Notes

Generation of Cationic and Neutral Iron Formate, HCOOFe, in the Gas Phase

Detlef Schröder and Helmut Schwarz*

Institut für Organische Chemie, Technische Universität Berlin, W-1000 Berlin 12, FRG

Received January 3, 1992

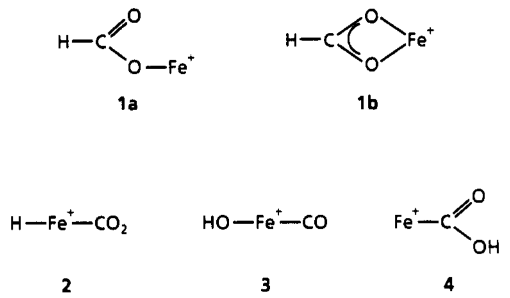
Summary: The title compound, $HCOOFe^+$, has been generated in the gas phase by reacting bare Fe^+ and/or ionized $Fe(CO)_5$ with methyl formate, and the species have been structurally characterized by using several mass-spectrometric techniques. The investigation of a specifically ^{18}O-labeled iron formate isotopomer rules out a symmetric bidentate carboxylate bonding to the metal ion; rather, the data are in keeping with either a unidentate or an asymmetric bidentate structure. Neutralization–reionization experiments provide for the first time evidence for the formation of the neutral HCOOFe counterpart, having a minimum lifetime of 0.8 μs.

Metal carboxylates play a decisive role in transition-metal chemistry in general,[1] and metal formates as well as acetates in particular are relevant ligands in many chemical and biological oxidation processes.[2] Furthermore, carboxylate complexes serve as intermediates in carbon dioxide activation by transition-metal complexes.[3] In spite of their undisputed importance, relatively little, if anything, is known about structural properties of the *isolated* molecules RCOOM or their corresponding cations $RCOOM^+$ (R = H, alkyl; M = bare transition metal). In this note we will describe the generation and structural characterization of the cationic iron formate $HCOOFe^+$ and its neutral counterpart HCOOFe in the gas phase.[4]

Experimental Section

Cationic iron formate, $HCOOFe^+$ (1), can be formed by reacting HCO_2CH_3 with $Fe(CO)_5$ in the presence of ionizing electrons in the chemical ionization (CI) source of a mass spectrometer or alternatively via an ion–molecule reaction of bare Fe^+ with HCO_2CH_3 using the technique of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. As both the instrument and its operation have been described repeatedly,[5] a short outline may suffice. Briefly, a mixture of methyl formate and $Fe(CO)_5$ was ionized by 100 eV of electrons in the CI source of a four-sector instrument of BEBE configuration (B stands for magnetic and E for electrostatic sector). A beam of the ion of interest, having 8-keV kinetic energy, was mass-selected at a resolution $m/\Delta m$ = 3000 by means of B(1)E(1) and for structural characterization subjected to a collisional activation (CA)[6] experiment (collision gas helium; 80% transmission, T) in a collision chamber located in the field-free region between E(1) and B(2). Ionic products were recorded by scanning B(2). In the neutralization–reionization (NR) experiment,[7] the 8-keV beam of mass-selected $[Fe,C,O_2,H]^+$ ions was neutralized in the first cell of a differentially pumped tandem collision cell (located in the field-free region between E(1) and B(2)) by colliding the ions with xenon (80% T). Unreacted ions were deflected away from the beam of neutral species by applying a voltage of 1000 V on the deflector electrode, which is placed between the set of tandem collision cells; subsequent reionization of $[Fe,C,O_2,H]$ occurred in the second collision cell by collision with oxygen (80% T). The resulting mass spectra were recorded by scanning B(2). In all experiments signal-averaging techniques were used to improve the S/N ratio. The data were accumulated by processing the spectra on-line with the AMD-Intectra DP10 computer system. In a further experiment, Fe^+ ions were formed via laser desorption–ionization[8] (Nd:YAG laser, Spectron Systems, 1064 nm) in the external ion source[9] of a Spectrospin CMS 47X mass spectrometer. The ions were transferred into the analyzer cell, decelerated and trapped in a magnetic field (Oxford Instruments, maximum field strength 7.05

Chart I



---

(1) Mehrota, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: London, 1983.

(2) For leading references, see: (a) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344. (b) Christon, G. *Acc. Chem. Res.* **1989**, *22*, 73. (c) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153. (d) Barton, D. H. R.; Doller, D. In *Dioxygen Activation and Homogeneous Catalytic Oxidation*; Simandi, L. T., Ed.; Elsevier: Amsterdam, 1991; p 1.

(3) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, Germany, 1988.

(4) (a) Laser spectroscopic investigations of neutral alkaline-earth carboxylates have been reported: O'Brien, L. C. O.; Brazier, C. R.; Kinsey-Nielsen, S.; Benrath, P. F. *J. Phys. Chem.* **1990**, *94*, 3543 and references therein. (b) For a mass-spectrometric study of $RCOOAg^+$ (R = alkyl), see: Busch, K. L.; Cooks, R. G.; Walton, R. A.; Wood, K. V. *Inorg. Chem.* **1984**, *23*, 4093.

(5) (a) Srinivas, R.; Sülzle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 368. (b) Srinivas, R.; Sülzle, D.; Koch, W.; DePuy, C. H.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 5970. (c) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243. (d) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621.

(6) (a) Levsen, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509. (b) Cooks, R. G., Ed. *Collision Spectroscopy*; Plenum: New York, 1978. (c) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1985**, 77. (d) Bordas-Nagy, J.; Jennings, K. R. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 105.

(7) (a) Terlouw, J. K.; Burgers, P. C.; van Baar, B. L. M.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 357. (b) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (c) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (d) Schwarz, H. *Pure Appl. Chem.* **1989**, *61*, 685. (e) Holmes, J. L. *Adv. Mass Spectrom.* **1989**, *11*, 53. (f) Terlouw, J. K. *Adv. Mass Spectrom.* **1989**, *11*, 984. (g) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *8*, 513. (h) McLafferty, F. W. *Science* **1990**, *247*, 925. (i) McLafferty, F. *Adv. Mass Spectrom.*, in press.

(8) Cody, R. B.; Burnier, R. C.; Reents, W. D., Jr.; Carlin, T. J.; McCrery, R.; Lengel, R. K.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Processes* **1980**, *33*, 37.

(9) Kofel, P.; Allemann, M.; Kellerhals, H.; Wanczek, K. P. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 97.

0276-7333/92/2311-2296$03.00/0

Table I. CA Mass Spectra of $[Fe,C,O_2,H]^+$ Ions from Different Organic Precursor Molecules and $Fe(CO)_5$[a]

	mass diff, amu										
precursor	−1	−17	−19	−28	−29	−30	−31	−44	−45	−46	−47
$HCOOCH_3$	1	2		12	22			31	100		
$HCOOCD_3$	1	2		13	24			28	100		
$HC^{18}OOCH_3$[b,c]	1	1	1	6	12	6	10			28	100
MeOH + CO[d]	<1	26		100	10			<1	28		

[a] Collision gas helium (80% transmission); data are given in percent base peak. [b] Synthesized according to a slightly modified procedure as originally described by: Hutchinson, C. R.; Mabuni, C. T. *J. Labelled Compounds Radiopharm.* **1977**, *13*, 571. The site-selective incorporation of the label (97 atom % ^{18}O) was confirmed by mass spectrometry. [c] The ratio between $Fe^{18}O^+$ and $Fe^{16}O^+$ (1.2 ± 0.05) was determined by four independent measurements. [d] This mixture gives rise to $Fe(CO)OH^+$ (**3**); the data were corrected for an isobaric $^{54}Fe^+$ interference.

T). The $^{56}Fe^+$ isotope was isolated using FERETS[10] and thermalized by collisions with argon ($p \approx 10^{-7}$ mbar). Methyl formate was introduced and reacted with Fe^+. The resulting $[Fe,C,O_2,H]^+$ species was further characterized by ion–molecule reactions (see below).

Results and Discussion

Although the loss of a methyl radical is a rare process in the gas-phase chemistry of transition-metal ions with organic substrates,[11,12] in the reaction of methyl formate (but not of higher alkyl formates) with $Fe(CO)_n{}^+$ ($n \leq 5$) or bare Fe^+, methyl radical loss is a facile reaction. This is, for example, indicated by the rate constant of $k_{\mathrm{exptl}} = 1.4 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} (±25%),[13] for the reaction of thermalized Fe^+ with HCO_2CH_3. The k_{ADO} rate constant[14] was calculated to be $k_{\mathrm{ADO}} = 1.6 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. Thus, methyl expulsion from the activated encounter complex occurs at near-collision rate:

$$HCO_2CH_3 + Fe^+ \rightarrow [HCO_2CH_3{\cdot}Fe^+]^* \rightarrow HCO_2Fe^+ + CH_3^{\bullet} \quad (1)$$

From a chemical point of view, in addition to the uni- and bidentate carboxylates **1a** and **1b**, three other isomers (**2**–**4**) are conceivable (Chart I).

Although the precursors HCO_2CH_3 and Fe^+ as well as the high reaction rate for the displacement of $CH_3^{\bullet}$ (eq 1) by Fe^+ already pointed to the carboxylate structure **1**, three different mass spectrometric techniques were used to verify this conjecture: (i) ion–molecule reactions of thermalized $[Fe,C,O_2,H]^+$ using FTICR, (ii) unimolecular and collision-induced dissociations of mass-selected $[Fe,C,O_2,H]^+$, and (iii) NR experiments. The last technique was recently shown to be of great promise in the structural characterization of transition-metal complexes.[15]

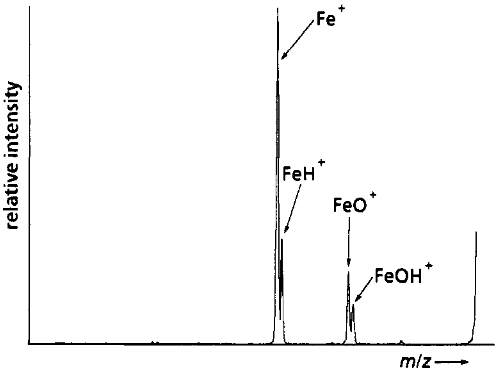
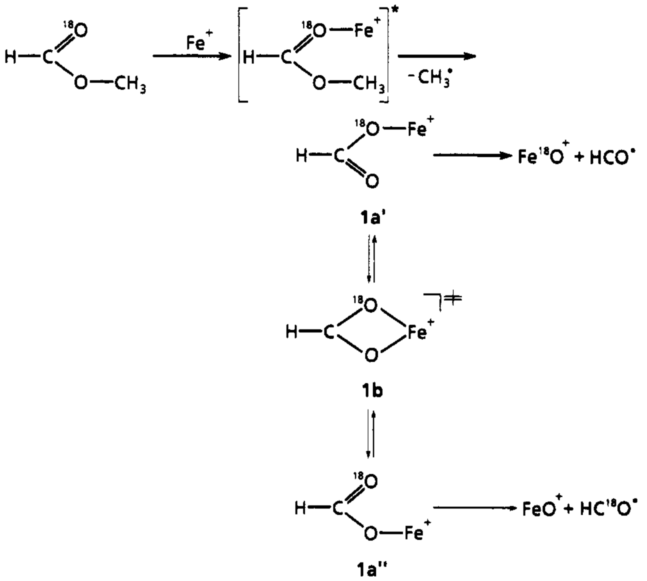


Figure 1. CA mass spectrum of HCO_2Fe^+ (He, 80% T).

Scheme I



In the ion–molecule reactions of thermalized $[Fe,C,O_2,H]^+$ with various substrates (i.e. methanol, water, acetone, and 1-butene), the dominant process corresponds to loss of CO_2; thus, a formal FeH^+ transfer to the neutral substrate takes place. While this reactivity can be explained in terms of structures **1**, **2** and **4** (but not **3**), the fact that $[Fe,C,O_2,H]^+$ does *not* undergo ligand exchange with $^{13}CO_2$ rules out the structure $H{-}Fe{-}CO_2{}^+$ (**2**). A further distinction is provided by the metastable ion (MI) and collision-induced dissociation processes. In the MI spectrum, we only observe losses of CO and CO_2 (30 and 100%, respectively). This is no surprise if one compares

---

(10) Forbes, R. A.; Laukien, F. H.; Wronka, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 23.

(11) Review: Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121.

(12) For examples of methyl loss from cationic iron complexes, see: (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445. (b) Fisher, E. R.; Schultz, R.-H.; Armentrout, P. B. *J. Phys. Chem.* **1989**, *93*, 7382. (c) Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics* **1989**, *8*, 2439. (d) Bjarnason, A.; Taylor, J. W.; Kinsinger, J. A.; Cody, R. B.; Weil, D. A. *Anal. Chem.* **1989**, *61*, 1889. (e) Karrass, S.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1990**, *98*, R1. (f) Prüsse, T.; Fiedler, A.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 8335. (g) Reference 5d.

(13) (a) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149. (b) Lin, Y.; Ridge, D. P.; Munson, B. *Org. Mass Spectrom.* **1991**, *26*, 550.

(14) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Processes* **1973**, *12*, 347.

(15) (a) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987**, *6*, 2268. (b) Drewello, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 177. (c) Eller, K.; Sülzle, D.; Schwarz, H. *Chem. Phys. Lett.* **1989**, *154*, 443. (d) Drewello, T.; Schwarz, H. *Chem. Phys. Lett.* **1990**, *171*, 5. (e) Schröder, D.; Sülzle, D.; Hrušák, J.; Böhme, D. K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *110*, 145. (f) Sülzle, D.; Schwarz, H.; Moock, K. H.; Terlouw, J. K. *Int. J. Mass Spectrom. Ion Processes* **1991**, *108*, 269.

(16) FeH^+ transfer is also observed in the reactions of iron(I) alkoxides with various substrates in the gas phase: (a) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543. (b) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 1566. (c) Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 910.

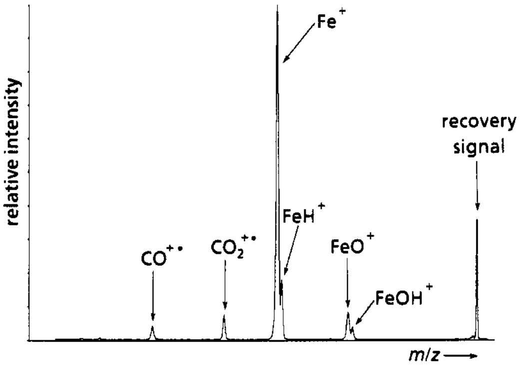


Figure 2. NR mass spectrum of HCO_2Fe^+ (Xe, 80% T//O_2, 80% T).

the heats of formation of the various conceivable product combinations[17] and also takes into account that in MI spectra reactions with the lowest energy paths often dominate.[18] In contrast, upon collisional activation high-energy processes are opened up and, in addition, the entropically favored direct-bond cleavage gains in importance.[6] This expectation is clearly reflected by the data reported in Table I as well as in the CA mass spectrum given in Figure 1. While all products shown in Figure 1 can be explained in terms of structure 1, the remaining isomers cannot account for the observed fragmentation pattern except if significant structural reorganization is allowed to precede the dissociations. The isomer **3** (HO–Fe–CO^+) is also ruled out by a comparison of the CA spectrum of $[Fe,C,O_2,H]^+$ generated from HCO_2H_3 and $Fe(CO)_n{}^+$ with the CA spectrum of the ion formed from ionizing a CH_3OH–CO–$Fe(CO)_5$ mixture. The CA spectrum so obtained is dominated by losses of $\Delta m = 17$ ($OH^\bullet$), $\Delta m = 28$ (CO), and $\Delta m = 45$ ($OH^\bullet$/CO); this pattern is in keeping with the structure HO–Fe–CO^+ (**3**).

For isomer **4** (Fe–$COOH^+$) one would expect a signal due to CO_2H^+ (*m/z* 45). This is not the case; consequently, **4** is not likely to be present.

A distinction between the unidentate and symmetric bidentate carboxylate structures, i.e. **1a** versus **1b**, is provided by studying a specifically ^{18}O-labeled methyl formate (Scheme I). The CA spectrum of the Fe^+ formate of this isotopomer (Table I) exhibits a structure-indicative difference for the formations of $Fe^{18}O^+$ (loss of $HCO^\bullet$) and FeO^+ (loss of $H^{18}CO^\bullet$), favoring the former by a factor of 1.2 ± 0.05. This difference is too high to be explained in terms of a heavy-atom kinetic isotope effect,[19] operative in the dissociation of the symmetric structure **1b**;[19] rather, it points to the unidentate connectivity of **1a**, which upon collisional activation undergoes partial oxygen equilibration prior to dissociation (Scheme I). Of course, an *asymmetric* bidentate carboxylate structure would give rise to the same result and, consequently, cannot be ruled out. However, irrespective of this unresolved question, our findings indicate a double-minimum potential for the *cationic* iron carboxylate **1a′** ⇄ **1b′** ⇄ **1a″** in which **1b′** may serve as a transition structure.[20]

Further support for our assignment that we are dealing with **1a** and not **2–4** is provided by the neutralization–reionization (NR) experiment. When mass-selected $[Fe,C,O_2,H]^+$ is subjected to a NR study, we obtain a quite intense recovery signal (Figure 2). As the minimum time between the two collision events (neutralization in the first cell; transit of the beam to the second cell followed by reionization) exceeds 0.8 μs, we have to conclude that the neutral species $[Fe,C,O_2,H]$ corresponds to a bound state.[7] In addition, the intense recovery signal points to a covalent bond between iron and the $[C,O_2,H]$ unit. This follows directly from the fact that weakly bonded complexes such as Fe(benzene) or Cu(HCN) cannot be reionized with high efficiency as most of the neutrals fall apart prior to reionization.[15] In contrast, covalently bonded systems such as $Fe(CH_x)$, OCuO, and HCCM (M = Fe, Co, Ni) give rise to strong recovery signals in the NR spectra of their corresponding cations.[15] Consequently, in the present case structures such as HO–Fe–CO and H–Fe–CO_2 are not likely to survive the multicollision experiments.

The comparison of the CA and NR mass spectra of $HCOOFe^+$ (**1a**) further reveals that, in addition to the common signals for Fe^+, FeH^+, FeO^+, and $FeOH^+$, the NR spectrum (Figure 2) contains signals corresponding to $CO_2{}^{\bullet+}$ and $CO^{\bullet+}$. These ions quite likely account for the neutral counterparts generated in the collision-induced fragmentation processes of **1a** leading to FeH^+ and $FeOH^{\bullet+}$, followed by reionization of CO_2 and CO, respectively. In the NR spectrum of the ^{18}O-labeled iron carboxylate $HCO^{18}OFe^+$ (**1a′**), the signals for $Fe^{18}O^+$ and FeO^+ have the same intensity. This observation requires that either the multicollision experiment brings about oxygen scrambling or the symmetric bidentate complex **1b** is the preferred structure for *neutral* iron formate. Ab initio MO calculations employing appropriate procedures are needed to resolve this important structural change when neutral and cationic iron formates are compared.

In conclusion, the combined application of several mass-spectrometric techniques strongly suggests that the Fe^+-mediated expulsion of a methyl radical from methyl formate gives rise to cationic iron formate. This species, most likely, is generated as the unidentate carboxylate **1a** rather than the symmetric structure **1b**. Neutralization of HCO_2Fe^+ (**1a**) can be brought about in a beam experiment, and the resulting *neutral* iron formate has a minimum lifetime of 0.8 μs.

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen-Stiftung is acknowledged.

Registry No. 1, 140110-93-6; 3, 138053-74-4; $Fe(CO)_5{}^+$, 59699-78-4; Fe^+, 14067-02-8; HCOOFe, 140110-92-5; $HCOOCD_3$, 23731-39-7; $HC^{18}OOCH_3$, 50417-96-4; MeOH, 67-56-1; CO, 630-08-0; FeH^+, 71899-96-2; FeO^+, 12434-84-3; $FeOH^+$, 15092-05-4; methyl formate, 107-31-3.

OM920003N

---

[17] On the basis of literature data, one obtains for the four most abundant processes the following heats of formation (kcal/mol) for the products: $FeOH^+$ + CO (185); FeH^+ + CO_2 (189); Fe^+ + $HCOO^\bullet$ (250); FeO^+ + $HCO^\bullet$ (276): (a) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465. (b) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*(1).

[18] Levsen, K. *Fundamental Aspects of Organic Mass Spectrometry*; Verlag Chemie: Weinheim, Germany, 1978.

[19] (a) Fry, A. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; ACS Monograph 167; Van Nostrand: New York, 1970. (b) Derrick, P. J.; Douchi, K. F. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1983; Vol. 24.

[20] For theoretical calculations on *neutral* Cu and Li carboxylates, forming symmetric bidentate structures as minima, see: (a) Sakaki, S.; Ohkubo, K. *Inorg. Chem.* **1988**, *27*, 2020. (b) Kaufmann, E. Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 4005.