much of the apolar bonding between I and II, perhaps by decreasing the structure of water,[9] thereby drastically reducing the rate of reaction between them. The effect of NaCl may be due to a similar decrease in water structure or to reduced electrostatic attraction between the reactants due to an increase in ionic strength.

Further studies utilizing this system to determine the thermodynamic characteristics of apolar bonding are in progress and will be discussed in a full paper.

(9) I. M. Klotz, "Horizons in Biochemistry," Academic Press Inc., New York, N. Y., 1962, pp 523–550.

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Eliminations of Neutral Metal Fluoride and Hydrogen Fluoride Fragments in the Mass Spectra of Transition-Metal Fluorocarbon Complexes

Sir:

A variety of fluorocarbon derivatives of transition metals have been prepared.[1] The mass spectra of a few such compounds have been investigated.[2–6] However, only in the mass spectra of the unusual cobalt complex[6] $[(CF_3)_2C_2S_2Co(CO)]_3$ and of the iron complex[7] $[(C_6F_5)_2PFe(CO)_3]_2$ has evidence been found by metastable ion analysis[8] for processes involving loss of neutral metal fluoride fragments. In the case of the cobalt complex, the reaction of this type involves fragmentation of the carbonyl-free trinuclear ion $C_{12}F_{18}S_6Co_3^+$ to the binuclear ion $C_{12}F_{16}S_6Co_2^+$. In this process a neutral CoF_2 fragment is lost.

This paper presents the data[9] in Table I which suggest that loss of neutral metal fluoride fragments is of widespread occurrence in the mass spectra of fluorocarbon transition metal derivatives. The compounds studied are of three different types: (a) fluoroorganosulfur derivatives[10] (*e.g.*, $C_2F_4S_2Fe_2(CO)_6$ (I) and $(CF_3)_2C_2S_2Fe_2(CO)_6$ (II)), (b) perfluoroaryl derivatives[11] (*e.g.*, $C_6F_5Fe(CO)_2C_5H_5$, p-$CF_3C_6F_4Fe(CO)_2C_5H_5$, and 3,4-$H_2C_6F_3Fe(CO)_2C_5H_5$, all of type III (R_f = perfluoroaryl)), and (c) metal π complexes of the fluorinated bicyclo[2.2.2]octatriene ("barrelene") derivative[12] $(CF_3)_2(CH_3)_4C_8H_2$ (IV) (*e.g.*, $C_{14}H_{14}F_6Fe(CO)_3$ and $C_5H_5CoC_{14}H_{14}F_6$). The limitation mainly to iron compounds is partially a consequence of the types of compounds available. The mass spectra of several fluorocarbon derivatives of molybdenum and tungsten have also been investigated, but the multiisotopic nature of these two metals has made observation of metastable ions involving metal-containing fragments in the mass spectra of their compounds much more difficult, since the intensity of any given ion is much less. The mass spectrum of the cobalt compound $C_5H_5CoC_{14}H_{14}F_6$ exhibits loss of C_5H_5CoF fragments rather than CoF_2 fragments (unlike $[(CF_3)_2C_2S_2Co(CO)]_3$).[6]

Table I. Some Metal Fluoride Eliminations[a]

Compound	Process	Neutral fragment lost	*m/e* Calcd	*m/e* Found
$C_2F_4S_2Fe_2(CO)_6$[b]	$C_2F_4S_2Fe_2(CO)_3^+ \longrightarrow C_2F_2S_2Fe(CO)_3^+$	FeF_2	196.5	196.5
$C_4F_6S_2Fe_2(CO)_6$[b]	$C_4F_6S_2Fe_2(CO)_3 \longrightarrow C_4F_4S_2Fe(CO)_3^+$	FeF_2	254.7	255 (s)
$C_6F_5Fe(CO)_2C_5H_5$[c]	$C_6F_4FeC_5H_4^+ \longrightarrow C_{11}H_4F_2^+$	FeF_2	113.0	113.2 (vw)
3,4-$H_2C_6F_3Fe(CO)_2C_5H_5$[c]	$C_6F_3H_2FeC_5H_5^+ \longrightarrow C_{11}H_7F^+$	FeF_2	99.2	99.3 (cw)
3,4-$H_2C_6F_3Fe(CO)_2C_5H_5$[c]	$C_6F_2H_2FeC_5H_4^+ \longrightarrow C_{11}H_6^+$	FeF_2	82.1	82.3 (vw)
p-$CF_3C_6F_4Fe(CO)_2C_5H_5$[c]	$C_7F_7FeC_5H_5^+ \longrightarrow C_{12}H_5F_5^+$	FeF_2	176.1	176.3 (vw)
p-$CF_3C_6F_4Fe(CO)_2C_5H_5$[c]	$C_7F_6FeC_5H_4^+ \longrightarrow C_{12}H_4F_4^+$	FeF_2	157.9	158 (w)
$C_{14}H_{14}F_6Fe(CO)_3$[d]	$C_{14}H_{14}F_6Fe^+ \longrightarrow C_{14}H_{14}F_4^+$	FeF_2	189.0	189 (m)
$C_5H_5CoC_{14}H_{14}F_6$[d]	$C_5H_5CoC_{14}H_{14}F_6^+ \longrightarrow C_{14}H_{14}F_5^+$	C_5H_5CoF	182.8	183 (w)
$C_5H_5CoC_{14}H_{14}F_6$[d]	$C_5H_5CoC_{10}H_8F_6^+ \longrightarrow C_{10}H_8F_5^+$	C_5H_5CoF	135.8	136 (s)

[a] The mass spectra from which these data were obtained were all taken at 70-ev electron energies on the Mellon Institute MS-9 mass spectrometer (Associated Electrical Industries, Ltd.). Inlet temperatures were in the range 200–250° and source pressures in the range 5×10^{-7} to 5×10^{-6} mm. [b] Reference 10. [c] Reference 11. [d] Reference 12.

The data on the perfluoroaryl and $(CF_3)_2(CH_3)_4C_8H_2$ derivatives in Table I indicate that elimination of metal fluoride fragments occurs only after the metal atom being eliminated has lost all of its carbonyl groups.[13] In both of the binuclear iron carbonyl derivatives of fluorinated organosulfur derivatives studied in this work ($C_2F_4S_2Fe_2(CO)_6$ and $C_4F_6S_2Fe_2(CO)_6$) loss of neutral FeF_2 fragments occurs from the tricarbonyl ions $(R_f)_2S_2Fe_2(CO)_3^+$. The apparent tendency for only carbonyl-free metals to be eliminated as their fluorides suggests that the first three carbonyl groups lost from the parent ions of $C_2F_4S_2Fe_2(CO)_6$ (I) and $C_4F_6S_2Fe_2(CO)_6$ (II) come off the same iron

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(1) For a review of fluorocarbon derivatives of transition metals, see P. M. Treichel and F. G. A. Stone, *Advan. Organometal Chem.*, **1**, 143 (1964).

(2) H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961).

(3) R. B. King, M. I. Bruce, J. R. Phillips, and F. G. A. Stone, *Inorg. Chem.*, **5**, 684 (1966).

(4) M. I. Bruce, *J. Organometal. Chem.* (Amsterdam), **10**, 95 (1967).

(5) M. I. Bruce, *Inorg. Nucl. Chem. Letters*, **3**, 157 (1967).

(6) R. B. King and T. F. Korenowski, *Chem. Commun.*, 771 (1966).

(7) J. M. Miller, *J. Chem. Soc., Sect. A*, 828 (1967).

(8) For a further discussion of metastable ions, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p xiii, and references cited therein.

(9) These mass spectra were run on the Mellon Institute MS-9 mass spectrometer (Associated Electrical Industries, Ltd.) under the direction of Mr. R. E. Rhodes. The standard conditions were 70-ev electron energies, 200–230° inlet temperature, resolution of 1000, 8-kv accelerating voltage, and sample introduction into the ion source with a metal probe.

(10) R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963).

(11) R. B. King and M. B. Bisnette, *J. Organometal. Chem.* (Amsterdam), **2**, 15 (1964)

(12) R. B. King, *J. Am. Chem. Soc.*, **84**, 4705 (1962).

(13) The stepwise loss of metal carbonyl groups is now a well-established feature of the mass spectra of metal carbonyl derivatives. For early observations of this phenomenon, see R. E. Winters and R. W. Kiser, *Inorg. Chem.*, **3**, 699 (1964); **4**, 157 (1965).

Table II. Some Hydrogen Fluoride Eliminations[a]

Compound	Process	Neutral fragment lost	*m/e*	
			Calcd	Found
$C_6F_5Fe(CO)_2C_5H_5$[b]	$C_6F_5FeC_5H_5^+ \longrightarrow C_6F_4FeC_5H_4^+$	HF	249.6	249.5 (w)
$C_6F_5Fe(CO)_2C_5H_5$[b]	$C_6F_5FeC_5H_4^+ \longrightarrow C_6F_4FeC_5H_3^+$	HF	229.5	229.5 (w)
$3.4\text{-}H_2C_6F_3Fe(CO)_2C_5H_5$[b]	$C_6F_3H_2FeC_5H_5^+ \longrightarrow C_6F_2H_2FeC_5H_4^+$	HF	213.5	213.6 (m)
$3,4\text{-}H_2C_6F_3Fe(CO)_2C_5H_5$[b]	$C_6F_2H_2FeC_5H_4^+ \longrightarrow C_6FH_2FeC_5H_3^+$	HF	193.9	194.0 (w)
$3,4\text{-}H_2C_6F_3Fe(CO)_2C_5H_5$[b]	$C_{11}H_7F_2^+ \longrightarrow C_{11}H_6F^+$	HF	120.5	120.9 (m)
$p\text{-}CF_3C_6F_4Fe(CO)_2C_5H_5$[b]	$C_7F_7FeC_5H_5^+ \longrightarrow C_7F_6FeC_5H_4^+$	HF	299.1	299.2 (w)
$C_{14}H_{14}F_6Fe(CO)_3$[c]	$C_{14}H_{14}F_6Fe^+ \longrightarrow C_{14}H_{13}F_5Fe^+$	HF	313	313 (vs)
$C_{14}H_{14}F_6Fe(CO)_3$[c]	$C_{13}H_{11}F_6^+ \longrightarrow C_{13}H_{10}F_5^+$	HF	242.2	242.5 (m)
$C_5H_5CoC_{14}H_{14}F_6$[c]	$C_{14}H_{14}F_5 \longrightarrow C_{14}H_{13}F_4^+$	HF	238.2	238.5 (m)

[a] See corresponding footnote in Table I. [b] Reference 11. [c] Reference 12.

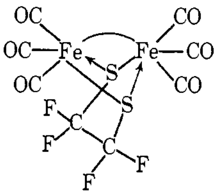
atom and that the ions $(R_f)_2S_2Fe_2(CO)_3^+$ have all three carbonyl groups bonded to the same iron atom leaving the other iron atom free of carbonyl groups and thus in a position to be eliminated as FeF_2. This is one of the first cases where a tentative decision has been possible between two alternative structures for an ion in the mass spectrum of a metal carbonyl derivative. Mass spectroscopy generally gives only information about the composition of the observed ions and not about their structure.

An interesting possibility is structure V for the ion $C_2F_2S_2Fe(CO)_3^+$ formed by FeF_2 elimination from $C_2F_4S_2Fe_2(CO)_3^+$ in the mass spectrum of $C_2F_4S_2Fe_2(CO)_6$ (I). This structure V is closely related to that of the cobalt complexes $C_5H_5CoS_2C_2R_2$ (VI, R = CF_3,[14] H,[15] and CN[16]). Similar possibilities (*e.g.*, VII) are available for the analogous ion $C_4F_4S_2Fe(CO)_3^+$ in the mass spectrum of $(CF_3)_2C_2S_2Fe_2(CO)_6$ (II). The mass spectrum of $(CF_3)_2C_2S_2Fe_2(CO)_6$ is also unique among all $R_2C_2S_2Fe_2(CO)_6$ compounds investigated[17] in exhibiting no parent ion but instead $C_4F_6S_2Fe_2(CO)_5^+$ as the highest *m/e* ion. Possibly $(CF_3)_2C_2S_2Fe_2(CO)_6$ is decarbonylated to $(CF_3)_2C_2S_2Fe(CO)_5$ (VIII) in the mass spectrometer[18,19] prior to ionization.

A further characteristic feature of the mass spectra of perfluoroaryl derivatives of the type $R_fFe(CO)_2C_5H_5$ (III) is the tendency for the carbonyl-free $(P - 56)^+$ ion to lose HF once or twice stepwise. Table II lists some metastable ions corresponding to these and other hydrogen fluoride eliminations. Such processes, while apparently usual for organic compounds containing both hydrogen and fluorine,[20] do not appear to have been observed previously for transition-metal organometallic compounds containing fluorine.

The metastable ions described in this paper clarify the fragmentation patterns of $R_fFe(CO)_2C_5H_5$ compounds. The two carbonyl groups are first lost stepwise from the parent ion giving the $R_fFeC_5H_5^+$ $(P - 56)^+$ ion. This ion can fragment further by the competitive processes of FeF_2 elimination and HF elimination. Other processes more typical of the mass spectra of cyclopentadienyliron dicarbonyl derivatives[21] also appear to occur in these perfluoroaryl compounds.

Complete details of the mass spectra of the compounds discussed in this paper will be reported in appropriate future full publications.



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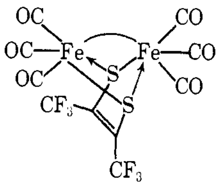

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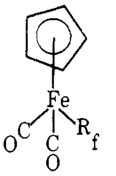

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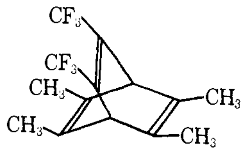

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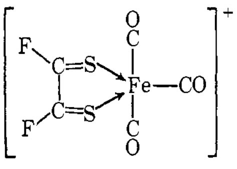

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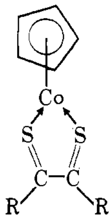

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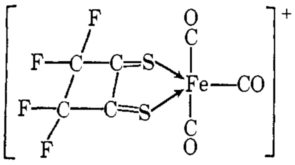

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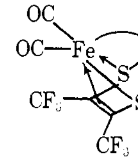

VIII

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(14) R. B. King, *J. Am. Chem. Soc.*, 85, 1587 (1963).

(15) R. B. King and C. A. Eggers, results presented to the Division of Inorganic Chemistry at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(16) J. Locke and J. A. McCleverty, *Inorg. Chem.*, 5, 1157 (1966).

(17) None of the other $R_2C_2S_2Fe_2(CO)_6$ compounds of which the mass spectra have been investigated has a carbon–carbon double bond bridge between the two sulfur atoms like $(CF_3)_2C_2S_2Fe_2(CO)_6$.

(18) Similar decarbonylation in the mass spectrometer has been observed for other metal carbonyl derivatives such as $C_6H_5COFe(CO)_2C_5H_5$, $\sigma\text{-}CH_3SCH_2Mo(CO)_3C_5H_5$, and $CF_3COMo(CO)_3C_5H_5$ (R. B. King, results presented to the Division of Physical Chemistry at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967). The inlet temperatures in the range 200–250° are undoubtedly responsible for this effect.

(19) The compound $(CF_3)_2C_2S_2Fe_2(CO)_6$, obtained from $Fe(CO)_5$ and bis(trifluoromethyl)dithietene by the previously published[10] procedure, has been reanalyzed using more carefully purified material. These new analytical data and the presence of the $\nu_{C=C}$ infrared band at 1653 (m) cm^{-1} confirm the originally proposed[10] formulation $(CF_3)_2C_2S_2Fe_2(CO)_6$ (II) rather than $(CF_3)_2C_2S_2Fe_2(CO)_5$ (VIII). The infrared spectrum of $(CF_3)_2C_2S_2Fe_2(CO)_6$ in the ν_{CO} region also exhibits three bands like other $R_2S_2Fe_2(CO)_6$ compounds.

(20) See ref 8, p 76.

(21) R. B. King, *J. Am. Chem. Soc.*, in press.

(22) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

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