for both FeO and CoO. This yields $\Delta H_f(FeOH^+)$ = 212 ± 6 kcal/mol, $D(Fe^+\text{-}OH)$ = 77 ± 6 kcal/mol, $\Delta H_f(CoOH^+)$ = 220 ± 6 kcal/mol, and $D(Co^+\text{-}OH)$ = 71 ± 6 kcal/mol.[24]

Photodissociation. $FeOH^+$ photodissociates readily to give Fe^+ as the only product, reaction 10. The photodissociation spectrum of $FeOH^+$ is shown in Figure 1 together with the photodissociation spectra of $FeCO^+$ [11] and $FeC_2H_4^+$ [14] for comparison. The spectra

$$FeOH^+ + h\nu \rightarrow Fe^+ + OH \qquad (10)$$

are remarkably similar with two absorption maxima observed near 290 and 335 nm. The $FeOH^+$ spectrum, however, has a photodissociation threshold of 390 ± 10 nm while both $FeCO^+$ and $FeC_2H_4^+$ are observed to have a low intensity long wavelength absorption tail from about 400 to 700 nm. Since the $Fe^+\text{-}OH$ bond appears to be considerably stronger than both the $Fe^+\text{-}CO$ and the $Fe^+\text{-}C_2H_4$ bonds,[25] it is reasonable to assume that the cutoff observed at 390 ± 10 nm for $FeOH^+$ is a thermodynamic one. This yields an absolute bond energy $D(Fe^+\text{-}OH)$ = 73 ± 3 kcal/mol, which is in excellent agreement with Murad's[2] value of 76 ± 5 kcal/mol and the deprotonation reaction value of 77 ± 6 kcal/mol.

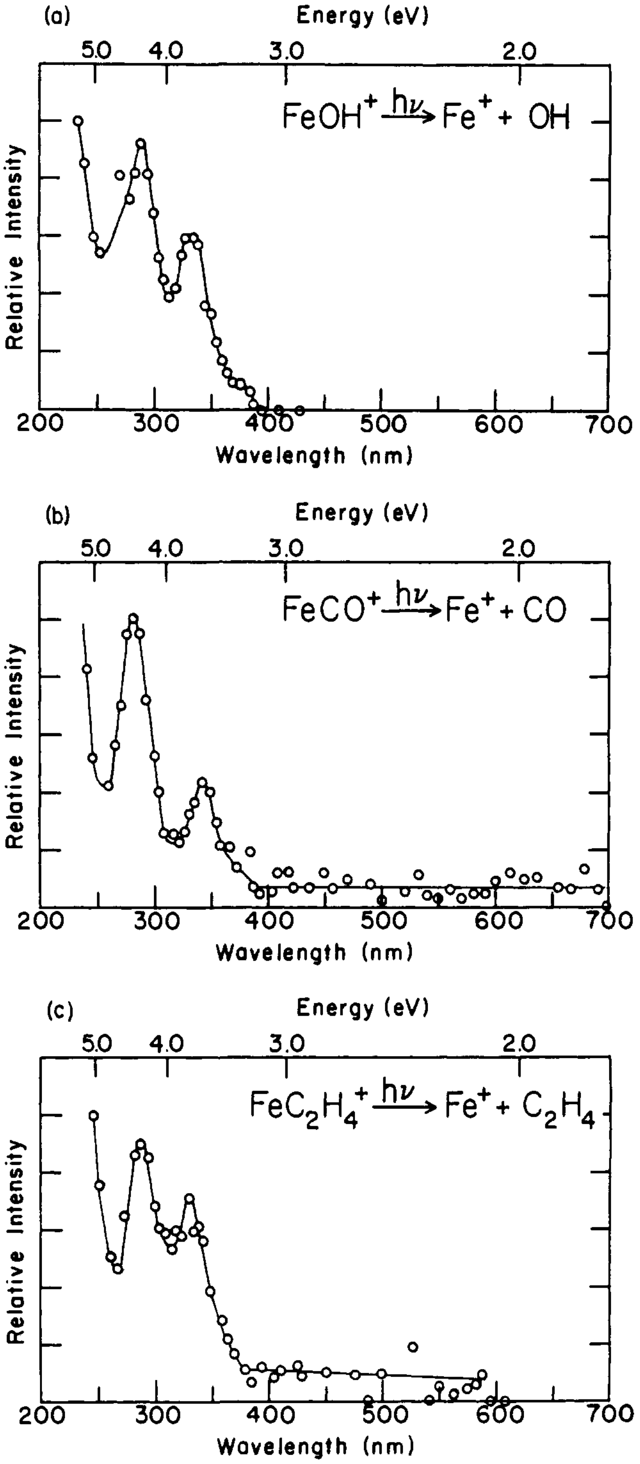


Figure 1. (a) Photodissociation spectrum of $FeOH^+$ obtained by monitoring reaction 10 as a function of wavelength at 10-nm resolution. No photodissociation at wavelengths greater than 390 nm is observed. (b) Photodissociation spectrum at 10-nm resolution of $FeCO^+$ generated by electron impact on $Fe(CO)_5$. The observation of photodissociation at wavelengths greater than 660 nm was confirmed by using a cutoff filter. A photodissociation threshold could not be determined due to the low intensity of light and of $FeCO^+$ absorption at longer wavelengths. Low light intensity also accounts for the scatter in the data at longer wavelengths. (c) Photodissociation spectrum at 10-nm resolution of $FeC_2H_4^+$ generated by the reaction of laser-desorbed Fe^+ with 1-butane. Dissociation in excess of 660 nm was observed by using cutoff filters, but it was not observed with the monochromator, possibly due to the low intensity of arc lamp light in this region.

$CoOH^+$, which was found to absorb more strongly than $FeOH^+$, photodissociates to give Co^+ as the only product, reaction 11. The photodissociation spectrum for $CoOH^+$ is shown in Figure 2 along with the photodissociation curve of $FeOH^+$ for comparison. The

$$CoOH^+ + h\nu \rightarrow Co^+ + OH \qquad (11)$$

$CoOH^+$ spectrum has an absorption maximum at 340 ± 10 nm, with the possibility of a low-intensity sideband near 375 nm. The cutoff for photodissociation is 400 ± 10 nm, which gives a $Co^+\text{-}OH$ bond energy of 71 ± 3 kcal/mol, again in excellent

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[23] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891.

[24] Our experiments were performed at an ambient temperature of ~298 K. The proton affinity values that are used in bracketing PA(MO) are referenced to 298 K, while the heats of formation which are used to calculate $\Delta H_f(MOH^+)$ and $D(M^+\text{-}OH)$ are referenced to 0 K. Since any correction for the difference between ΔH_{f0} and ΔH_{f298} would be small relative to the other errors involved in this experiment, we have chosen to make use of these values as stated in the literature with no correction for temperature.

[25] There is a discrepancy in the literature between the bond strengths of C_2H_4 and CO to Fe^+. The reported values are $D(Fe^+\text{-}C_2H_4)$ = 34 ± 2 kcal/mol (Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492) and $D(Fe^+\text{-}CO)$ = 37.6 kcal/mol (ref 13). Ligand displacement reactions, however, show that C_2D_4 readily displaces CO from $FeCO^+$ (Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808) indicating that $D(Fe^+\text{-}C_2H_4) > D(Fe^+\text{-}CO)$. Our observation of photodissociation in excess of 660 nm for both ions does not address this problem but does set an upper limit of $D(Fe^+\text{-}L) \leq 43 \pm 3$ kcal/mol for both species.

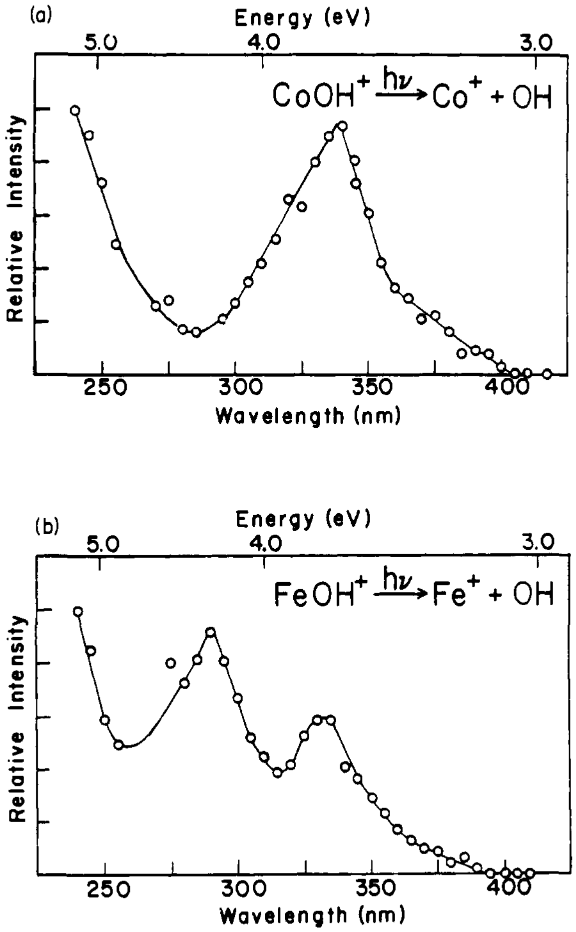

Figure 2. (a) Photodissociation spectrum of $CoOH^+$ obtained by monitoring reaction 11 as a function of wavelength at 10-nm resolution. (b) Photodissociation spectrum of $FeOH^+$ obtained by monitoring reaction 10 as a function of wavelength at 10-nm resolution.

agreement with the value obtained by deprotonation reactions.

Several possibilities exist for the assignment of the MOH^+ absorption bands. Assuming that MOH^+ is linear, d-orbital splitting could account for two absorption bands.[26] However, absorptions due to d–d transitions are generally of low intensity,[27] while $FeOH^+$ and $CoOH^+$ have reasonably intense absorptions with molar absorptivities on the order of 2000–5000 l mol^{-1} cm^{-1} determined relative to benzoyl ion.[28] The fact that little or no shift in the absorption maxima is observed between $FeCO^+$, $FeC_2H_4^+$, and $FeOH^+$ indicates that the absorption is probably not due to charge transfer. (Absorption at wavelengths less than 250 nm, however, can be assigned as charge transfer.[29]) The most probable explanation for the $FeOH^+$ and $CoOH^+$ absorption is that it arises primarily from absorption of the metal ion itself. The atomic absorption spectrum of Fe^+ has lines between 105 and 770 nm, with the most intense series of lines clustered around 240 nm and a weaker cluster around 270 nm.[30] For Co^+, which has lines from 125 to 500 nm, the most intense absorption occurs around 260 nm, with a weaker absorption maximum around 290 nm.[30] This compares favorably with the MOH^+ absorption, with shifts for ligand affects. Surprisingly, an even better agreement occurs between MOH^+ absorption and the absorption spectrum of the metal atom. The atomic spectrum of Fe has the most intense series of lines clustered around 250, 270, and 340 nm,[30] while the most intense series of lines for atomic Co is around 340 nm, with other intense clusters at 240 and 390 nm.[30] On the basis of these preliminary studies, the nature of the MOH^+ absorption bands is unclear; however, comparisons to metal atom and ion line spectra do serve to indicate that metal absorption in this region of the spectrum could account for the MOH^+ absorption bands.

Conclusion

Deprotonation reactions suggest that both FeO and CoO have a proton affinity of 219 ± 5 kcal/mol. This gives an M^+–OH bond energy of 77 ± 6 and 71 ± 6 kcal/mol for $FeOH^+$ and $CoOH^+$, respectively. These values are in good agreement with the values of $D(Fe^+–OH) = 73 \pm 3$ kcal/mol and $D(Co^+–OH) = 71 \pm 3$ kcal/mol which were obtained from photodissociation thresholds. In the $CoOH^+$ photodissociation spectrum, an absorption maximum is observed at 340 ± 10 nm. For $FeOH^+$, two absorption maxima are observed at 290 ± 10 and 335 ± 10 nm. The $FeOH^+$ absorption maxima are located within ±10 nm of the absorption maxima in the photodissociation spectra of $FeCO^+$[11] and $FeC_2H_4^+$.[14] These preliminary results seem to indicate that the bands are the result of absorption of the bare metal ion rather than due to crystal field splitting or metal–ligand charge transfer. Further studies are currently underway in our laboratory to test the validity of this statement by studying the photodissociation of a variety of metal–ligand species.

In conclusion, while in theory the use of deprotonation reactions to determine metal–ligand bond strengths appears to be a fairly straightforward procedure, in fact, these experiments may in many cases be hampered by competing reactions of the inorganic species with the base. The determination of metal–ligand bond strengths using photodissociation thresholds, however, appears to be a relatively simple technique which gives accurate results and which may be applied to many inorganic species.

Acknowledgement 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 the National Science Foundation (CHE-8002685) for providing funds for the purchase of the FTMS. In addition, one of us (C.J.C.) thanks Phillips Petroleum for providing fellowship support.

Registry No. FeO, 1345-25-1; CoO, 1307-96-6; Fe(OH), 12315-09-2; Co(OH), 12314-24-8; Fe^+, 14067-02-8; Co^+, 16610-75-6; OH^-, 14280-30-9.

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