are indicated by previous equilibrium studies involving titanium(III), thiocyanate, and chloride ions, which give the stability constants for the complexing of thiocyanate and chloride ions with titanium(III) as 1.5 ± 0.1^{26} $dm^3\ mol^{-1}$ and $0.07-0.2^{27}$ $dm^3\ mol^{-1}$ at 25 °C, respectively.

Acknowledgment. The authors appreciate the financial support from the University of Ife research committee.

Registry No. $Ru(NH_3)_5Br^{2+}$, 21388-15-8; $Ru(NH_3)_5I^{2+}$, 25483-95-8; Ti(III), 22541-75-9; Cl^-, 16887-00-6; N_3^-, 14343-69-2; SCN^-, 302-04-5.

References and Notes

(1) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).
(2) J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).
(3) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).
(4) H. Diebler and H. Taube, *Inorg. Chem.*, **4**, 1029 (1965).
(5) J. H. Espenson and R. T. Wang, *Chem. Commun.*, 207 (1970).
(6) A. Adegite, J. F. Iyun, and J. F. Ojo, *J. Chem. Soc., Dalton Trans.*, 115 (1977).
(7) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).
(8) (a) A. Ohyoshi, K. Yoshikuni, H. Ohtsuyama, Y. Yamashita, and S. Sakaki, *Bull. Chem. Soc. Jpn.*, **50**, 666 (1977); (b) T. D. Hand, M. R. Hyde, and A. G. Sykes, *Inorg. Chem.*, **14**, 1720 (1975); (c) A. McAuley and J. Hill, *Q. Rev., Chem. Soc.*, **23**, 18 (1969); (d) K. Kustin and J. Swinehart, *Prog. Inorg. Chem.*, **13**, 101 (1970).
(9) V. W. Cope, R. G. Miller, and R. T. M. Fraser, *J. Chem. Soc. A*, 301 (1967).
(10) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976).
(11) A. Haim, *Inorg. Chem.*, **7**, 1475 (1968).
(12) P. Chalilpoyil, K. M. Davies, and J. E. Earley, *Inorg. Chem.*, **16**, 3344 (1977).
(13) K. M. Davies and J. E. Earley, *Inorg. Chem.*, **17**, 3350 (1978).
(14) M. Orhanovič and J. E. Earley, *Inorg. Chem.*, **14**, 1478 (1975).
(15) K. Gleu and K. Rehm, *Z. Anorg. Allg. Chem.*, **227**, 237 (1936).
(16) N. Akinyugha, J. Ige, J. F. Ojo, O. Olubuyide, and R. Simoyi, *Inorg. Chem.*, **17**, 218 (1978).
(17) A. Adegite, J. E. Earley, and J. F. Ojo, *Inorg. Chem.*, in press.
(18) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972).
(19) T. W. Kallen and J. E. Earley, *Inorg. Chem.*, **10**, 1152 (1971).
(20) P. Chaudhuri and H. Diebler, *J. Chem. Soc., Dalton Trans.*, 596 (1977).
(21) R. L. Pecsok and A. N. Fletcher, *Inorg. Chem.*, **1**, 155 (1962).
(22) J. A. Broomhead, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 826 (1964).
(23) J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, **7**, 2519 (1968).
(24) T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973).
(25) R. T. Wang and J. E. Espenson, *J. Am. Chem. Soc.*, **93**, 380 (1971).
(26) H. Diebler, *Z. Phys. Chem. (Frankfurt am Main)*, **68**, 64 (1969).
(27) H. J. Gardner, *Aust. J. Chem.*, **26**, 2357 (1967).

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

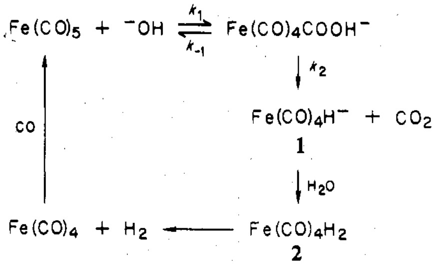
Reaction of Iron Pentacarbonyl with Oxygen-18-Enriched Hydroxide. Decarboxylation vs. Oxygen Exchange in the [Fe(COOH)] Intermediate

D. J. Darensbourg,* M. Y. Darensbourg, N. Walker,
J. A. Froelich, and H. L. C. Barros

Received December 27, 1978

Recently iron pentacarbonyl in basic media has been demonstrated to effectively catalyze the water–gas shift and hydroformylation reactions.[1-3] These processes proceed by nucleophilic attack of hydroxide ion at a carbon center in $Fe(CO)_5$ resulting in formation of the intermediate $[Fe(CO)_4(COOH)^-]$ (see Scheme I). Subsequently this species undergoes decarboxylation to afford $Fe(CO)_4H^-$ (**1**) and carbon dioxide. Protonation of **1** leads to $Fe(CO)_4H_2$ (**2**) which can sustain reductive elimination of H_2 with addition of CO to re-form $Fe(CO)_5$ or react with olefins to give products of hydroformylation.[1,4,5] Evidence for hydroxide ion attack at a metal-bound carbon monoxide ligand has been obtained from oxygen-exchange studies.[6-11]

Scheme I



We report here reactivity studies of $Fe(CO)_5$ with oxygen-18-enriched hydroxide ion in an attempt to characterize this rather interesting and important process more completely.

Experimental Section

Materials. Iron pentacarbonyl was obtained from Strem Chemicals and was purified by vacuum distillation prior to use. $H_2{}^{18}O$ (99.0% by weight oxygen-18) was obtained from Norsk Hydro (Norway).

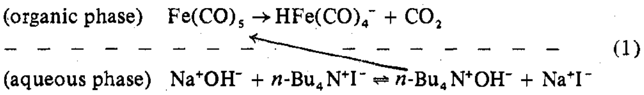
Preparation of [PPN][HFe(CO)$_4$]. The synthesis of $[PPN][HFe(CO)_4]$ was carried out in dry Schlenkware under a nitrogen atmosphere.[12] In a given run, 1.0 mmol of $Fe(CO)_5$ was dissolved in methanol and 4.0 mmol of $Na^{16}OH$ in 0.4 mL of $H_2{}^{18}O$ was added (upon equilibration the NaOH is 83.9% by weight oxygen-18). Stirring of the solution for 0.5 h and the addition of 1.0 mmol of PPNCl yielded a precipitate which redissolved in hot ethanol/ethyl acetate. Light yellow crystals were obtained upon cooling. An identical preparation of $[PPN][HFe(CO)_4]$ was performed by employing $H_2{}^{16}O$ for comparative purposes.

In order to decrease the base concentration during the synthesis of $[PPN][HFe(CO)_4]$, the reaction was carried out under phase-transfer conditions.[10] One millimole of $Fe(CO)_5$ and 0.028 mmol of $n\text{-}Bu_4NI$ in 5.0 mL of benzene were stirred vigorously with 5.0 mmol of NaOH in 0.40 mL of $H_2{}^{18}O$ (NaOH 80.8% by weight oxygen-18) for 14 h at room temperature. Volatiles were removed under vacuum (including much unreacted $Fe(CO)_5$) followed by workup as a methanol solution (vide supra) resulting in isolation of a small quantity of $[PPN][HFe(CO)_4]$.

Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear-absorbance potentiometer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}. Sodium chloride solution cells (0.1 mm) were used with the appropriate solvent in the reference cell.

Results and Discussion

The infrared spectra in the ν(CO) region of $[PPN][HFe(CO)_4]$ prepared from both oxygen-18-labeled and unlabeled aqueous NaOH are illustrated in Figure 1. Analysis of these spectra indicates that there was no significant enhancement of ν(CO) vibrations attributable to $C^{18}O$-bound ligands when the reaction was run in highly enriched $Na^{18}OH/H_2{}^{18}O$. Therefore, the rate of the intermediate, $[Fe(CO)_4COOH^-]$, proceeding to $Fe(CO)_4H^-$ and CO_2 is rapid relative to reversible loss of ^-OH with concomitant oxygen exchange. Since it has previously been noted that the process leading to metal–hydride formation, when compared with that of oxygen-exchange, can be accelerated as a function of the added base concentration,[11] it was of interest to carry out the reaction under phase-transfer conditions where the hydroxide ion concentration is small (eq 1).[10] The large, lipophilic quaternary ion is soft in the HSAB sense,[13] thus preferring to ion-pair with the softer iodide ion instead of the hydroxide ion (i.e., the aqueous-phase reaction as written in eq 1 lies far to the left). Nevertheless, a small quantity of OH^- is transferred into the organic phase resulting in a low-yield production of



$$\begin{array}{ll} \text{(organic phase)} & Fe(CO)_5 \rightarrow HFe(CO)_4^- + CO_2 \\ \hline \text{(aqueous phase)} & Na^+OH^- + n\text{-}Bu_4N^+I^- \rightleftharpoons n\text{-}Bu_4N^+OH^- + Na^+I^- \end{array} \qquad (1)$$

0020-1669/79/1318-1401$01.00/0 © 1979 American Chemical Society

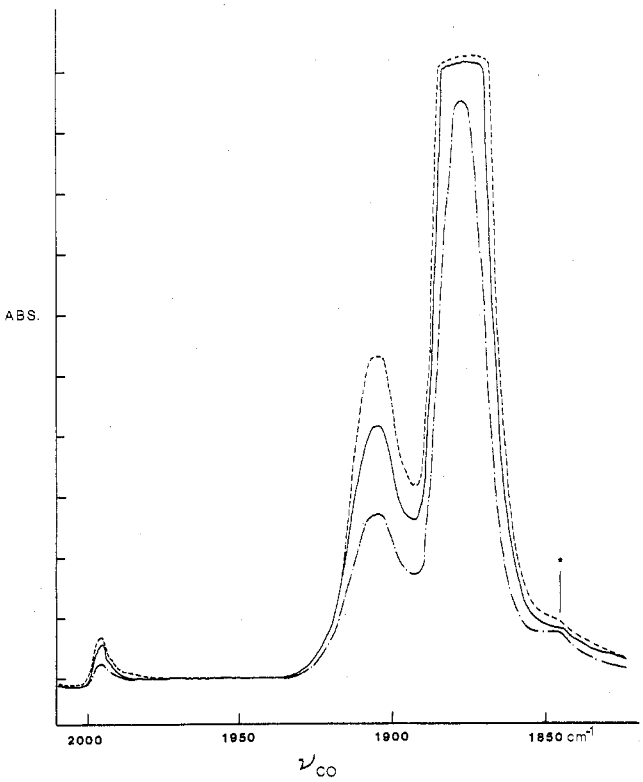


Figure 1. Infrared spectra in the ν(CO) region of [PPN][$HFe(CO)_4$] in tetrahydrofuran: —, prepared from $Na^{16}OH$; - - -, prepared from $Na^{18}OH$; –·–, prepared from $Na^{18}OH$ under phase-transfer conditions. Peak marked by asterisk corresponds to a mono-$C^{18}O$-labeled $HFe(CO)_4^-$ species (see ref 12 for the analogous ^{13}CO assignment since both $C^{18}O$ and ^{13}CO substitutions result in essentially identical ν(CO) shifts).

$HFe(CO)_4^-$ (~10%). Even under these mildly basic conditions oxygen exchange was only barely discernible (<2% oxygen-18 enrichment in $HFe(CO)_4^-$ (see Figure 1)).[14]

The consequences of these investigations clearly point out the propensity of $Fe(CO)_5$ to proceed to the anionic carbonyl hydride species $HFe(CO)_4^-$ as opposed to undergoing oxygen exchange under the conditions of the water–gas shift catalysis. This would suggest that in this catalytic system as in its $Ru_3(CO)_{12}$ analogue,[2] reductive elimination of H_2 may be the rate-determining step in hydrogen production following initial attack of ^-OH at the carbon center in $Fe(CO)_5$.

Consistent with observations made on other metal carbonyl derivatives, substitution of CO by phosphine ligands in $Fe(CO)_5$ retards metal hydride formation.[10]

Acknowledgment. Partial financial support from the National Science Foundation through Grant CHE 78-01758 for this project is greatly appreciated.

Registry No. [PPN][$HFe(CO)_4$], 56791-54-9; $Fe(CO)_5$, 13463-40-6; NaOH, 1310-73-2.

References and Notes

(1) Kang, H. C.; Mauldin, C. H.; Cole, T.; Sleigeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323.
(2) Ford, P. C.; Rinker, R. G.; Ungermann, C.; Laine, R. M.; Landis, V.; Moya, S. A. *J. Am. Chem. Soc.* **1978**, *100*, 4595.
(3) King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 2925.
(4) Species **2** is known to be a catalyst for olefin isomerization and hydrogenation.[5]
(5) (a) Sternberg, H. W.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1957**, *79*, 6116. (b) Schroeder, M. A.; Wrighton, M. S. *Ibid.* **1976**, *98*, 551.
(6) Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 1841.
(7) Darensbourg, D. J.; Drew, D. *J. Am. Chem. Soc.* **1976**, *98*, 275.
(8) Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 4726.
(9) Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5940.
(10) Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 338.
(11) Darensbourg, D. J.; Froelich, J. A. *Inorg. Chem.* **1978**, *17*, 3300.
(12) Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297.
(13) Pearson, R. G. "Hard and Soft Acids and Bases"; Dowden, Hutchinson, and Ross: Stroudsburg, PA, 1973.
(14) It would nonetheless be anticipated that as the reaction proceeds further, more highly enriched $HFe(CO)_4^-$ would be formed.

Contribution from the Lash Miller Chemical Laboratories and
Erindale College, University of Toronto,
Toronto, Ontario, Canada

The Matrix Optical Spectra of Sodium Molecules Containing from Two to Four Atoms

Geoffrey A. Ozin* and Helmut Huber

Received December 4, 1978

A thorough appreciation of small-particle chemistry and physics demands a fundamental knowledge of the size dependence of the electronic, bonding, and structural properties of metallic clusters, especially their convergence behavior toward the bulk metal.[1] Activity–selectivity patterns of high-dispersion metallic catalysts, for example, are understood to be electronic and/or geometric in origin and in principle the metallic substrate and its chemisorption characteristics can be *theoretically modeled* by finite naked clusters M_n and these clusters interacting with ligands, M_nL.[2] Particularly important directions here involve the establishment of appropriate boundary conditions for localized bonding discussions of metal–surface chemistry.[3] Recent *experimental realizations* of model "ligand-free" cluster systems can be seen, for example, in the optical ($Cr_{2,3}$,[4] $Mo_{2,3}$,[4] $Ni_{2,3}$,[5] $Cu_{2,3,4}$,[6] $Ag_{2,3,4,5,6}$,[7] Cr_2Mo,[4] $CrMo_2$[4]), Mössbauer (FeCo;[8a] FeNi;[8a] FeCu;[8a] $Sn_{2,3,4}$;[9] FeMn, Fe_2Mn, $FeMn_2$;[8b] $Fe_{2,3}$[10]), Raman ($Ag_{2,3}$,[11] Mg_2[12]), resonance Raman (Ca_2[13]), fluorescence (Sn_2,[14] Pb_2,[15] $Ag_{2,3}$[16]), and ESR (MgAg,[17] Na_3,[18] Ag_3[19]) spectral studies of a wide range of unimetallic and bimetallic molecules. With the evolution of such unique sets of spectroscopic data concerning few-atom clusters, one can appreciate the necessity for complementary, high-quality, semiempirical,[1,3] and first-principles molecular orbital cluster calculations.[3,20]

In view of the supersonic nozzle beam generation[21a] and laser photoionization mass spectroscopic detection of sodium clusters containing as many as 13 atoms[21b] (which has led to the longest known series of reliable metal cluster ionization potentials), the preparation of gaseous lithium clusters containing up to 15 atoms by evaporation of lithium metal in a high pressure of an inert gas,[22] the ESR detection of matrix entrapped Na_3,[18] the ab initio CI calculations for Na_3[23] as well as numerous other electronic structure calculations of small clusters of alkali metal atoms,[18] and our current interest in group 1A/1B bimetallic cluster systems[24] (the latter, we believe, representing a new synthetic pathway to group 1B cluster anions), we thought it worthwhile to establish the metal concentration and substrate dependence of sodium atom/inert gas condensation–aggregation processes. By employing ultraviolet–visible absorption spectroscopic monitoring of the molecular sodium aggregates so generated, we have managed to tentatively assign some of the optical excitation energies associated with $Na_{2,3,4}$. Such observations should prove to be of considerable worth in the evaluation of future IR/Raman/fluorescence/ESR/two-photon-ionization spectroscopic measurements of Na_n clusters, as well as providing stringent guidelines for assessing the reliability of various metal cluster computational techniques.