Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

FRAGMENTATION OF METALLOCENES IN THE LOW-TEMPERATURE PLASMA

I. COMPARATIVE STUDY OF THE ARC DISCHARGE PLASMA ION COMPOSITION AND THE MASS SPECTRA OBTAINED UNDER THE ELECTRON IMPACT

N. V. ZAKURIN, S. P. GUBIN AND V. P. BOCHIN

Institute of Organo-Element Compounds, Kurchatov Institute of Atomic Energy, Academy of Sciences, Moscow (U.S.S.R.)

(Received December 16th, 1969)

SUMMARY

Abundance and relative intensities of positive ions generated during the fragmentation of some metallocenes under action of the electron impact and arc discharge plasma were investigated by the mass-spectroscopic method. Identities and differences in the behaviour of metallocenes under the conditions described were elucidated and the mechanisms of fragmentation were postulated.

Recently the fragmentation of the transition metal cyclopentadienyl compounds under the electron impact has become a subject of elaborate study. Generally these investigations were directed towards molecular energy characteristics: non-adiabatic ionization potential of the entire molecule[1] or of its separate fragments[2], values of the bond energies[3], etc. Mass-spectral investigations have revealed a number of interesting pecularities in the behaviour of metallocene, *e.g.* the formation of the "three layer sandwiches"[4], the ligand-to-metal migration of substituents[5], etc. More recently investigation of the negative ions composition has been undertaken concerning in general the mass-spectra of carbonyls[6] and transition metal cyclopentadienyl carbonyls[2]. Transition metal π-complexes (being readily available, volatile and stable) may be conveniently employed for the quantitative determination of the isotopic abundances for multiisotopic elements[7] and as charge material for ionic source electromagnetic separator.

In the present work we estimated ionic abundance of a weakly ionized arc discharge plasma produced by vapours of some transition metal cyclopentadienyl derivatives. Pecularities of the metallocene fragmentation in plasma with respect to their cleavage under the electron impact are discussed in detail.

EXPERIMENTAL

Experiments were conducted on a mass separator of the Kurchatov Atomic Energy Institute of the USSR Academy of Sciences. Main characteristics of the mass separator being: magnetic field: quasi-homogenic, stepwise; beam divergence: 180°; trajectory radius: 900 mm; dispersion per 1% of mass: 9 mm; registration range of masses: from 5 to 300. The ionic source design is described in ref. 9. Pressure in a discharge region was about 10^{-2} mm. Electron temperature at a discharge axis was of several eV[10]. The electron beam (180×2 mm^2) was operated by means of an ionic optic system. All the experiments were conducted at an accelerating potential of 30 kV and an additional electrode was supplied with 4–10 kV potential.

Signal from ion receiver passed through a fast-scanning oscillograph with a modulating of the accelerating potential followed via an amplifier with a slow scanning of the analysing magnetic field into automatic EPP-09 recording system. Minor ion current registered was 50–60 μA. Average scattering of peak intensities in recording the mass spectra was 15–20 relative percent. We assume that the main reasons of scattering were the instability of ion source operation and inhomogenous rate of the magnetic field scanner.

Besides the small number of recharge acts occurring between the accelerating and focusing electrodes, and except for the small number of ions generated from the slit edge material of the gas discharge camera, the ion abundance of the beam beyond the region of arc discharge corresponds to that of the compound under study. Moreover, the real ion abundance varies owing to the ion–molecule reactions taking place in the plasma bulk: in the axis the light fragmental ions predominate while in the peripheral zone there are more molecular ones. This is a result of the large axial–peripheral temperature gradient within the plasma bulk and thus the conditions of ionization and excitation differ.

In none of the experiments a change in discharge parameters like voltage, current and the heated cathode emission current had ever altered the quantitative picture of the spectrum. It only changes the relative intensities of some ions in comparison with those of the others. As the discharge voltage varied from 100 to 300 V the relative ion peak intensities changed from 5 to 15%.

The following stable cyclopentadienyl transition metal compounds were used as the working substances: ferrocene, $(C_5H_5)_2Fe$; 1,1'-diacetylferrocene, $(CH_3CO\text{-}C_5H_4)_2Fe$; ruthenocene, $(C_5H_5)_2Ru$; cyclopentadienylmanganese tricarbonyl, $C_5H_5\text{-}Mn(CO)_3$; and cyclopentadienylallylpalladium, $C_5H_5PdC_3H_5$. All the compounds were prepared and purified by the procedures described[10]. These are crystalline solids which can be readily sublimed without decomposition (their $\Delta T \equiv T_{\text{dec.}} - T_{\text{subl.}}$ is about 100–300°). All the substances were studied under analogous conditions, *i.e.*, same design of the ionic source, same discharge parameters, vacuum in the chamber, metal ion currents, etc. Table 1 shows the current intensities (with respect to the ion current of the most widely employed metal isotope taken as 100%) observed after the analysis of ion abundance of the ion source arc discharge plasma in mass separator. These results are compared with the mass spectra of the same compounds obtained by a method of electron impact using MI 1311 and MKh 1306 instruments at the ionizing electrons energy of 70 eV and evaporator temperature as high as 110°.

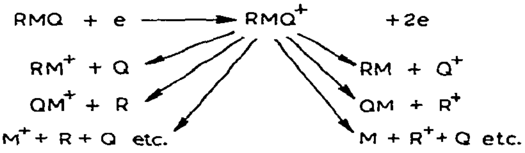
To attain the larger ion currents and enhance the activity of molecular ionization an attempt was made to employ an ion source with oscillating electrons (cathode and anode being under the same potential). It increased the stability of arc discharge and diminished the substance expense but sharply lost the quality of mass spectra. The oscillating electrons caused a complete destruction to composing elements (carbon and iron in case of ferrocene) even under mild conditions of the ion source operation.

RESULTS AND DISCUSSION

Fragmentation under electron impact (mass spectra)

The character of fragmentation of metallocenes investigated under electron impact does not differ essentially from the dependencies described earlier[1-8]. All the compounds show an intensive molecular ion peak in the spectra. It should be noted that it is most intense for the first three metallocenes (ferrocene, diacetylferrocene and ruthenocene). The two latter compounds have different peak intensity ratios: in the spectrum of $C_5H_5Mn(CO)_3$ the peak of the $(C_5H_5Mn)^+$ ion is the most intense; and the peak of the cyclopropyl cation $(C_3H_3)^+$ is the most intense in the spectrum of $C_3H_5PdC_5H_5$. As can be seen from the data of Table 2, relative intensity of the molecular ion peak for metallocenes investigated depends on the known chemical stability of the corresponding metallocene cations[11]. The first three terms of a series showed the formation of cations in solution and reversibility of the process (neutral metallocene→corresponding cation) whereas no evidence of reversible oxidation has been yet revealed for the last terms of a series. The oxidation of cyclopentadienylmanganesetricarbonyl for example has been shown to involve much further molecular destruction. Thus, the thermodynamic stability of the metallocene cations in the gaseous phase (judged from the relative peak intensity of molecular ions) is in qualitative agreement with the chemical stability of the same cations in solution.

Results presented in Table 2 may lead to the conclusion that there are different mechanisms of metallocene fragmentation:



$R = C_5H_5$; $Q =$ other ligands

The generated molecular ion may further decay either with the preservation of the constant positive charge at the metal-containing ions or with a predominant formation of the metal-containing neutral fragments. The latter course of decay is most pronounced in case of π-cyclopentadienyl-π-allylpalladium.

The pecularities of ruthenocene fragmentation under electron impact are that unlike all other compounds, the ruthenocene mass spectrum shows almost no metal free ions. Moreover, a comparatively intense peak of the bipositive ruthenocinium cation found in the ruthenocene mass spectrum entirely agrees with the chemical data published[12]. All these results testify to a stronger ruthenium–carbon bond in comparison with other investigated metallocenes.

Fragmentation in the arc discharge plasma

As seen from Tables 1 and 3 the metallocene fragmentation in the arc discharge is considerably different from that observed under electron impact. It may be due to the following reasons:

(*a*) Whereas the arc discharge plasma provides multiple collisions, only one takes place in the electron impact mass spectra.

(*continued p.* 542)

TABLE 1

MASS SPECTROGRAMS OF THE FRAGMENTS GENERATED UNDER ELECTRON IMPACT IN AN ION SOURCE OF A MASS SPECTRO

m/e	$(C_3H_5)_2{}^{104}Ru$			$(C_5H_5)_2{}^{56}Fe$				$(CH_3COC_5H_4)_2{}^{56}Fe$
	Ion	Elec. impact[a]	Arc disch.[b]	Ion	Elec. impact[a]	Arc disch.[b]	Arc disch.[c]	Ion
270								$(CH_3COC_5H_4)_2Fe$
255								$C_5H_4COCH_3FeC_5H_4CO$
240								$(C_5H_4CO)_2Fe$
234	$(C_5H_5)_2Ru$	1667						
227								$C_5H_4COCH_3FeC_5H_4$
216								
213								$C_5H_4COFeC_5H_4$
208	$C_8H_{10}Ru$	43						
206	C_8H_8Ru	83						
205								$C_5H_4COCH_3FeCOCH_3$
204								
199								$(C_5H_4)_2CH_3Fe$
193	C_7H_5Ru	5						
188								
186				$(C_5H_5)_2Fe$	1050	7		$(C_5H_5)_2Fe$
185								$C_{10}H_9Fe$
184								$C_{10}H_8Fe$
183								$C_{10}H_7Fe$
180	C_6H_4Ru	58						
176								
175								
169	C_5H_5Ru	600						
163								$C_5H_4COCH_3Fe$ $C_5H_4COFeCH_3$
162								
155	C_4H_3Ru	30						
152								
151								
148								
143	C_3H_3Ru	86						
142	C_3H_2Ru	46						
141	C_3HRu	233						
140								
139				$C_6H_{11}Fe$		7		
137								
134				C_6H_6Fe		7		
130	C_2H_2Ru	20		$C_{10}H_{10}$		7		
129				$C_{10}H_9$	42	7		$C_{10}H_9$
128				$C_{10}H_8$	33	21		$C_{10}H_8$
127				$C_{10}H_7$		3.5		
126				$C_{10}H_6$		23		
125								
121				C_5H_5Fe	266	151	64	C_5H_5Fe
120								
117	$[C_{10}H_{10}Ru]^{++}$	125						
116	CRu		36					
115				C_9H_7		3.5		
110								
106								

METER AND UNDER CONDITIONS OF ARC DISCHARGE PLASMA

		$C_5H_5{}^{55}Mn(CO)_3$			$C_3H_5{}^{110}PdC_5H_5$		
Elec. impact[a]	Arc disch.[b]	Ion	Elec. impact[a]	Arc disch.[b]	Ion	Elec. impact[a]	Arc disch.[b]
390	87						
30							
10							
187	115						
					$C_3H_5PdC_5H_5$	147	
20							
22							
		$C_5H_5Mn(CO)_3$	25	5			
92							
					C_6H_6Pd	12.5	
22							
20							
77	170						
22							
		$C_5H_5Mn(CO)_2$	3				
					C_5H_5Pd	126	12.5
44							
					C_4H_4Pd	5.2	
					C_3H_5Pd	143	82.5
		C_5H_5MnCO	23				
						7.0	
					C_2H_3Pd	8.7	
40	48						
22	20						
					CH_3Pd	10.5	
65	51						
		C_5H_5Mn	113	40			
					Pd	100	100
					$C_3H_5C_5H_5$		

(*Continued*)

TABLE 1 *(continued)*

m/e	$(C_3H_5)_2{}^{104}Ru$			$(C_5H_5)_2{}^{56}Fe$				$(CH_3COC_5H_4)_2{}^{56}Fe$
	Ion	Elec. impact[a]	Arc disch.[b]	Ion	Elec. impact[a]	Arc disch.[b]	Arc disch.[c]	Ion
104	Ru	100	100					
102				C_8H_6		2.3		
101				C_8H_5		7.0		
95				C_3H_3Fe	33	35		C_3H_3Fe
94				C_3H_2Fe	46	21		C_3H_2Fe
93				C_3HFe		11.5		C_3HFe
92								C_3Fe
91								
83								
80				C_2Fe		35		C_2Fe
79								
78	C_6H_6		9					
77	C_6H_5		2.2	C_6H_5		18		
76	C_6H_4		1.5	C_6H_4		11.5		C_6H_4
75	C_6H_3		3	C_6H_3		7		C_6H_3
74	C_6H_2		7.7	C_6H_2		3.5		
73	C_6H		4.4	C_6H		14.0		
72	C_6		1.6					
71								CH_3Fe
66	C_5H_6	>0	14	C_5H_6	>0	70	52	C_5H_6
65	C_5H_5	>0	31	C_5H_5	>0	87	57	C_5H_5
64	C_5H_4	>0	12	C_5H_4		46	7.1	C_5H_4
63	C_5H_3		26	C_5H_3	>0	70	31	C_5H_3
62	C_5H_2		23	C_5H_2		53	14	C_5H_2
61	C_5H		20	C_5H		39	4.7	C_5H
60	C_5		4.4	C_5		11.5	0	
56				Fe	100	100	100	Fe
55								
52	C_4H_4		11	C_4H_4		11.5	3.5	C_4H_4
51	C_4H_3		22	C_4H_3		16	23.5	C_4H_3
50	C_4H_2		26	C_4H_2		55	65.7	C_4H_2
49	C_4H		21	C_4H		32	19	C_4H
48	C_4		12.5	C_4		7	13	C_4
44				CO_2			162	
42								
41								
40								
39	C_3H_3		30	C_3H_3		40	62	C_3H_3
38	C_3H_2		26	C_3H_2		75	71	C_3H_2
37	C_3H		26	C_3H		70	66	C_3H
36	C_3		22	C_3		41	23	C_3
32								
28				CO			47	

---

[a] Electron impact, energy of ionizing electrons 70 eV. [b] Arc discharge, ~0.2–0.3 amp, discharge voltage 100–300 V, accelerating voltage 30 kV, vacuum in a camera of mass separator $1\text{–}2\cdot10^{-5}$ mm. [c] Arc discharge with addition of the reper gas, CO_2

		$C_5H_5{}^{55}Mn(CO)_3$			$C_3H_5{}^{110}PdC_5H_5$		
Elec. impact[a]	Arc disch.[b]	Ion	Elec. impact[a]	Arc disch.[b]	Ion	Elec. impact[a]	Arc disch.[b]
12.5	6.1						
28	8.9	C_3H_3Mn	1.3				
7.5		C_3H_2Mn C_5H_5CO	8				
12.5		C_3HMn	2				
					C_7H_7	19	
		MnCO	1.6				
22	9.8		1.4				
					C_6H_7	17.5	
					C_6H_6	8.7	
					C_6H_5	17.5	
	5.4						
	3.9						
69	8.8						
5	10.4	C_5H_6	2.4	45	C_5H_6	121	165
7.5	15.5	C_5H_5	2.6	30	C_5H_5	63	32.5
8.7	12.6	C_5H_4	0.8	2.5	C_5H_4	14	
10	17.2	C_5H_3	1.6	7.5	C_5H_3	72	8
1.2	9.0	C_5H_2	0.5	1.5	C_5H_2	16	
	40	C_5H	0.4	1	C_5H	7	
		$[C_5H_5Mn]^{2+}$ C_5	1.6	0	C_5	1.8	
100	100						
		Mn	100	100			
	2.4						
2	6.5	C_4H_3	>0	4			
	6.8	C_4H_2	>0	2.5			
	2.7	C_4H		1.5			
	1.2						
					C_3H_6	37	3.2
					C_3H_5	100	26
					C_3H_4	105	265
3.5	42	C_3H_3	9	22.5	C_3H_3	568	866
	18.4	C_3H_2	1.7	20	C_3H_2	82	133
	10.5	C_3H	0.8	5	C_3H	31	43
	2.3				C_3	3.5	6.2
		CO	25	245			

TABLE 2

RELATIVE ION INTENSITIES IN THE MASS-SPECTRA OF METALLOCENES INVESTIGATED (ELECTRON IMPACT)

Metallocene	Intensities[a]		
	Molecular ion	$C_5H_5M^+$ ion	Total (of metal-free ions)
$(C_5H_5)_2Fe$	67	17	4.8
$(CH_3COC_5H_4)_2Fe$	29	8.1[b]	7.5
$(C_5H_5)_2Ru$	54	16.2	0
$C_5H_5Mn(CO)_3$	7.7	35	14.5
$C_3H_5PdC_5H_5$	8.4	7.2[c]	73

[a] Total intensity of all the peaks observed in a mass spectrum is taken as 100%. [b] Total peak intensity of $C_5H_5Fe^+$ and $(CH_3COC_5H_4Fe)^+$ ions. [c] Ion peak intensity of (C_3H_5Pd) is 8.2%.

TABLE 3

RELATIVE ION INTENSITIES IN THE MASS-SPECTRA OF METALLOCENES INVESTIGATED (ARC DISCHARGE)

Metallocene	Intensities[a]		
	Molecular ion	$C_5H_5M^+$ ion	Total (of metal-free ions)
$(C_5H_5)_2Fe$	0.5	12.5	69
$(C_5H_5)_2Fe$[b]		9.5	75.9
$(CH_3COC_5H_4)_2Fe$	10.5	6.2	32.5
$(C_5H_5)_2Ru$			72.5
$C_5H_5Mn(CO)_3$	0.94	0.93	73.5
$C_3H_5PdC_5H_5$		0.72[c]	88.8

[a] Total intensity of all peaks in a mass spectrum was taken as 100%. [b] Experiment was conducted with an additional input of carbon dioxide in the arc discharge area. [c] Peak intensity of $(C_3H_5Pd)^+$ ion is 4.7.

(*b*) The electron energy spectrum of an arc discharge under analysis involves the entire region from 0 to 1 keV[10].

These conditions should result in the more profound dissociative ionization, recombination and ionization of a neutral molecule by the heavy fragmental ions. But the results obtained show that a major process of ion formation still involves dissociative ionization under the impact of electrons: there are no ions in the spectra having lesser carbon atoms than in the original molecule, the molecular ion intensities are weak and occasionally not even seen, the rearrangement ions appear generally in the region of light masses.

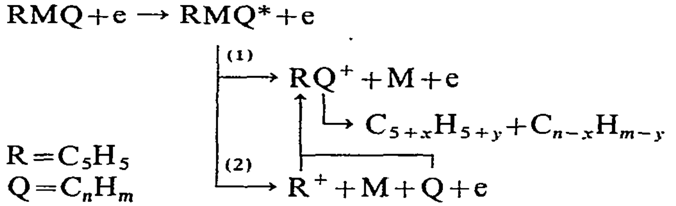
Comparing the results of Tables 2 and 3 one can see that passing from electron impact to arc discharge sharply increases the total metal-free ion intensity (the more profound dissociation products). However, this difference is more pronounced in ferrocene and ruthenocene than in cyclopentadienylallylpalladium splitting in an arc discharge in a manner slightly different from that under electron impact. From metallocenes investigated such a behaviour is characteristic of cyclopentadienylallylpalladium. It should be pointed out that in spite of such rigid conditions of cleavage, the metallocene spectra exhibit however noticeable intensities of molecular ion peaks.

This serves as another proof of high thermodynamic stability of metallocene cations.

Relatively high vapour pressure of metallocenes in the arc discharge area (10^{-2} mm) as compared to the pressure in an ion source of mass spectrometer (10^{-6} mm) and an increased contribution of the enthropy term in the free energy equation should be expected to generate the ion/molecule reaction products during the cleavage under arc discharge. Analogous reaction might be assumed to give rise to the ruthenium and iron carbides (7.3 and 0.8%).

Attention should be paid at an ion abundance of the products free of the metal atoms.

Two mechanisms can be advanced based on appearing hydrocarbon ions with the mass heavier than that of CH fragment:



In case (1) an excited metallocene molecule eliminating an uncharged metal atom gives rise to an over-all hydrocarbon fragment RQ^+. The latter may dissociate to the ions with both maximal and minimal contents of C and H. Since $C_5H_5Mn(CO)_3$ can split neither by the electron impact nor arc discharge based on the first course producing no hydrocarbon ions with the number of carbons greater than 5, one may be assured of an exclusively first route leading to hydrocarbon ions with the greater number of carbon atoms.

The second mechanism represents an example of ion/molecule reaction, and probably involves generation of ions with the larger number of hydrogen atoms than in the starting hydrocarbon radical.

Experiments were conducted with a simultaneous input of a foreign (reper) gas and the compound under study into the arc discharge region (CO_2, Ar and Xe were employed as reper gases). Ferrocene and ruthenocene vapours were investigated. The mass spectra became more simple (Table 1) and contained no peaks of molecular ions and fragmental ions in all the cases. It can be assumed that these conditions facilitate the cleavage of metal–hydrocarbon radical bonds.

Finally it should be pointed out that as in the case of other substances[13], the mass-spectroscopic study of metallocenes can provide a basis for predicting the abundance of fragmental ions in the arc discharge plasma.

ACKNOWLEDGEMENTS

The authors thank Mrs. V. S. Zolotareva and V. G. Zaikina for assistance in the present work and useful advices.

REFERENCES

1 L. Friedman, A. P. Irsa and G. Wilkinson, *J. Amer. Chem. Soc.*, 77 (1955) 3689.
2 R. G. Dennig and R. A. D. Wentworth, *J. Amer. Chem. Soc.*, 88 (1966) 4619.
3 R. E. Winters and R. W. Kiser, *J. Organometal. Chem.*, 4 (1965) 190.
4 E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, 47 (1964) 1525.
5 A. Mandelbaum and M. Cais, *Tetrahedron Lett.*, (1964) 3847.
6 R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, 69 (1965) 1618; *J. Chem. Phys.*, 44 (1966) 1964.
7 A. Carrick and F. Glockling, *J. Chem. Soc., A*, (1967) 40.
8 D. J. Claney and J. J. Spilners, *Anal. Chem.*, 34 (1962) 1839.
9 P. M. Morosov and B. N. Makov, *Proc. 2nd. Unit. Int. Conf. Peaceful Uses Atomic Energy*, Vol. 4, Geneva, 1958, p. 447 (P/2303).
10 P. M. Morosov, Doctoral Thesis, 1958, Moscow.
11 M. Rosenblum, *Chemistry of the Iron Group Metallocenes, Ferrocene, Ruthenocene, Osmocene*, Part I, Interscience, New York, 1965, p. 48–49.
12 A. N. Nesmeyanov, A. A. Lubovich, L. P. Yur'eva, S. P. Gubin and E. G. Perevalova *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1967) 935.
13 C. E. Melton, *J. Chem. Phys.*, 37 (1962) 562.