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Gas-Phase Generation and Structural Characterization of the $Fe(CO_2)^+$ Cluster

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Summary: The hitherto unknown $Fe(CO_2)^+$ *cluster is conveniently available by ion–molecule reactions of "bare"* Fe^+ *with β-butyrolactone in the gas phase. By using the technique of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry, collision-induced dissociation and ligand exchange experiments are conducted and the results suggest an* $Fe^+–(CO_2)$ *structure for the cluster with a bond dissociation energy of 8 ± 2 kcal/mol. While this small binding energy is advantageous for using the* $Fe(CO_2)^+$ *cluster as an ideal precursor to generate other interesting* Fe^+ *complexes, as expected all attempts failed to bring about an* Fe^+*-mediated coupling of* CO_2 *and RH (R = H,* CH_3*) to the corresponding carbonic acids.*

Introduction

Photosynthesis, i.e. the sunlight promoted conversion of carbon dioxide and water to carbohydrates, is the most important chemical reaction on earth. However, in chemical industry only a few processes[1,2] take advantage of the excessive availability of CO_2, whose accumulation in the atmosphere also has generated major concern.[3] The reason for the failure is 2-fold in that carbon dioxide activation[2] is difficult to achieve on both thermochemical and kinetic grounds: The molecule's low heat of formation makes it a thermochemical sink, and the small polarity and polarizability confer chemical inertness to CO_2. Consequently, activation of carbon dioxide represents a challenge as important and demanding as the selective chemical transformation of alkanes. Of course, the simultaneous coupling of CO_2 with molecular hydrogen or methane (eq 1) is rightly viewed as the ultimate goal in

$$CO_2 + RH \rightarrow RCO_2H \qquad R = H, CH_3 \qquad (1)$$

CO_2 activation. Unfortunately, the formations of both formic acid (R = H) and acetic acid (R = CH_3) are endothermic by 3 and 9 kcal/mol, respectively,[4] and the successful transformation poses a scientific problem that has been met piecemeal at best.

The coordination of CO_2 to a transition metal has long been thought of as a means not only to avoid the thermochemical constraint but also to bring about catalytic conversion. Not surprisingly, this appealing concept has resulted in numerous theoretical[5] and experimental[6] studies on the properties of transition-metal carbon dioxide complexes, and there are also several reports on the attempted reactivity of these CO_2 complexes with organic molecules. While most of the experimental work is confined to reactions in solution,[7] gas-phase studies on the reactions of main group and transition-metal ions with CO_2 are relatively scarce and only recently emerging.[8] In the present article we will describe our results on the hitherto unknown $Fe(CO_2)^+$ cluster, and we will focus on the generation and characterization of $Fe(CO_2)^+$. The iron(I) cation was chosen on the ground that this transition-metal ion exhibits unique properties with regard to the *coupled* activation of molecular oxygen and C–H/C–C bonds.[9]

Experimental Section

The apparatus (a Spectrospin CMS-47 X equipped with an external ion source) and its operation have been described in detail previously.[10] The Fe^+ ion is formed via laser desorption/

[⊛] Abstract published in *Advance ACS Abstracts,* March 1, 1994.

(1) (a) Behr, A. *Chem.-Ing.-Tech.* **1985,** *57,* 893. (b) Behr, A. *Chem. Eng. Technol.* **1985,** *10,* 16.

(2) (a) Inoue, S.; Koinuma, H. *Rev. Inorg. Chem.* **1984,** *6,* 291. (b) Walther, D. *Coord. Chem. Rev.* **1987,** *79,* 135. (c) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 661. (d) Behr, A. *Carbondioxide Activation by Metal Complexes*; VCH Publishers: Weinheim, 1988. (e) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988,** *88,* 747. (f) Ayers, W. M., Ed. *Catalytic Activation of Carbon Dioxide*; ACS Symposium Series 363; American Chemical Society: Washington, D.C., 1988. (g) Galindo, A.; Pastor, A.; Pérez, D. J.; Carmona, E. *Organometallics* **1993,** *12,* 4443. (h) Reetz, M. T.; Konen, W.; Strack, T. *Chimia* **1993,** *47,* 493. (i) Leitner, W. *Angew. Chem.* **1994,** *106,* 183.

(3) (a) Williams, J., Ed. *Carbon Dioxide, Climate and Society*; IIASA Proceedings Series; Pergamon, New York, 1978, Vol. 1. (b) Lemons, J. *Environ. Sci. (Beijing)* **1985,** *28,* 60.

(4) Thermochemical data were taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* 1988, *17,* Suppl. 1.

(5) (a) Sakaki, S.; Kitaura, K.; Morokuma, K. *Inorg. Chem.* **1982,** *21,* 760. (b) Sakaki, S.; Dedieu, A. *Inorg. Chem.* **1987,** *26,* 3278. (c) Marcos, E. S.; Caballol, R.; Trinquier, G.; Barthelat, J.-C. *J. Chem. Soc., Dalton Trans.* **1987,** 2373. (d) Rosi, M.; Sgamellotti, A.; Tarantelli, F.; Floriani, C. *J. Organomet. Chem.* **1987,** *332,* 153. (e) Caballol, C.; Marcos, E. S.; Barthelat, J.-C. *J. Phys. Chem.* **1987,** *91,* 1328. (f) Sakaki, S. *J. Am. Chem. Soc.* **1991,** *112,* 7813. (g) Sodupe, M.; Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1992,** *192,* 185.

(6) For examples of this kind of complex and recent FTIR and NMR studies, see: (a) Pilato, R. S.; Housmekerides, E.; Jernakoff, P.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990,** *9,* 2333. (b) Carmona, E.; Hughes, A. K.; Munoz, M. A.; O'Hare, D. M.; Perez, J. P.; Poveda, M. L. *J. Am. Chem. Soc.* **1991,** *113,* 9210. (c) Jegat, C.; Fouassier, M.; Tranquille, M.; Mascetti, J. *Inorg. Chem.* **1991,** *30,* 1529. (d) Jegat, C.; Fouassier, M.; Mascetti, J. *Inorg. Chem.* **1991,** *30,* 1521. (e) Aresta, M.; Gobetto, R.; Quaranta, E.; Tommasi, I. *Inorg. Chem.* **1992,** *31,* 4286. (f) Jegat, C.; Fouassier, M,; Tranquille, M.; Mascetti, J.; Tommasi, I.; Aresta, M.; Ingold, F.; Dedieu, A. *Inorg. Chem.* **1993,** *32,* 1279.

(7) For examples of this kind of reaction, see: (a) Burkhart, H.; Hoberg, H. *Angew. Chem., Int. Ed. Engl.* **1982,** *21,* 76. (b) Keim, W., Ed. *Catalysis in* C_1*-Chemistry*; Reidel: Dordrecht, The Netherlands, 1983. (c) Alvarez, R.; Carmona, E.; Cole-Hamilton, D. J.; Galindo, A.; Gutierrez-Puebla, E.; Monge, A.; Poveda, M. L.; Ruiz, J. *J. Am. Chem. Soc.* **1985,** *107,* 5529. (d) Antberg, M.; Frosin, K.-M.; Dahlenburg, L. *J. Organomet. Chem.* **1988,** *338,* 319. (e) Hoberg, H.; Balleseteros, A.; Sigan, A.; Jegat, C.; Milchereit, A. *Synthesis* **1991,** 395.

(8) (a) Dheandhanoo, S.; Chatterjee, B. K.; Johnsen, R. *J. Chem. Phys.* **1985,** *83,* 3327. (b) Lessen, D. E.; Asher, R. L.; Brucat, P. J. *J. Chem. Phys.* **1991,** *95,* 1414. (c) Gregor, I. K.; Gregot, R. C. *Rapid Commun. Mass Spectrom.* **1992,** *6,* 221. (d) Yeh, C. S.; Willey, K. F.; Robbins, D. L.; Pilgrim, J. S.; Duncan, M. A. *J. Chem. Phys.* **1993,** *98,* 1867.

(9) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1420.

(10) (a) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989,** *93,* 243. (b) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990,** *112,* 621. (c) Eller, K. Ph.D. Thesis, Technische Universität Berlin, D83, 1991.

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Scheme 1

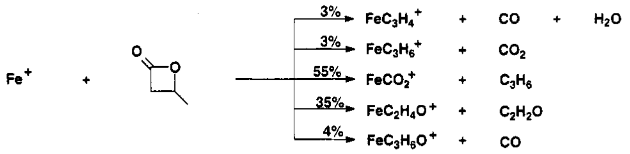

Chart 1

$Fe^+–(CO_2)$ **1** $O{=}Fe^+–CO$ **2** $C{=}Fe^+–(O_2)$ **3**

Scheme 2

$$Fe(CO_2)^+ + L \longrightarrow Fe(L)^+ + CO_2$$

$L = C_2H_4, CO, H_2O, C_3H_8, C_2H_6, CH_4, Xe$

$$Fe(CO_2)^+ + Ar \not\longrightarrow Fe(Ar)^+ + CO_2$$

Table 1. Bond Dissociation Energies (BDEs) of FeL$^+$ Complexes

ligand(L)	BDE(Fe^+–L) (kcal/mol)	ligand(L)	BDE(Fe^+–L) (kcal/mol)
C_2H_4	34.0 ± 2.0[20]	C_2H_6	15.3 ± 1.8[23]
CO	31.3 ± 1.8[21]	CH_4	13.7 ± 0.8[18]
H_2O	30.6 ± 1.2[18]	Xe	9.0 ± 2.0[21]
C_3H_8	19.0 ± 2.0[22]	Ar	7.1[24]

ionization[11] by focusing the beam of a Nd:YAG laser (Spectron systems, fundamental frequency 1064 nm) onto a stainless steel target which is affixed in the external ion source.[12] The ions are extracted from the source and transferred into the analyzer cell by a system of electrostatic potentials and lenses. After deceleration, the Fe^+ ions are trapped in the field of a superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.05 T. For the reaction of Fe^+, the metal's most abundant isotope ($^{56}Fe^+$) was isolated by using FERETS[13] and allowed to react with β-butyrolactone, which was present at a pressure of (6.5–9.6) × 10^{-9} mbar; reaction times are typically 0.25–10 s. For collisional cooling of excited states possibly formed in the generation process and the removal of kinetic energy remaining from the transfer, argon or helium was present as a buffer gas at a static pressure of (1–2) × 10^{-7} mbar. The pressure of the various gases and the β-butyrolactone were measured with an (uncalibrated) ionization gauge (Balzers IMG 070). For the collision-induced decomposition (CID)[14] and the ligand displacement[15] experiments, performed in order to obtain structural information on the $Fe(CO_2)^+$ ion, argon and the other gases were introduced in the ICR cell through a pulsed valve.[16] High resolution and double-resonance experiments were performed as described earlier,[10a,17a] and great care was applied to avoid any off-resonance excitation of the ions of interest while ejecting unwanted signals.[17b,c] All functions of the instrument were controlled by a Bruker Aspect 3000 minicomputer. Methane (99.95%), ethane (99.99%), xenon (99.99%), and carbon monoxide (99.97%) (all purchased from Linde), argon (99.999%, purchased from AGA), and propane (99.95%, purchased from Messer Griesheim) were used without further purification. β-Butyrolactone was subjected to multiple pump–freeze–thaw cycles in order to remove uncondensable gases. $^{13}CO_2$ was *on-line*-synthesized by gently warming a mixture of $Ba^{13}CO_3$ (98%, from Sigma Chemical Co.) and H_2SO_4.

Results and Discussion

When "bare" Fe^+ is reacted with β-butyrolactone, the reaction products depicted in Scheme 1 are observed. High resolution experiments demonstrate that the signal at *m/z* 100 corresponds to a doublet with the elemental compositions $Fe(CO_2)^+$ and $Fe(C_2H_4O)^+$ (intensity ratio 1.57:1).

For the structure of $Fe(CO_2)^+$ there are three basic types conceivable (Chart 1): (i) an iron–carbon dioxide cluster **1**, for which two modes of complexation (*end*-on versus *side*-on) are feasible; (ii) the iron cation inserted into the O–C bond of carbon dioxide, thus giving rise to the oxo–carbonyl structure **2**; (iii) finally, a carbide–oxygen complex **3**, in which the O_2 subunit has, again, two options (*end*-on versus *side*-on) to interact with the metal center. While an unambiguous distinction of the three connectivities **1**–**3** is possible, based on the experiments we are going to describe next, the problem of the actual coordination of CO_2 (in **1**) or O_2 (in **3**) cannot be solved experimentally with the methods presently available to us.

If $Fe(CO_2)^+$ is mass-selected and subjected to collisional activation with argon, over the entire kinetic energy regime applied, the organometallic complex exclusively decomposes to Fe^+ and CO_2. There is no indication at all for the formations of either FeO^+ or FeC^+. Consequently, neither structure **2** nor **3** is formed in the reaction of Fe^+ with β-butyrolactone (Scheme 1). This follows immediately from a consideration of thermochemical data,[4,18] as these structures are expected to give rise to FeO^+ (from **2**) and FeC^+ (from **3**), respectively. Further, when $Fe(CO_2)^+$ is reacted with $^{13}CO_2$ for 3 s, we observe a complete ligand exchange (eq 2).

$$Fe(CO_2)^+ + {}^{13}CO_2 \rightarrow Fe({}^{13}CO_2)^+ + CO_2 \qquad (2)$$

This is precisely expected to occur for a loosely bound ion–dipole cluster like **1**, but not for **2** and **3**.[19]

By employing ligand exchange reactions, we have tried to bracket the bond dissociation energy (BDE) of Fe^+–(CO_2) (**1**). As indicated in Scheme 2, ligands L (with L = C_2H_4, CO, H_2O, C_3H_8, C_2H_6, CH_4, and Xe) replace CO_2 from thermalized **1**, while in the reaction of $Fe(CO_2)^+$ with Ar no ligand exchange is observed. These results imply that BDE(Fe^+–(CO_2)) is larger than BDE(Fe^+–Ar), which is calculated to 7.1 kcal/mol,[24] and smaller than the experimentally determined binding energies of all other ligands L studied. From the data in Table 1 and the occurrence versus nonoccurrence of ligand exchange

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[11] (a) Freiser, B. S. *Talanta* **1985**, *32*, 697. (b) Freiser, B. S. *Anal. Chim. Acta* **1985**, *178*, 137.

[12] Kofel, P.; Allemann, M.; Kellerhals, Hp. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 97.

[13] Forbes, R. A.; Laukien, F. M.; Wronka, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 23.

[14] (a) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 193. (b) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96. (c) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436.

[15] Halle, L. F.; Houriet, R.; Kappes, M.; Stanley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293.

[16] (a) Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 5876.

[17] (a) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413. (b) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 257. (c) Heck, A. J. R.; de Koning, L. J.; Pinkse, F. A.; Nibbering, N. M. M. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 406.

[18] Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1993**, *97*, 596.

[19] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

[20] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492.

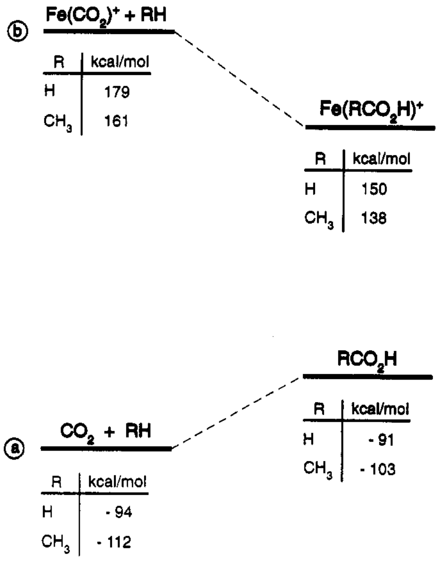
[21] Schultz, R. H.; Crellin, K. C.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590.

[22] Schultz, R. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 729.

[23] Schultz, R. H.; Armentrout, P. B. *J. Phys. Chem.* **1992**, *96*, 1662.

[24] (a) Bauschlicher, C. W., Jr. *Chem. Phys. Lett.* **1990**, *165*, 272. (b) Bauschlicher, C. W., Jr.; Partridge, H.; Langhoff, S. R. *J. Phys. Chem.* **1992**, *96*, 2475.

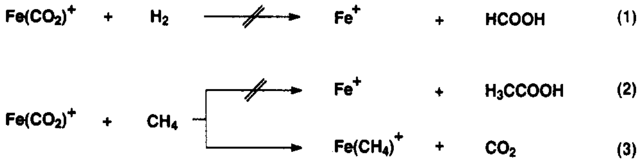
Scheme 3



processes (Scheme 2) we arrive at BDE(Fe^+–(CO_2)) = 8 ± 2 kcal/mol. It is obvious that the ready availability of 1 together with the small binding energy of the cluster will make $Fe(CO_2)^+$ an ideal precursor for the gas-phase generation of transition-metal complexes which are otherwise not so easily accessible.[25]

Finally, we would like to address the problem depicted in eq 1, i.e. the coupling of CO_2 and RH (R = H, alkyl) to generate carbonic acids. As indicated in Scheme 3a, this basic reaction is endothermic, leaving aside the existence of additional barriers imposed by high-lying transition structures of the four-center process. On the other hand, as indicated qualitatively by the data given in Scheme 3b, in the presence of atomic Fe^+, the same reactions are strongly exothermic, which is a consequence of the small binding energy of CO_2 and the much larger BDEs of Fe–(RCO_2H).[26,27]

Scheme 4



However, as repeatedly demonstrated, a favorable exothermicity does by no means provide a guarantee that the reaction will occur on the time scale of the experiment.[28] This is also born out by the reaction of $Fe(CO_2)^+$ with H_2 and CH_4 (Scheme 4). While no products are observed at all with H_2, in the ion–molecule reaction of $Fe(CO_2)^+$ with CH_4 it is the simple ligand exchange which wins over the formation of CH_3CO_2H. In retrospect, this negative result is not unexpected. If one assumes that the presence of the weakly interacting CO_2 in ligand 1 does not significantly alter the electronic structure of the metal ion, in a first approximation the reactivity of $Fe(CO_2)^+$ is expected to resemble that of Fe^+. For ground-state Fe^+, however, it has been amply demonstrated[29] that this metal is not capable of spontaneously activating H_2 or CH_4 via oxidative addition. Thus, it remains to be seen if third-row transition-metal ions, which activate methane,[30] are better candidates to bring about the activation of CO_2 and RH (R = H, CH_3).

In conclusion, the $Fe(CO_2)^+$ cluster is easily accessible, its connectivity and the BDE have been established, and the suitability of the cluster for the formation of other interesting clusters is obvious. However, further efforts are necessary to reach the ultimate goal, i.e., the coupled activation of CO_2 and RH.

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(25) Schröder, D.; Fiedler, A.; Schwarz, J.; Schwarz, H. *Inorg. Chem.*, submitted for publication.

(26) The thermochemical numbers used in Scheme 3b are based on a reasonable estimate of BDE(Fe^+–RCO_2H) = 40 kcal/mol. Actually, the Fe^+ complex of CH_3CO_2H has been generated in the gas phase: Schröder, D.; Fiedler, A.; Hrušák, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992,** *114,* 1215.

(27) For other gas-phase examples of changing the reaction energetics by complexing the reactants and products to a transition-metal ion, see: (a) Schröder, D.; Eller, K.; Prüsse, T.; Schwarz, H. *Organometallics* **1991,** *10,* 2052. (b) Karrass, S.; Schröder, D.; Schwarz, H. *Chem. Ber.* **1992,** *125,* 751.

(28) The extremely small reaction rate of the spin-allowed, highly exothermic reaction $FeO^+ + H_2 \rightarrow Fe^+ + H_2O$ may serve as an example: Schröder, D.; Ryan, M. F.; Fiedler, A.; Schwarz, H. *J. Phys. Chem.* **1994,** *98,* 68.

(29) For reviews, see: (a) Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russel, D. H., Ed.; Plenum Press: New York, 1989. (b) Armentrout, P. B. *Annu. Rev. Phys. Chem.* **1990,** *41,* 313.

(30) (a) Irikura, K. I.; Beauchamp, J. L. *J. Phys. Chem.* **1991,** *95,* 8344. (b) Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 820. (c) Wesendrup, R.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.*, in press.