Inorganica Chimica Acta, 133 (1987) 243–246

Chemical Ionization Mass Spectra of some Dicarbonyl Cyclopentadienyl Iron Derivatives

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(Received February 2, 1987)

Abstract

The chemical ionization mass spectra of the title compounds have been studied by using some protonating gas systems; information on the basicity of the compounds has been obtained and the reactivity of the gaseous ions has been compared with the behaviour in the condensed phase; the possibility of some novel reaction is suggested by the mass spectra.

Introduction

Chemical ionization (CI) mass spectrometry is now a well established technique in the study of organic substrates; by contrast the CI mass spectrometry of organometallic compounds is largely an unexplored field [1], even if this technique is potentially able to give information on the basicity and reactivity of the systems under investigation. We have undertaken a systematic investigation of the CI mass spectra of this class of compounds and previous results [2], together with those now reported, give a first idea of the scope and capability of the technique. The high degree of fragmentation often found in the CI mass spectra of organometallic compounds gives a precious investigation tool on the reactivity of these systems in the gas phase; analogies have been found with the reactions in the condensed phase, but also novel reactions have been observed; it seems that CI mass spectrometry could be extensively used as a rapid way to explore the reactivity of organometallic compounds.

Results and Discussion

Chemical Ionization Mass Spectra

CpFe(CO)$_2$X (X = Cl, Br, I)

Tables I, II and III report the mass spectra of these halogen derivatives; no notable discrepancy has been

TABLE I. Mass Spectra of (η^5-Cp)Fe(CO)$_2$Cl

m/z	EI	H_2	CH_4	i-Bu	Assignment
213		<1.0	0.7	4.5	$[MH]^+$
212	38	1.6	0.3		$[M]^+$
187		65.0	47.8	31.6	$[Cp_2FeH]^+$
186		98.0	40.6	100	$[Cp_2Fe]^+$
184	33				$[M\text{-}CO]^+$
178		77.8	65.2	7.3	$[CpFe(CO)_2H]^+$
156	100				$[M\text{-}2CO]^+$
149	3	27.7	12.5		$[M\text{-}(Cl + CO)]^+$

TABLE II. Mass Spectra of (η^5-Cp)Fe(CO)$_2$Br

m/z	EI	H_2	CH_4	i-Bu[a]	Assignment
257		58.4	13.8	33.6	$[MH]^+$
256	33.0	43.1	2.9		$[M]^+$
229			4.4		$[MH\text{-}CO]^+$
228	47.1	23.1	2.5		$[M\text{-}CO]^+$
200	100.0				$[M\text{-}2CO]^+$
187		6.1	24.5	26.4	
186		21.5	24.5	87.7	
178		70.5	58.0	51.9	$[CpFe(CO)_2H]^+$
177	3.0	100.0	100.0	100.0	$[CpFe(CO)_2]^+$

[a] Using i-Bu as reagent gas, a $m/z = 313$ ion formulated as $(M + C_4H_9)$ was observed.

TABLE III. Mass Spectra of (η^5-Cp)Fe(CO)$_2$I

m/z	EI	H_2	CH_4	i-Bu	Assignment
305	32.8	24.8	38.8	100	$[MH]^+$
304		35.5	16.5		$[M]^+$
277			6.9	3.6	$[MH\text{-}CO]^+$
276	34.5	12.6	4.0		$[M\text{-}CO]^+$
249		8.7	3.7		$[MH\text{-}2(CO)]^+$
248	36.2	11.8	3.2		$[M\text{-}2(CO)]^+$
187		12.9	13.6	10.6	$[Cp_2FeH]^+$
186		14.4	16.0	31.5	$[Cp_2Fe]^+$
178		10.0	8.5	2.5	$[CpFe(CO)_2H]^+$
177	1.3	100.0	100.0	51.1	$[CpFe(CO)_2]^+$

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0020-1693/87/$3.50

observed with the previously reported [3] electron impact mass spectra. When the reagent gas is H_2 or CH_4, the molecular ion is observed with a fairly high intensity; this ion is formed by a charge exchange reaction, due to the low ionization energy of these compounds [4] compared to the recombination energy of the reactant gases [5]. This ionization mechanism is accompanied by the proton transfer reaction responsible for the formation of the protonated molecule. When isobutane (i-Bu) is used as the reagent gas, the low recombination energy [5] of this reactant system prevents the charge exchange reaction and only the protonated molecule is observed. The absence of the protonation reaction when the reagent gas is NH_3, indicates that the gas phase proton affinities of these three compounds are between 827 and 857 kJ/mol, *i.e.* between the gas phase proton affinities of i-Bu and NH_3.

As shown in Tables I–III, the mass spectra become simpler as the reactant gas is changed from CH_4 or H_2 to i-Bu; with this last gas, almost the total ion current is due to the protonated molecule and to its fragment ion at $m/z = 177$ $[CpFe(CO)_2]^+$; a search for the metastable ions in the second field-free region evidentiates an unique fragmentation pathway of the protonated molecule, corresponding to the transition $MH^+ \rightarrow 177$; the relative abundance of this ion is low in the electron impact spectra.

When H_2 or CH_4 is used as the reactant gas, ions obtained by loss of some CO groups from the protonated molecule are observed; this suggests that the loss of CO groups, a typical reaction of metal-carbonyls in mass spectrometry, competes with the formation of the ion at $m/z = 177$ only when more energetic protonating systems are used (*i.e.* when the MH^+ ion is formed with a sufficient excess of internal energy). The different behaviour of the protonated molecule and of the molecular ion itself suggests that the neutral fragment formed in the transition leading to the ion at $m/z = 177$ is a stable molecule XH. This particular fragmentation pathway of the protonated molecules, indicates that their protonation site is the iron or the halogen atom. It has been reported that the addition of concentrated sulphuric acid to the chloro derivative leads to the evolution of gaseous HCl [6]; a very close analogy between the reactivities in these two different conditions is therefore evident. When NH_3 is used as the ionizing gas, $[NH_4]^+$ or $[(NH_3)_2H]^+$ ions are added to the molecular compounds; these processes can be followed by loss of CO groups. In the absence of any specific fragmentation pathway of the addition ions it is not possible to draw any conclusion concerning the interaction site of the compounds with the ions of the reagent gas.

Finally we wish to draw attention to the presence, with high relative abundance, of the ions $[Cp_2Fe]^+$ and $[Cp_2FeH]^+$; these ions must be formed by collisions between molecules of substrate; their presence, also at low partial pressure of the sample, is related to the well known high stability of such structures.

TABLE IV. Mass Spectra of $(\eta^5\text{-Cp})Fe(CO)_2Si(CH_3)_3$

m/z	*EI*	H_2	CH_4	i-Bu	Assignment
265				5.0	$[M + 15]^+$
251			13.2	100.0	$[MH]^+$
250	56.7	51.4	48.8	60.0	$[M]^+$
235	12.7	100.0		37.5	$[M\text{-}Me]^+$
223			0.9		$[MH\text{-}CO]^+$
222	45.0	10.6	7.8	19.5	$[M\text{-}CO]^+$
207	8.0				$[M\text{-}(Me + CO)]^+$
194	100.0	22.6	3.0	10.0	$[M\text{-}2(CO)]^+$
186		10.2	12.3	11.2	$[Cp_2Fe]^+$
178		4.3	0.5	7.4	$[CpFe(CO)_2H]^+$
177		5.8	1.6	22.0	$[CpFe(CO)_2]^+$

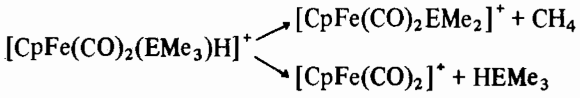
TABLE V. Mass Spectra of $(\eta^5\text{-Cp})Fe(CO)_2Sn(CH_3)_3$

m/z	EI	H_2	CH_4	i-Bu	Assignment
343		1.3	7.3	44.8	$[MH]^+$
342	20.0	25.6	25.2	6.9	$[M]^+$
327	100.0	100.0	100.0	100.0	$[M\text{-}CH_3]^+$
299	18.0	4.5	0.4		$[M\text{-}(CO + CH_3)]^+$
271	82.0	5.0	0.2		$[M\text{-}(2CO + CH_3)]^+$
186		38.5	0.8	22.4	$[Cp_2Fe]^+$
177		6.3	15.0	2.3	$[CpFe(CO)_2]^+$
165	78.0	21.8	3.7	1.9	$[SnCH_3]^+$

$CpFe(CO)_2E(CH_3)_3$ ($E = Si$ and Sn)

Tables IV and V report the mass spectra of these compounds. The differences found in these spectra are related to the protonating ability of the reagent gases; in fact, when H_2 is used, one observes a low relative abundance of the protonated molecule, but a wide fragmentation occurs which, mainly, leads to the $[M\text{-}CH_3]^+$ ion. The relative abundance of the $[PH]^+$ ion increases as the protonating ability of the reagent gas decreases, *i.e.* as the amount of internal energy transferred to the protonated molecule decreases.

The relative abundance of the $[M\text{-}CH_3]^+$ ion is higher in CI then in EI; in the CI mass spectra we find again the $m/z = 177$ ion, corresponding to $[CoFe(CO)_2]^+$, which is absent in the EI mass spectra. It clearly follows that the fragmentation pathways of the protonated molecules (neglecting the scarcely represented loss of CO groups) are:



$$[CpFe(CO)_2(EMe_3)H]^+ \begin{cases} \rightarrow [CpFe(CO)_2EMe_2]^+ + CH_4 \\ \rightarrow [CpFe(CO)_2]^+ + HEMe_3 \end{cases}$$

where the break of the E–C or Fe–E bond occurs respectively, as observed in the condensed phase by reaction of nucleophilic agents with the same or related compounds [7]. Again, the existence of specific fragmentation pathways induced by the protonation, indicates the iron atom, or more probably the IV group element, as the site of the proton attack.

The peculiar reactions, observed when ammonia is used as the reagent gas, are discussed later; now we note only that the $[NH_4]^+$ ion is able to protonate the silicon derivative, which is therefore the more basic compound among those examined.

$CpFe(CO)_2EPh_3$ (E = Ge and Sn)

The mass spectra of these compounds are reported in Tables VI and VII. The relative abundances of the ions M^+ and MH^+ cannot be exactly established owing to the low intensity of the spectra, due to the low volability of these aryl derivatives, and to the low relative abundance of the ions in the molecular ion region; there is however, clear evidence for the protonation reaction with each reagent gas, also confirmed by the presence of the $[M\text{-}Ph]^+$ ion, absent in EI.

In comparison with the methyl derivatives, the abundance of $[EPh_3]^+$ ions is much higher; their formation is therefore an important fragmention pathway of the protonated molecules; this reaction is favoured in the aryl derivatives by the lower ionization energy of triphenyl radicals.

Finally the presence of ions due to substitution reactions of one or more phenyl groups by methyl groups when methane is used as reagent gas should be noted. The presence of these ions, which are of higher abundance with tin and are found also in some manganese derivatives [2], indicates that the ions produced by CI are able to further react with the gas within the ion source.

TABLE VI. Mass Spectra of $(\eta^5\text{-}Cp)Fe(CO)_2GePh_3$

m/z	EI	H_2	CH_4	i-Bu	Assignment
479		1.5	1.7	2.1	$[MH]^+$
478	3.1	10.2	7.0	8.2	$[M]^+$
450	5.6	6.4			$[M\text{-}CO]^+$
422	13.7	5.1			$[M\text{-}(2CO)]^+$
401		100.0	100.0	56.8	$[M\text{-}Ph]^+$
345	10			100.0	$[CpFeGePh_2]^+$
301	100	85.9	74.0		$[GePh_3]^+$
239			47.7		$[GePh_2CH_3]^+$
225		64.1	93.0		$[GePh_2H]^+$
224	5.2				$[GePh_2]^+$
177		10.4	22.0	12.0	$[CpFe(CO)_2]^+$

TABLE VII. Mass Spectra of $(\eta^5\text{-}Cp)Fe(CO)_2SnPh_3$

m/z	EI	H_2	CH_4	i-Bu	Assignment
529		<0.1	<0.5	3.3	$[MH]^+$
528	7.0	0.1	1.5	0.9	$[M]^+$
500	18.9			3.3	$[M\text{-}CO]^+$
451		1.8	12.5	100.0	$[M\text{-}Ph]^+$
395	22.1				$[M\text{-}(2CO + Ph)]^+$
386	43.9				$[M\text{-}(Ph + C_5H_5)]^+$
351	100.0	100.0	100.0	24.3	$[SnPh_3]^+$
289			67.5	9.0	$[SnPh_2CH_3]^+$
227			70.0	1.9	$[SnPh(CH_3)_2]^+$
177		1.8	6.0	4.3	$[CpFe(CO)_2]^+$

Reactions with Ammonia

It is well known that $[NH_4]^+$, $[(NH_3)_2H]^+$ and, with lower abundance, $[(NH_3)_3H]^+$ constitute the reactive ions when NH_3 is used as the reagent gas. Very few classes of organic compounds are protonated by these ions; $[NH_4]^+$ ions normally act as an electrophile for ketones, aldehydes, ethers and anhydrides, but are unreactive towards alkanes, alkenes, alcohols and aromatic compounds. The few examples of organometallic compounds studied with ammonia confirm [1e, 1f] the low reactivity of this reagent system; in fact, only ions with $[NH_4]^+$ or $[N_2H_7]^+$ added to the substrate are present and their degree of fragmentation is very low.

The compounds now examined are instead capable of reacting with ammonia; an examination of the mass spectra shows that the ions formed in these reactions are not subject to appreciable fragmentation (for instance, ions containing CO groups are formed and there is no evidence for their fragmentation via CO loss, even if this reaction is very common). We can schematize the observed reactions as follows:

$$CpFe(CO)_2ER_3 + [NH_4]^+ \longrightarrow [CpFe(CO)_2(ER_2)NH_3]^+ + RH$$

$$CpFe(CO)_2ER_3 + [NH_4]^+ \longrightarrow [CpFe(CO)_2ER_2]^+ + NH_3 + RH$$

$$CpFe(CO)_2ER_3 + [NH_4]^+ \longrightarrow [H_3NER_3]^+ + CpFe(CO)_2H$$

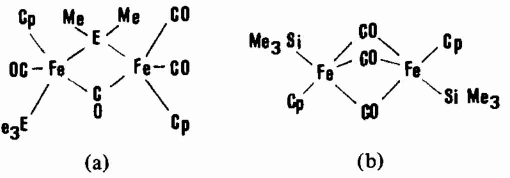
Obviously, both the nature of the neutral products and the structure of the ions are only reliable hypotheses; anyway, it is clear that the bonds E–C and Fe–E are again the more reactive sites. To our knowledge, similar reactions have not been reported in the condensed phase and, therefore, it could be of interest to explore the reactivity of such systems with ammonia.

Reactions Between Molecules of Substrate

When in the ion source the sample partial pressure increases, reactions leading to the formation of high mass ions become evident; these ions are present only in CI conditions, since the reduced mean free path allows collisions between substrate molecules; the mechanism of formation of these ions is confirmed by the strong dependence of their relative abundance upon the sample partial pressure (this partial pressure cannot be measured directly into the ion source, but it can be increased raising the sample temperature). The ready decrease in relative abundance of these polynuclear ions as the inlet temperature decreases, as well as their absence by EI, confirms that they are not due to a solid state reaction.

With $CpFe(CO)_2EMe_3$ (E = Si and Sn) the observed binuclear ions are assignable to $[Cp_2Fe_2(CO)_n\text{-}EMe_3EMe_2]^+$ (n = 4, 3, 2, 1) and $[Cp_2Fe_2(CO)_4\text{-}EMe_3]^+$; the silicon derivative shows further ions assigned to $[Cp_2Fe_2(CO)_n(SiMe_3)_2]^+$ (n = 3, 2, 1) and $[Cp_2Fe_2(CO)_4SiMe_2H]^+$.

A larger variety of ions has been observed with the silicon derivative, in agreement with the smaller tendency of tin derivatives to get bridge bonding between metal centers already noted in the condensed phase [8]; this feature has been ascribed to the larger size of the tin atom. Among the above reported assignments, the last only corresponds to an already known structure where the $SiMe_2$ bridge bonds two metal centers.



(a) (b)

Scheme 1.

In Scheme 1 are reported reasonable structures for the other binuclear ions.

Considering the positive charge of the ion, the iron atoms achieve a stable electronic configuration in structure (a), while such a configuration is achieved by a neutral compound in structure (b). The evidence for these structures in the gas phase suggests that they might exist also in the condensed phase; these results could be considered as a challenge for the synthetic inorganic chemistry.

The halogen derivatives behave differently: the chloro-derivative gives only $[CpFe(CO)_2]_2$ and its fragments; the iodo-derivative shows ions assigned to the dimer $[CpFe(CO)_2I]_2$ and its fragments; the bromo-derivative gives rise to ions assigned to the dimer as well as to $[CpFe(CO)_2]_2$, and to their fragments.

Experimental.

The iron complexes were prepared by published procedures [9]. Mass spectra were obtained with a Finnigan-Mat 112S mass spectrometer equipped with a chemical ionization ion source.

The reactant gases were reagent grade products and their pressure in the ionization box was kept between 0.05 and 0.1 torr; significant variation of the mass spectra was not observed over this pressure range. The ion source temperature was 170 °C.

Acknowledgement

This work was supported financially by the Italian Ministero della Pubblica Istruzione.

References

1 (a) D. F. Hunt, J. W. Russell and R. L. Torian, *J. Organomet. Chem., 43,* 175 (1972); (b) W. P. Anderson, N. Hsu, C. W. Stanger and B. Munson, *J. Organomet. Chem., 69,* 249 (1974); (c) W. J. A. Vandenheuvel, R. W. Walker, S. B. Nagelberg and B. R. Willeford, *J. Organomet. Chem., 190,* 73 (1980); (d) J. Muller and C. Hansch, *J. Organomet. Chem., 262,* 323 (1984); (e) M. R. Blake, J. L. Garnett, I. K. Gregor and D. Nelson, *J. Organomet. Chem., 193,* 219 (1980); (f) M. R. Blake, J. L. Garnett, I. K. Gregor and D. Nelson, *J. Organomet. Chem., 188,* 203 (1980); (c) G. Cetini, P. Michelin-Lausarot, L. Operti, G. A. Vaglio, M. Valle and P. Volpe, *Transition Met. Chem., 8,* 380 (1983); (h) A. Turco, A. Morvillo, V. Vettori and P. Traldi, *Inorg. Chem., 24,* 1123 (1985).

2 D. Perugini, G. Innorta, S. Torroni and A. Foffani, *J. Organomet. Chem., 308,* 167 (1986).

3 M. I. Bruce, *Int. J. Mass Spectrom. Ion Phys., 1,* 141 (1968).

4 G. Innorta, A. Foffani and S. Torroni, *Inorg. Chim. Acta, 19,* 263 (1976).

5 A. G. Harrison, 'Chemical Ionization Mass Spectrometry', CRC Press, Boca Raton, 1983.

6 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.,* 3653 (1962).

7 R. D. Gorsich, *J. Am. Chem. Soc., 84,* 2486 (1962); R. E. J. Bichler, H. C. Clark, B. K. Hunter and A. T. Rake, *J. Organomet. Chem., 69,* 367 (1974).

8 K. Triplett and M. D. Curtis, *Inorg. Chem., 15,* 431 (1976).

9 R. B. King, 'Organometallic Syntheses', Vol. 1, Academic Press, New York, 1965; R. Ugo, S. Cenini and F. Bonati, *Inorg. Chim. Acta, 1,* 451 (1967); D. Seyferth, H. P. Hofmann, R. Burton and J. F. Helling, *Inorg. Chem., 1,* 227 (1962).