Electron Induced Processes on Iron Pentacarbonyl Molecule

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Abstract. Iron pentacarbonyl molecule (Fe(CO)5) was studied using a crossed molecular and electron beam experiment. The experimental appearance energies of positive ions via electron ionization and corresponding dissociative electron ionization were determined and used to estimate the thresholds for dissociative reactions as well as the experimental bond dissociation energies for CO ligands losses. The ion efficiency curves for formation of Fe(CO)n n = (4 – 0) ions via dissociative electron attachment were measured and we have discussed the mechanism of the reaction.

Introduction

The importance of the electron induced processes on molecules is increasing in the last few years due to their importance in such fields as plasma technologies for new materials, nanotechnology, fusion science, medicine and many more [Christophorou et al., 2002; Arumanayagam et al., 2010]. Metal organic molecules are primarily used in plasma and nano-scale technologies such as FEBID (Focused Electron Beam Induced Deposition). Understanding of chemical and physical processes between electrons, molecules and surfaces are crucial for these applications. The iron pentacarbonyl is one of the molecules used in FEBID applications for many years. Although many electron induced processes regarding Fe(CO)5 molecule were studied up until today, there still exist needs for better understanding of the processes of dissociative ionization (DI), dissociative electron attachment (DEA), especially the description of ligand bond energies and the reaction possibilities. The improved knowledge of the structure and energetics of the metal-organic molecules may lead to synthesis of new metal organic compounds suitable for nanotechnologies.

Present work is focused on the investigation of important ionization processes for formation of positive ions via electron ionization (EI) and dissociative ionization (DI) and processes of negative ion formation via electron attachment (EA) and dissociative electron attachment (DEA) reactions. These processes can be schematically described as

\[
\begin{align*}
\text{EI:} & \quad M + e^- \rightarrow M^+ + 2e^- \\
\text{DI:} & \quad M + e^- \rightarrow (M - R)^+ + R + 2e^- \\
\text{EA:} & \quad M + e^- \rightarrow M^- \\
\text{DEA:} & \quad M + e^- \rightarrow M^- \rightarrow (M - R)^+ + R
\end{align*}
\]

where M is representing a molecule, R a free radical and (M – R)^+ represent fragment ions. The investigation of these processes for Fe(CO)5 molecule was performed by several authors [Winters et al., 1964; Winters et al., 1966; Foffani et al., 1964; Bidinosti et al., 1967; Junk et al., 1968; Clements et al., 1976; Compton et al., 1976; Conard et al., 1978; Sunderlin et al., 1992], however, there exist spread of the values of appearance energies for particular reaction channels (for positive ions). These differences make it difficult to estimate the bond dissociation energies of ligands. The present experimental technique, which applies electron monochromator allows better electron energy resolution in the ion efficiency curves and more precise determination of the appearance energies in comparison to previous studies.

Experiment

The experimental investigation of the electron induced processes on Fe(CO)5 was performed using crossed electron and molecular beam apparatus, located at Department of Experimental Physics of Comenius University in Bratislava [Stano et al., 2003]. The molecular beam is created by effusion
of the vapors of the liquid Fe(CO)$_5$ sample via a small capillary into the reaction region. There it collides with the electron beam, which has perpendicular orientation to the molecular beam. Electron beam is formed using a trochoidal electron monochromator, with the resolution of electron energy used in this study of around 250 meV. The calibration of the electron energy scale was made for EI using Ar$^+$/Ar reaction with threshold at 15.76 eV [Lias, S. G., NIST Chemistry WebBook] and for EA and DEA studies using the SF$_6$/$\text{SF}_6$ reactions with peak at $\approx$ 0 eV [Christophrou et al., 2000]. A weak electric field extracts the produced ions from the reaction region into the ion optics of the quadrupole mass analyzer. The mass separated ions (according to m/z) are detected with the electron multiplier.

Two different modes of operation of the experiment were applied, the first one, the mass spectrum was recorded at constant electron energy. For positive ions standard mass spectrum was recorded at electron energy $\approx$ 70 eV. In the case of negative ions the mass spectra depend more strongly on the energy of the electrons due to resonant character of the reactions in the energy scale (0–10 eV), therefore the knowledge of the positions of the resonances for EA and DEA reaction for particular molecule is important. In the second mode, we have measured the ion efficiency curves for particular ions (for given m/z) as function of the incident electron energy.

For positive ions we have tried to estimate the experimental threshold for EI and DI processes, which is an important information about the reactions. The thresholds were evaluated using a fitting procedure based on generalized Wannier law [Wannier, 1953] for the EI and DI threshold. We determined experimental appearance energies (AE) of fragments fitting following function:

$$S(\varepsilon) = b ; \varepsilon < AE$$
$$S(\varepsilon) = b + a(\varepsilon - AE)^d ; \varepsilon > AE$$

where $\varepsilon$ represents electron energy and $b, a, d$ are variable fitting parameters.

**Results**

The mass spectrum of positive ions formed via EI and DI of $\approx$ 70 eV electrons is shown in the Fig. 1. The spectrum was recorded at mass resolution of about 400 and electron current of $\approx$ 1 $\mu$A. The isotopic pattern of Fe is very prominent in the mass spectrum.

The determination of the appearance energies for EI and DI reactions were performed for almost all peaks in the mass spectrum (Fig. 1) except the low intensity peaks for which we were not able to evaluate it or for the isotopic peaks. In evaluation we had to consider the overlap of some ions within a

![Figure 1](image-url). The mass spectrum of positive ions formed via EI and DI of Fe(CO)$_5$ at incident electron energy of $\approx$ 70 eV.
Table 1. Summarized experimental appearance energies (AE) compared with values from other authors: 1) Conard et al., [1978], 2) Winters et al., [1964], 3) Foffani et al., [1964], 4) Bidinosti et al., [1967], 5) Junk et al., [1968], 6) Clements et al., [1976]. The uncertainty of AE for present data is 0.25 eV.

<table>
<thead>
<tr>
<th>m/z (Th)</th>
<th>Positive ion</th>
<th>Neutral</th>
<th>AE (eV)</th>
<th>AE — other experiments (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>196</td>
<td>Fe(CO)$_5^+$</td>
<td>CO</td>
<td>8.45</td>
<td>8.53$^{1)}$, 8.53$^{2)}$, 8.14$^{3)}$, 8.16$^{3)}$, 8.4$^{4)}$, 8.4$^{5)}$, 8.4$^{6)}$</td>
</tr>
<tr>
<td>168</td>
<td>Fe(CO)$_4^+$</td>
<td>CO</td>
<td>9.00</td>
<td>9.3$^{1)}$, 10.2$^{2)}$, 8.34$^{3)}$, 8.73$^{3)}$, 9.17$^{5)}$, 9.3$^{6)}$</td>
</tr>
<tr>
<td>140</td>
<td>Fe(CO)$_3^+$</td>
<td>2CO</td>
<td>10.28</td>
<td>10.08$^{1)}$, 10.3$^{2)}$, 9.89$^{3)}$, 10.01$^{4)}$, 10.04$^{5)}$, 10.1$^{6)}$</td>
</tr>
<tr>
<td>124</td>
<td>Fe(CO)$_2^+$</td>
<td>2CO + O</td>
<td>17.66</td>
<td>18.2$^{5)}$</td>
</tr>
<tr>
<td>112</td>
<td>Fe(CO)$_2^+$</td>
<td>3CO</td>
<td>10.95</td>
<td>11.24$^{1)}$, 11.8$^{2)}$, 10.92$^{3)}$, 11.27$^{4)}$, 11.12$^{5)}$, 11.5$^{6)}$</td>
</tr>
<tr>
<td>96</td>
<td>Fe(CO)$_2^+$</td>
<td>3CO + O</td>
<td>19.97</td>
<td>20.2$^{1)}$</td>
</tr>
<tr>
<td>84</td>
<td>Fe(CO)$_2^+$</td>
<td>4CO</td>
<td>12.82</td>
<td>13.18$^{1)}$, 14$^{2)}$, 12.9$^{3)}$, 13.39$^{4)}$, 13.76$^{5)}$, 14$^{6)}$</td>
</tr>
<tr>
<td>72</td>
<td>FeO$^+$</td>
<td>4CO + C</td>
<td>22.95</td>
<td>22.5$^{5)}$</td>
</tr>
<tr>
<td>70</td>
<td>Fe(CO)$_3^{2+}$</td>
<td>2CO</td>
<td>23.57</td>
<td>24$^{1)}$</td>
</tr>
<tr>
<td>68</td>
<td>Fe$^{2+}$</td>
<td>4CO + O</td>
<td>21.94</td>
<td>23.65$^{1)}$, 23.6$^{5)}$</td>
</tr>
<tr>
<td>56</td>
<td>Fe$^{2+}$</td>
<td>5CO</td>
<td>14.65</td>
<td>15.51$^{1)}$, 16.1$^{2)}$, 14.7$^{3)}$, 15.31$^{4)}$, 15.99$^{5)}$, 16.2$^{6)}$</td>
</tr>
<tr>
<td>48</td>
<td>Fe(CO)$_2^{2+}$</td>
<td>3CO + O</td>
<td>36.36</td>
<td>36$^{4)}$, 36$^{5)}$, 36$^{6)}$</td>
</tr>
<tr>
<td>42</td>
<td>Fe(CO)$_2^{2+}$</td>
<td>4CO</td>
<td>30.06</td>
<td>30.24$^{1)}$, 30.2$^{2)}$, 30.2$^{5)}$, 30.2$^{6)}$</td>
</tr>
<tr>
<td>28</td>
<td>CO$^+$</td>
<td>Fe(CO)$_3^+$</td>
<td>14.29</td>
<td>14.29$^{5)}$, 14.29$^{6)}$</td>
</tr>
</tbody>
</table>

Figure 2. Ion efficiency curves as a function of incident electron energy and the theoretical fits for estimation of appearance energies of ions from Fe(CO)$_n^+$ (n = 5 – 0) ions. Measurement at m/z = 54 Th is for the isotopic peak of $^{54}$Fe$^+$.

peak, for example at m/z = 56 Th the Fe$^+$ and Fe(CO)$_2^+$ ions were detected. The values of appearance energies determined from experiment with proposed ionic and neutral products are summarized in the Table 1 and compared with previous works. An uncertainty of appearance energies of ± 0.25 eV was evaluated for all reactions and is based on the energy distribution of the electrons in the beam.
Table 2. DEA to Fe(CO)$_5$ description of the negative ions, tentative assignment of neutral products and position of the resonances.

<table>
<thead>
<tr>
<th>Negative ion</th>
<th>Neutral</th>
<th>Threshold (eV)</th>
<th>Peak center (eV)</th>
<th>Negative ion</th>
<th>Neutral</th>
<th>Threshold (eV)</th>
<th>Peak center (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CO)$_4$</td>
<td>CO</td>
<td>≈ 0</td>
<td>≈ 0</td>
<td>Fe(CO)$_5^-$</td>
<td>4CO</td>
<td>≈ 4</td>
<td>≈ 5.8</td>
</tr>
<tr>
<td>Fe(CO)$_3^-$</td>
<td>2CO</td>
<td>≈ 0</td>
<td>≈ 1.3 ≈ 3.45</td>
<td>Fe$^-$</td>
<td>5CO</td>
<td>≈ 6</td>
<td>≈ 8.7</td>
</tr>
<tr>
<td>Fe(CO)$_2^-$</td>
<td>3CO</td>
<td>≈ 2.4</td>
<td>≈ 4.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. Ions efficiency curves for negative ions created from Fe(CO)$_5$. The theoretical thresholds of excited states of neutral parent molecule from Kotzian et al. [1989] are indicated in the upper graph.

The formation of the negative ions from Fe(CO)$_5$ by DEA proceeds via transient negative ion (Fe(CO)$_5$)$_{h-}$. The sequential dissociation of CO ligands was observed with increasing incident electron energy:

$$\text{Fe(CO)}_5 + e^{-} \rightarrow (\text{Fe(CO)}_5)_h^-> \rightarrow \text{Fe(CO)}_4^-> + \text{CO} \rightarrow \text{Fe(CO)}_3^-> + 2\text{CO} \rightarrow \ldots \rightarrow \text{Fe}^- + 5\text{CO}$$

The measured ion efficiency curves of negative ions are shown in Fig. 3. Only negative ions formed via CO ligand cleavage were detected with final decomposition to atomic Fe$. The parent negative ion of the molecule was not detected. The reason most probably is the short life time of this ion against dissociation in comparison to the flight time through the quadrupole mass spectrometer ($\approx 50 \mu$s). The comparison of experimental data with theoretical results of Fe(CO)$_5$ electron excitation states and experimental study of UV–Vis absorption spectroscopy on neutral molecule [Kotzian et al., 1989] can help to identify the resonances as single particle and core excited (in region, where excited states are available). Some basic parameters of resonances are collected in Table 2.

Discussion

The ionization energy of Fe(CO)$_5$ molecule according to present experiment is 8.45 eV, which agrees well with the previously published IEs (Table 1). Several new positive ions, not mentioned in earlier studies, were identified in the mass spectrum. The low intensity peak at m/z = 100 was assigned to FeO(CO)$^+$ ion and the peak at m/z = 48 to a doubly charged ion FeC(CO)$_2^+$+. The peak at m/z = 28 was as well not discussed by previous authors, who probably assigned it to N$_2$$. The comparison of
LACKO ET AL.: ELECTRON INDUCED PROCESSES ON IRON PENTACARBONYL

The intensities of m/z 28 and 32 and taking into account the AE of the m/z = 28 peak (lower than the ionization energy of N₂ molecule of 15.58 eV [Lias, S. G., NIST Chemistry WebBook]) indicated that this could be CO⁻ ion formed from the ligand. The isotopic pattern investigation of peak m/z = 27 indicates that a small amount of Fe²⁺ ion can contribute to the intensity of m/z = 28 peak. Similar effect was observed in case of m/z = 56 for Fe⁺ and Fe(CO)₂⁺ ion.

From the appearance energies of the Fe(CO)₅⁺ ions the bond dissociation energies for (CO)nFe⁺ – CO (n = 4 – 0) can be estimated:

\[ \text{BDE}[(\text{CO})n\text{Fe}^+ \text{ – CO}] = \text{AE}[\text{Fe(CO)}_{n+1}^+] \text{ – AE}[\text{Fe(CO)}_{n}^+] \]

Present experimental values are compared with values obtained by other authors (Fig. 4). The electronic states assigned on the x-axis are from our preliminary DFT calculations with PBE/def2-TZVPd functional and basis set.

The DEA to Fe(CO)₃ resulted in formation of Fe(CO)₅⁻ (n = 4 – 0) ions, which is in agreement with previous works [Winters et al., 1966; Compton et al., 1976; Sunderlin et al., 1992]. From the thresholds for the formation of negative ions we are able to evaluate either electron affinity of the neutral fragment X formed via dissociation of M or bond dissociation energy (BDE) of fragment X in the molecule M:

\[ \varepsilon_{\text{thrs}} \geq \text{BDE}(M – X) – \text{EA}(X) \]

If the electron affinity of X is known, we are able to estimate upper limit of BDE for (CO)nFe – CO (n = 4 – 0) bonds in neutral molecule. The electron affinities in present calculations are from our DFT calculations. These values can be compared with other theoretical calculations. We were able to estimate only BDE of (CO)₄Fe – CO bond, where the value of BDE[(CO)₄Fe – CO] ≤ 2.13 eV.

**Conclusion**

Dissociative processes of metal organic compounds induced by electron impact play an important role in the field of FEBID nanotechnologies. A crossed electron and molecular beam apparatus was used to study processes relevant to interaction of secondary electrons in FEBID techniques. We have

**Figure 4.** Bond dissociation energies of (CO)nFe⁺ – CO (n = 4 – 0) for positive ions, comparison of experimental and theoretical results.
studied products of EI, DI and DEA reactions to Fe(CO)\textsubscript{n}, one of the important molecules in field of FEBID technologies. We have observed some new products and estimated the appearance energies of most positive ions. From the appearance energies we have estimated the bond dissociation energies of CO ligand in positive ions. The negative ions created via dissociative electron attachment resulted in formation of Fe(CO)\textsubscript{n} \quad n = 4 – 0 ions. Using thresholds values for DEA reactions and theoretical calculation, some of bond parameters for neutral molecule were estimated.

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References


