Acknowledgment. This work was supported by the National Science Foundation. Numerous helpful discussions with Dr. Jay Winkler are a pleasure to acknowledge.

---

(11) Contribution No. 6988.

(12) Present address: Los Alamos National Laboratory, Los Alamos, NM 87545.

Arthur Amos Noyes Laboratories[11]
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

Mark T. Paffett[12]
Fred C. Anson*

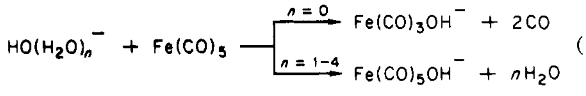
Received February 15, 1984

Generation of Metallocarboxylic Acid Anions in the Gas Phase

Sir:

We describe here the formation and reactivity of several metallocarboxylic acid anions, $M(CO)_nCOOH^-$, in the gas phase and discuss the implications of these findings for homogeneous catalysis of the water gas shift reaction (WGSR) by transition-metal carbonyls.[1-3]

As part of a larger program of study of the reactions of bare and partially solvated gas-phase ions with transition-metal compounds using the flowing afterglow method,[4] we have recently observed a remarkable effect of reactant ion hydration on the reaction between OH^- and $Fe(CO)_5$ (eq 1).[5] Bare



$$HO(H_2O)_n^- + Fe(CO)_5 \begin{cases} \xrightarrow{n=0} Fe(CO)_3OH^- + 2CO \\ \xrightarrow{n=1-4} Fe(CO)_5OH^- + nH_2O \end{cases} \quad (1)$$

hydroxide ion and each of the cluster ions shown above all react with $Fe(CO)_5$ at or near the collision rate.[6] In the former case, a coordinatively unsaturated iron tricarbonyl hydroxide ion results by expulsion of two CO ligands[7] while the hydrated species all yield a hydroxide adduct by exclusive loss of water molecules. We find this behavior to be general for several other group 6 metal carbonyls (eq 2–4). Several analogous

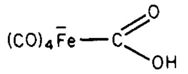
$$Cr(CO)_{3,4}OH^- \xleftarrow{n=0} HO(H_2O)_n^- + Cr(CO)_6 \xrightarrow{n=1-4} Cr(CO)_6OH^- \quad (2)$$

$$Mo(CO)_{3,4}OH^- \xleftarrow{n=0} HO(H_2O)_n^- + Mo(CO)_6 \xrightarrow{n=1-4} Mo(CO)_6OH^- \quad (3)$$

$$W(CO)_{3,4}OH^- \xleftarrow{n=0} HO(H_2O)_n^- + W(CO)_6 \xrightarrow{n=1-4} W(CO)_6OH^- \quad (4)$$

examples of solvent-induced mechanism changes in gas-phase proton-transfer and substitution reactions have been reported.[8-10] In the present case, the observed maintenance of high reaction rates with even up to *four* solvent water molecules *without* solvent retention by the product ions must be a reflection of the strongly exothermic attachment of OH^- to the metal carbonyls.[11] Indeed, the observation of a fast reaction between $OH(H_2O)_4^-$ and $Fe(CO)_5$ permits an estimate of a lower limit to $D°[Fe(CO)_5–OH^-]$ of ≥ 50 kcal/mol.[12]

Several gas-phase ion–molecule reactions of $Fe(CO)_5OH^-$ have been observed in the flowing afterglow that support a structural formulation as the iron carboxylic acid **1**. $Fe(CO)_5OH^-$ is not observed to undergo binary neutral switching type reactions with molecules possessing large permanent dipole moments (i.e., CH_3NO_2, $\mu_D = 3.86$ D)[13] such as might be expected if it were an electrostatically bound cluster ion, $[Fe(CO)_5 \cdots OH^-]$.[11,14] Furthermore, $Fe(CO)_5OH^-$ and its deuterated analogue,[5] $Fe(CO)_5OD^-$, both undergo hydrogen–deuterium exchange in the presence of carboxylic acids and H_2S (eq 5–7). We take this observation as evidence against an isomeric formate structure, $[Fe(CO)_4O_2CH]^-$, since exchange of a formyl hydrogen under these conditions is unlikely.



1

$$(CO)_4FeCOOD^- + HCO_2H \rightarrow (CO)_4FeCOOH^- + HCO_2D \quad (5)$$

$$(CO)_4FeCOOH^- + CH_3CO_2D \rightarrow (CO)_4FeCOOD^- + CH_3CO_2H \quad (6)$$

$$(CO)_4FeCOOD^- + H_2S \rightarrow (CO)_4FeCOOH^- + HSD \quad (7)$$

We therefore assign the iron carboxylic acid structure, **1**, to $Fe(CO)_5OH^-$ and, by analogy, we presume the other metal carbonyl/OH^- adducts in eq 2–4 to be anionic metallocarboxylic acids. Their occurrence as relatively stable gas-phase species has an important bearing on the continuing efforts to determine the mechanisms by which certain metal carbonyls may catalyze the water gas shift reaction in alkaline solution.[1-3] In particular, although $Fe(CO)_4COOH^-$ has been postulated as a key intermediate in WGSR catalysis by $Fe(CO)_5$,[15-17] it has never been observed directly and the exact

---

(1) Ford, P. C., Ed. "Catalytic Activation of Carbon Monoxide"; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 152.

(2) King, R. B., Ed. "Inorganic Compounds with Unusual Properties"; American Chemical Society: Washington, DC, 1979; Adv. Chem. Ser. No. 173.

(3) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685–1693 and references cited therein.

(4) All experiments were carried out in our recently constructed flowing afterglow apparatus which consists of a 100 cm × 7.6 cm i.d. ion-flow reactor with a quadrupole mass spectrometer detector (P(He) = 0.300 torr, $\bar{v} = 9100$ cm s^{-1}, $T = 300 \pm 2$ K). For general discussions of flowing afterglow, see: Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopf, A. *Adv. At. Mol. Phys.* **1969**, *5*, 1–56. Smith, D.; Adams, N. G. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, **1979**; Chapter 1.

(5) Most of the studies reported here have actually employed $DO(D_2O)_n^-$ reactant ions in order to avoid potential ambiguities arising from the equal mass-to-charge ratios for $^{35}Cl^-$ and $HO(H_2O)^-$.

(6) Measured bimolecular rate coefficients (in units of 10^{-9} cm^3 molecule^{-1} s^{-1}): 2.3 ($n = 0$); 2.3 ($n = 1$); 2.1 ($n = 2$); 1.8 ($n = 3$); 0.97 ($n = 4$).

(7) Similar reactions with $Fe(CO)_5$ and other mononuclear metal carbonyls are observed for a variety of gas-phase anions: Lane, K. R.; Sallans, L.; Squires, R. R., manuscript in preparation. For an earlier report on reactions between gaseous anions and $Fe(CO)_5$ see: Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808–4814.

(8) Bohme, D. K.; Rakshit, A. B.; Mackay, G. I. *J. Am. Chem. Soc.* **1982**, *104*, 1100–1101 and references cited therein.

(9) Bartmess, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 2483–2484.

(10) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 809–810.

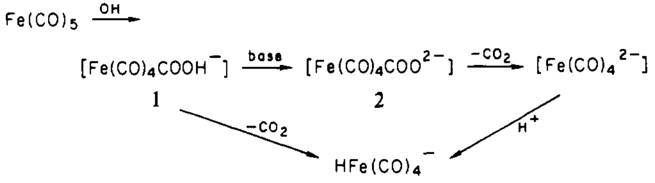
(11) Bohme, D. K. In "Ionic Processes in the Gas Phase"; Ferreira, M. A. A., Ed.; D. Reidel Publishing Co.: Dordrecht, 1984.

(12) Based upon data from: Payzant, J. D.; Yamdagni, R.; Kebarle, P. *Can. J. Chem.* **1971**, *49*, 3308–3314. Arshadi, M.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1483–1485. ($D°[4(H_2O)–OH^-] = 72.2$ kcal/mol; estimated entropy contribution of 73.9 eu for reaction 1 ($n = 4$).)

(13) McClellan, A. L. "Table of Experimental Dipole Moments"; Rahara Enterprises: El Cerrito, CA, 1979; Vol. 2.

(14) Fahey, D. W.; Bohringer, H.; Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1982**, *76*, 1799–1805.

manner in which it decarboxylates to yield $Fe(CO)_4H^-$ (eq 8) still remains controversial.[18-20]



(8)

In the early work with this system it was presumed that CO_2 loss proceeded directly from the free metallocarboxylic acid anion **1**.[15-17] However, several recent investigations[18-20] have concluded that decarboxylation requires a second equivalent of base and proceeds via dianion **2**. Our results suggest that on a millisecond time scale, *isolated* $Fe(CO)_4COOH^-$ is stable with respect to decarboxylation. This must be due to a substantial kinetic barrier to CO_2 loss since formation of $Fe(CO)_4H^-$ from $Fe(CO)_4COOH^-$ can be estimated to be slightly exothermic (ca. −17 kcal/mol).[21] Furthermore, our experiments indicate that, in the absence of bulk solvation, decarboxylation is not catalyzed by a lone water molecule nor by stronger neutral bases such as amines since $Fe(CO)_4COOH^-$ sustains many collisions with H_2O in the course of its formation and detection in our instrument and undergoes no observable reaction with Me_2NH. Additional support for the contention that decarboxylation of $Fe(CO)_4COOH^-$ requires strong-base catalysis is given by the collision-induced-dissociation (CID) spectrum of this ion, which we have obtained in our recently developed flowing afterglow–triple quadrupole apparatus.[22] Fragmentation of **1** occurs upon low-energy collisional activation by successive loss of only CO ligands *and not* CO_2 (eq 9).[23] Thus, $Fe(CO)_4COOH^-$ resists decarboxylation even when it possesses relatively large amounts of excess internal energy; i.e., the barrier for CO_2 loss exceeds that for CO loss.

$$Fe(CO)_4COOH^- \xrightarrow{CID} Fe(CO)_{5-n}OH^- + nCO \quad (9)$$

In summary, several examples of metallocarboxylic acid anions have been produced by reactions between hydroxide–water clusters and metal carbonyls in the gas phase. The previously unobserved $Fe(CO)_4COOH^-$ ion has been found to be a relatively stable species on a millisecond time scale which is resistant toward decarboxylation either when collisionally activated or when in the presence of weak neutral bases such as amines. These results corroborate previous contentions[18-20] that decarboxylation of the $(CO)_4FeCOOH^-$ intermediate in the $Fe(CO)_5$-catalyzed WGSR requires strong-base catalysis.[24] The full details of these experiments will be published elsewhere.

Acknowledgment. We gratefully acknowledge the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support in this research.

---

(15) Kang, H.; Mauldin, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323–8325.

(16) Pettit, R.; Cann, K.; Cole, T.; Mauldin, C.; Slegeir, W. *Adv. Chem. Ser.* **1979**, *No. 173*, 121–130.

(17) Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623–1628.

(18) Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* **1982**, *104*, 500–504.

(19) Darensbourg, D. J.; Froelich, J. A. *Inorg. Chem.* **1978**, *17*, 3300–3304.

(20) Bercaw, J. E.; Goh, L.; Halpern, J. *J. Am. Chem. Soc.* **1972**, *94*, 6534–6536.

(21) Based upon an upper limit to $\Delta H_f[Fe(CO)_4COOH^-] \leq -257$ kcal/mol from the occurrence of reaction 1 ($n = 4$) and an estimate for $\Delta H_f[Fe(CO)_4H^-] = -180 \pm 6$ kcal/mol: Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.*, in press. Since the measured rate of reaction 1 ($n = 4$) was large, it is reasonable to expect that reaction should also occur for even larger $OH(H_2O)_n{}^-$ reactant ions. Therefore, the actual enthalpy of decarboxylation is likely to be even more positive than the present estimate.

(22) Squires, R. R.; Lane, K. R.; Lee, R. E.; Wright, L. G.; Wood, K. V.; Cooks, R. G. submitted for publication in *J. Am. Chem. Soc.*

(23) Ion axial (kinetic) energy ca. 20 eV; argon collision gas pressure approximately 2 mtorr. We presume that loss of the first CO from the activated ion is accompanied by migratory deinsertion of hydroxyl in the metal fragment and that subsequent CO dissociations occur from $(CO)_xFe\text{–}OH^-$ ($x < 5$).

(24) During the preparation of this manuscript we became aware of a recent reinvestigation of $Fe(CO)_5$ in basic solutions that points to a base-independent pathway for $Fe(CO)_4COOH^-$ decarboxylation. It was suggested that on the time scales available in condensed-phase reactions, β elimination of CO_2 may occur through a protic solvent-catalyzed mechanism. We are grateful to Professor P. C. Ford for disclosure of these results prior to publication.

Department of Chemistry **Kelley R. Lane**
Purdue University **Larry Sallans**
West Lafayette, Indiana 47907 **Robert R. Squires***

Received March 14, 1984