Ionization Efficiency Data and Fragmentation Mechanisms for Ferrocene, Nickelocene, and Ruthenocene

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Ionization efficiency (IE) data for the M^+, MCp^+, and MCp_2^+ ions of ferrocene ($FeCp_2$), nickelocene ($NiCp_2$), and ruthenocene ($RuCp_2$) are interpreted by a deconvolution–convolution technique to yield ionic bond dissociation energies in the 6—7 eV range for $D(CpM^+–Cp)$ and in the 4—5 eV range for $D(M^+–Cp)$. Additional direct experimental evidence in support of these values was obtained from IE data for appropriate metastable ion transitions.

Probable errors in the interpretation of IE data for other molecular systems are discussed with reference to the approach for metallocenes presented here.

THE mass spectra of the dicyclopentadienyls of iron ($FeCp_2$), nickel ($NiCp_2$), and ruthenium ($RuCp_2$), and the appearance potentials (AP's) of their principal ions have been reported by Friedman *et al.*[1] and Müller and D'Or.[2] Both investigations indicate the existence of a stable molecule-ion and a strong metal–cyclopentadienyl bond. They report that the ionic bond dissociation energy for the loss of the first Cp ring, $D(CpM^+–Cp)$, is 6—7 eV, while that for the loss of the second Cp ring, $D(M^+–Cp)$, is <1 eV. Such low values for $D(M^+–Cp)$ seem intuitively and theoretically to be in error. We have re-investigated the mass spectra and fragmentation mechanisms of $FeCp_2$, $NiCp_2$, and $RuCp_2$ with emphasis on the interpretation of the ionization efficiency (IE) data.

RESULTS

The mass spectra observed here for these compounds are in excellent agreement with those reported by Friedman *et al.*[1] and Müller and D'Or.[2] The principal ions from 50 eV electrons and their intensities are listed in Table 1. The spectra are simple, *i.e.* MCp_2^+, MCp^+, and M^+ account for 90, 85, and 70% of the total number of ions produced from $FeCp_2$, $NiCp_2$, and $RuCp_2$, respectively.

The IP's and AP's determined by the Warren method[3] for the principal ions are listed in Table 2. All the values are lower than those reported by Friedman *et al.*,[1] who used the vanishing current method[4] to interpret their IE data. The IP's listed are also lower than those reported by Müller and D'Or,[2] who used Warren's method[3] for IE data interpretation. The AP values are in general lower for fragment ions from $FeCp_2$ and $NiCp_2$, but higher for ions from $RuCp_2$.

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[1] L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Amer. Chem. Soc.*, 1955, **77**, 3689.

[2] J. Müller and L. D'Or, *J. Organometallic Chem.*, 1967, **10**, 313.

[3] J. W. Warren, *Nature*, 1950, **165**, 810.

[4] T. Mariner and W. Bleakney, *Phys. Rev.*, 1947, **72**, 807.

The higher values were those obtained for low abundance ions.

The deconvolution of the IE data,[5,6] using the total-ion IE data as the reference, gave the AP values listed in Table 3. The IP(MCp_2) was used to calibrate the electron energy scale in each case. A double break was found in all the M^+ IE data and also for the $RuCp^+$ data.

Evidence for metastable ion transitions was observed for the reactions indicated in Table 4. The IE data in these cases were interpretable only by the linear extrapolation method [7] because of the low metastable ion current intensities.

DISCUSSION

The molecular ions of the metallocenes are very stable, as indicated by the relatively high abundance of the MCp_2^+ and MCp_2^{2+} ions shown in Table 1. Since the abundance of those ions containing residues of ruptured Cp rings is low, the Cp ring must also be quite stable. The residue observed in highest abundance is C_3H_3, and its structure is presumed to be cyclic.

TABLE 1

Fragmentation pattern for ferrocene, nickelocene, and ruthenocene, 50 eV electrons

Ion	M=Fe	M=Ni	M=Ru
MCp_2^+	100	100	100
$CpMC_3H_3^+$	<1	1	2
MCp^+	33	62	29
$MC_3H_3^+$	5	13	6
M^+	15	12	4
MCp_2^{2+}	6	8	5
Cp_2^+	<1	≪1	≪1

On the basis of the AP's listed in Table 2, it is tempting to conclude that the rupture of the $CpM^+{-}Cp$ bond (6—7 eV) greatly reduces the stability of the remaining $M^+{-}Cp$ bond (0—2 eV). This is intuitively difficult to accept, and there is no theoretical evidence that such a conclusion is correct. In a search for evidence that some pertinent information was unobserved in the experiments, the $FeCp_2$ IE data were examined in detail.

TABLE 2

Ionization and appearance potentials (eV) of the principal ions from $FeCp_2$, $NiCp_2$, and $RuCp_2$ determined by Warren's method

Ion	M=Fe	M=Ni	M=Ru
MCp_2^+	6·77 ± 0·02	6·49 ± 0·03	7·54 ± 0·02
$CpMC_3H_3^+$		12·6 ± 0·1	14·6 ± 0·2
MCp^+	13·93 ± 0·08	12·63 ± 0·05	14·8 ± 0·5
$MC_3H_3^+$	18·06 ± 0·10	16·7 ± 0·1	19·6 ± 0·2
M^+	13·96 ± 0·05	13·26 ± 0·10	16·4 ± 0·5
Cp_2^+	13·96 ± 0·10		

When the IE curves for $FeCp_2^+$, $FeCp^+$, and Fe^+ were normalized to full scale for 50 eV electrons, the IE curves in the left portion of Figure 1 were obtained. The linear portions of the $FeCp^+$ and Fe^+ curves are approximately parallel and separated by 6—7 eV. One concludes that most of the Fe^+ is produced in a reaction whose energy requirement is 6—7 eV higher than that required to produce $FeCp^+$. Such a conclusion is compatible with the observed 50 eV spectrum.

When the normalization energy was reduced to 26 eV, the central portion of Figure 1 was obtained. The linear portions of the $FeCp^+$ and Fe^+ curves remain approximately parallel, but the voltage difference between the curves is reduced to 2—3 eV.

When the normalization energy was reduced to AP + 2·0 eV, the $FeCp^+$ and Fe^+ curves were nearly superimposed, as shown in the right portion of Figure 1.

The apparent energy relationship between the $FeCp^+$ and Fe^+ IE curves thus depends upon the energy at which the recorder deflections are normalized. In contrast to this, the energy relationship between the $FeCp_2^+$ and $FeCp^+$ IE curves is essentially the same (*ca.* 7 eV) for all three sets of IE curves. Since $FeCp_2^+$ has only one precursor, $FeCp_2^0$, these comparisons suggest that $FeCp^+$ also has only one precursor, but Fe^+ has more than one.

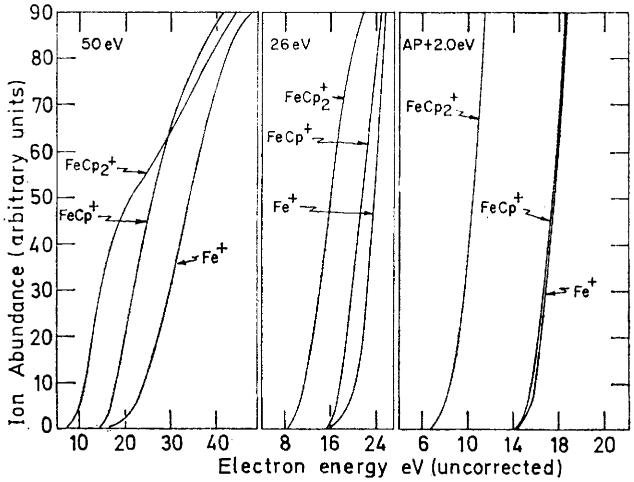

FIGURE 1 Ferrocene IE curves normalized to full scale deflection at the various electron energies indicated in each portion

The conclusion above is supported by the results of deconvolution experiments which show that the M^+ IE curve for each of the metallocenes has two components. It is reasonable to assume that these two components result from the reactions (1) and (2).

$$MCp_2 + e^- \longrightarrow M^+ + Cp_2 + 2e^- \qquad (1)$$

$$MCp_2 + e^- \longrightarrow M^+ + 2Cp + 2e^- \qquad (2)$$

The observations of metastable transitions and the values determined for their AP's also support the idea of two different reactions producing M^+ and also help identify them. Consider the metastable transitions (3) and (4). There is little doubt about the identity of the neutral product in (4), since the measured AP's of

$$MCp_2^+ \longrightarrow M^+ + Cp_2 \text{ (or 2Cp)} \qquad (3)$$

$$MCp^+ \longrightarrow M^+ + Cp \qquad (4)$$

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[5] G. D. Flesch and H. J. Svec, *J. Chem. Phys.*, 1971, **54**, 2681.

[6] G. D. Flesch and H. J. Svec, *J. Chem. Phys.*, 1971, **55**, 4310.

[7] P. T. Smith, *Phys. Rev.*, 1930, **36**, 1293.

(4), Table 4, agree well with the measured AP's of (2), Table 2. Comparison of AP's also identifies the neutral product in (3). If the neutral product in (3) were 2Cp, the AP's of (3) and (4) should be nearly the same. However, from the data in Table 4 it is seen that the AP for (3) is *ca.* 4 eV lower than that for (4). This strongly suggests that the neutral fragment in (3) is Cp_2.

TABLE 3

Ionization and appearance potentials (eV) of the principal ions from $FeCp_2$, $NiCp_2$, and $RuCp_2$ determined from deconvolution data *

Ion	M=Fe	M=Ni	M=Ru
MCp_2^+	6·75	6·50	7·50
MCp^+	14·25	13·00	14·75 18·25
M^+	14·00 18·00	13·00 17·75	16·50 20·00

* The values are given only to the nearest 0·25 V because of the nature of the deconvolution procedure. The uncertainties are thus estimated to be ±0·25 eV.

TABLE 4

Metastable ion transitions observed and their appearance potentials (eV) determined by linear extrapolation

	M=Fe [a]	M=Ni [a]	M=Ru [b]
$MCp_2^+ \longrightarrow MCp^+ + Cp$	14·0	13·0	14·2
$MCp_2^+ \longrightarrow M^+ + Cp_2$	14·4	14·3	
$MCp_2^+ \longrightarrow Cp_2^+ + M$	13·8	13·3	
$MCp^+ \longrightarrow M^+ + Cp$	18·9	17·7	
$MCp_2^+ \longrightarrow CpMC_3H_3^+ + C_2H_2$			14·1
$CpMC_3H_3^+ \longrightarrow MCp^+ + C_3H_3$			16·5

[a] Estimated uncertainty, ±0·5 eV. [b] Estimated uncertainty, ±1 eV.

There is further evidence to support the identification of Cp_2. Hedaya and his co-workers [8] have shown that one of the products of the flash vacuum pyrolysis of $NiCp_2$ is $C_{10}H_{10}$, which they identify as 9,10-dihydrofulvalene, with an IP of 7·75 eV. From our $FeCp_2$ data we calculate * an IP of 7·9 eV for the ion we identify as Cp_2^+. Presumably this ion is the same as that observed by Hedaya *et al.*

Still further evidence for Cp_2 being the neutral product in (3) is the AP for the metastable ion transitions leading to Cp_2^+. From the data in Table 4 it is seen that the AP for this transition is nearly the same as that for (3). This could be true only if the neutral in (3) is Cp_2 rather than 2Cp, since IP (Cp_2) ≈ IP (M).

The evidence above explains and identifies the two components in the M^+ IE curves, but does not apply to the other two-component curve—that for $RuCp^+$. In this case the components are probably due to reactions (5) and (6). The presence of reactions (6) is not surprising, since the $RuCp_2$ mass spectrum contains many ions

$$RuCp_2^+ \longrightarrow RuCp^+ + Cp \qquad (5)$$

$$\begin{tikzcd} RuCp_2^+ \arrow[r] & CpRuC_3H_3^+ + C_2H_2 \arrow[d] \\ & RuCp^+ + C_3H_3 \end{tikzcd} \qquad (6)$$

with residues due to ruptures of Cp rings. The observations of metastable transitions, Table 4, are evidence that the stepwise losses of C_3H_3 and C_2H_2 in reaction (6) occur.

The evidence above has clarified the interpretation of the fragmentation of the ions from metallocenes as it occurs in the mass spectrometer. On the basis of this evidence the simple mechanisms shown in Figure 2 are proposed to describe the fragmentation to produce the principal ions at 25 eV.

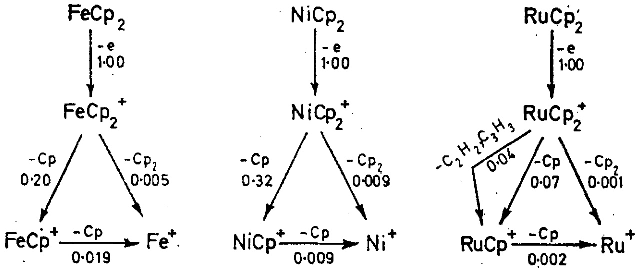

FIGURE 2 Fragmentation mechanisms for $FeCp_2$, $NiCp_2$, and $RuCp_2$ for 25 eV electrons. The neutral moiety ejected from each ion and the fraction of the total ions involved are shown next to the arrow for each reaction

As indicated above, the low-energy process leading to M^+ requires a rearrangement to form Cp_2. Such a rearrangement must have a low activation energy in order that the product ions be observed. The calculations of Ballhausen and Dahl [9] for protonated ferrocene suggest that the activation energy for this rearrangement in the ferrocene molecule ion is probably <0·5 eV.

Using the IE data and fragmentation mechanisms presented above, the ionic bond dissociation energies for $FeCp_2$, $NiCp_2$, and $RuCp_2$ have been calculated and are summarized in Table 5. The values of 6—7 eV for $D(CpM^+–Cp)$ agree with the values found by earlier workers,[1,2] while the 4—5 eV values for $D(M^+–Cp)$ are

TABLE 5

Ionic bond dissociation energies (eV) in $FeCp_2$, $NiCp_2$, and $RuCp_2$

Bond	M=Fe	M=Ni	M=Ru
$CpM^+–Cp$	7·2,[a] 7·5 [b]	6·1,[a] 6·5 [b]	7·3,[a] 7·2 [b]
$M^+–Cp$	3·8,[b] 4·9 [c]	4·8,[b] 4·7 [c]	5·2 [b]

[a] Calculated from data in Table 2. Estimated uncertainty is 0·2—0·5 eV. [b] Calculated from deconvolution data in Table 3. Estimated uncertainty is 0·5 eV. [c] Calculated from metastable data in Table 4. Estimated uncertainty is 1 eV.

$$\begin{array}{lll} * \; FeCp_2 + e^- \longrightarrow Fe^+ + Cp_2 + 2e^- & AP = 13{\cdot}96 \pm 0{\cdot}05\ eV \\ FeCp_2 + e^- \longrightarrow Cp_2^+ + Fe + 2e^- & AP = 13{\cdot}96 \pm 0{\cdot}10\ eV \\ Fe \longrightarrow Fe^+ + e^- & IP = 7{\cdot}90 \pm 0{\cdot}01\ eV \\ \hline Cp_2 \longrightarrow Cp_2^+ + e^- & IP = 7{\cdot}9 \pm 0{\cdot}1\ eV \end{array}$$

[8] E. Hedaya, D. W. McNeil, P. Schizzel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, 1968, **90**, 5284.

[9] C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, 1961, **15**, 1333.

quite reasonable and in keeping with both intuitive and theoretical expectations.

A value for D(Cp–Cp) was calculated from the deconvolution AP data of Table 3. For each metallocene, the lower AP value for M^+ is assigned to reaction (1) and the higher value to reaction (2), and D(Cp–Cp) is found to be $4{\cdot}1 \pm 0{\cdot}6$ eV. This is a reasonable value for the breaking of a single C–C bond.

Conclusions.—This report emphasizes the importance of proper reaction identification in determining bond dissociation energies from IE data. Failure to do so in the case of M^+ from MCp_2 has resulted for years in an erroneous interpretation of the ionic bond dissociation energies of metallocenes.

A reasonable interpretation of long ' tails ' in fragment ion IE curves has also been presented. The IE data here and in previous reports [5,6,10] are persuasive evidence that many such tails result from contributions of two or more decomposition reactions whose energy requirements are different. In nearly every case where we have investigated IE curves with long ' tails ' we have found deconvolution and/or metastable ion evidence to support the idea of multi-energy paths for decomposition. The more complex the molecule, the greater is the probability for such multi-energy pathways to occur, and the more difficult is the delineation of the reactions.

A logical conclusion of the multi-energy pathways explanation for the long ' tail ' in an IE curve is that only data points within 1—2 eV of the initial onset are useful in determining the AP of the lowest energy reaction associated with the curve. Higher-energy reactions contributing to the ' tail ' might be resolved with a monoenergetic source of electrons. However, with a conventional ion source there is little doubt that deconvolution of the ' tail ' portion is the best method of obtaining the AP's of the higher energy reactions contributing to the ' tail '. Deconvolution may establish that a second reaction occurs even though no significant ' tail ' is observed, as in the case of $RuCp^+$.

EXPERIMENTAL

The 60° sector mass spectrometer used in this study has been previously described,[11] but it has been modified by the addition of magnetic electron multiplier ion detectors. The ion-accelerating voltage was 2200 V and the ionizing current was 2 μA. The mass spectra were obtained at 50 eV using magnetic field scanning.

The IE data were plotted continuously with an X–Y recorder connected directly to the ion current and electron energy monitors. These data were used to determine the initial onset potentials by an adaptation of Warren's method.[3] Additional IE data were recorded over the 18 eV energy range immediately above the ionization potential (IP) of a particular metallocene. These data were used in the deconvolution procedures.[5,6]

The metallocenes were obtained from commercial sources. The $NiCp_2$ and $RuCp_2$ were used without purification, while the $FeCp_2$ was sublimed *in vacuo* to improve its purity.

The sample vessel and direct-flow inlet lines were operated at room temperature for $FeCp_2$ and $NiCp_2$, but for $RuCp_2$ they were heated to *ca.* 65 °C by means of a heating tape. The ion-source temperature was <100 °C, which is well below the temperature at which these compounds thermally decompose.[12]

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[10] G. D. Flesch, R. M. White, and H. J. Svec, *Internat. J. Mass Spectroscopy and Ion Phys.*, 1969, **3**, 339.

[11] H. J. Svec and G. D. Flesch, *Internat. J. Mass Spectroscopy and Ion Phys.*, 1968, **1**, 41.

[12] S. Pignatorro and F. P. Lossing, *J. Organometallic Chem.*, 1968, **11**, 571.