Studies by ESCA on the Thermal Decomposition of Fenitrothion

Fumio Horide, Kozo Tsuji, Masao Sasaki* and Masao Minobe*

Pesticides Research Laboratory, Takarazuka Research Center, Sumitomo Chemical Co., Ltd., Konohana-ku, Osaka 554, Japan
*Takatsuki Research Center, Sumitomo Chemical Co., Ltd., Tsukahara, Takatsuki 569, Japan

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INTRODUCTION

There are several papers1-9) on the thermal decomposition of organophosphorus pesticides. In our previous paper1) among them, we have elucidated the thermal decomposition mechanism of fenitrothion by means of DTA (differential thermal analysis), EGA (evolved gas analysis), HPLC (high performance liquid chromatography), elementary analysis etc. Fenitrothion in the air showed three exothermic peaks at 150-190°C (I), 210-235°C (II) and 270-285°C (III) on the DTA diagram, but the first peak disappeared in a nitrogen atmosphere. Based on the results the authors have proposed a three-step thermal decomposition mechanism of fenitrothion in the air:

First step (150-190°C); fenitroxon formation with sulfur dioxide gas evolution, that is, a reaction of fenitrothion with oxygen

Second step (210-235°C); dimethyl sulfide gas evolution through S-methyl-fenitrothion and polymetaphosphate formation

Third step (270-285°C); carbonization of phenolic rings and gas evolution from S-methyl-bis-fenitrothion as a by-product

In order to elucidate the thermal decomposition mechanism of fenitrothion on the sample surface this time, we carried out ESCA (Electron Spectroscopy for Chemical Analysis) measurement for the samples heated up to 190, 235 and 285°C in the air, the temperatures corresponding to the ones after peaks (I), (II) and (III) in the DTA diagram, respectively. The present paper describes the results of our study by means of ESCA on the thermal decomposition of fenitrothion on the sample surface.

ESCA is employed to determine the binding energy of an inner shell electron by measuring the kinetic energy of an electron released by soft X-ray irradiation, and applied to the surface analysis about 50Å in depth. The binding energy of each electron in organic compounds shows a chemical shift depending on the binding atom or atoms, and is related to the molecule structure. A chemical binding state of an element in the molecule can be determined by the binding energy obtained by ESCA.

EXPERIMENTAL

I. Materials

The compounds used in this study were synthesized at the Pesticides Research Laboratory, Takarazuka Research Center, Sumitomo Chemical Co., Ltd.

<table>
<thead>
<tr>
<th>Compound (abbreviation)</th>
<th>Chemical name</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenitrothion (MEP)</td>
<td>O,O-Dimethyl O-(3-methyl-4-nitrophenyl)phosphorothioate</td>
<td>96.8%</td>
</tr>
<tr>
<td>S-Methyl-fenitrothion (S-Me-MEP)</td>
<td>O,S-Dimethyl O-(3-methyl-4-nitrophenyl)phosphorothiolate</td>
<td>98.1%</td>
</tr>
</tbody>
</table>

II. Apparatus

Thermal decomposition of MEP on the surface was measured with an ESCA apparatus, Shimadzu-Du Pont model 650B equipped with a data processing system (ESCAPAC-660) at -50 to -100°C. Samples were mainly heated with a Shimadzu DT-30 thermal analyzer, and about 10 mg of a sample was taken into an appropriate aluminum pan and heated up to the prescribed temperature at a rate of 10°C/min in the air. The residue was then subjected to ESCA measurement.

RESULTS AND DISCUSSION

Figure 1 shows S2p (S2p: electron in the 2p orbital of S atom) spectra of MEP and S-Me-MEP measured by ESCA. Binding energies of S2p3/2 electrons (3/2: spin quantum number) of MEP and S-Me-MEP were determined 162.5 eV and 163.9 eV, respectively; the difference in the binding energy was able to distinguish MEP from
S-Me-MEP. The shoulder near 163 eV in the S$_{2p}$ spectrum of MEP is attributed to S$_{2p1/2}$ electrons. ESCA spectra were measured for samples heated up to 190, 235 and 285°C in the air with a DT-30 thermal analyzer. S$_{2p}$ spectra of these samples are shown in Fig. 2. Peaks in S$_{2p}$ spectra were observed in a range of 163.5–164.5 eV. These values were similar to the binding energy of S-Me-MEP. Figure 3 shows N$_{1s}$ spectra of the samples. A sample heated up to 190°C gave peaks of 406.0–406.5 eV in binding energy, the values being very close to 405.9 eV of MEP. Samples heated up to 235 and 285°C, however, showed a peak of 401.5–401.7 eV in binding energy. This suggests that a binding state of the nitrogen atom in MEP gradually changed with temperature up to 235°C.

On the other hand, the binding energies of the nitrogen atom in C$_6$H$_5$NO$_2$, (CH$_3$)$_2$NO and C$_6$H$_5$SCN were 405.1, 402.2 and 398.4 eV, respectively, indicating that the NO$_2$ group in

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**Table 1** ESCA data on MEP heated at various temperatures in the air.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Heat temperature (°C)</th>
<th>MEP (untreated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>190</td>
<td>235</td>
</tr>
<tr>
<td>O$_{1s}$ BE (eV)</td>
<td>532.8</td>
<td>532.8</td>
</tr>
<tr>
<td>HW (eV)</td>
<td>2.30</td>
<td>2.95</td>
</tr>
<tr>
<td>PA (eV·cps)</td>
<td>6612</td>
<td>32684</td>
</tr>
<tr>
<td>N$_{1s}$ BE (eV)</td>
<td>406.0</td>
<td>401.5</td>
</tr>
<tr>
<td>HW (eV)</td>
<td>1.80</td>
<td>2.85</td>
</tr>
<tr>
<td>PA (eV·cps)</td>
<td>795</td>
<td>1413</td>
</tr>
<tr>
<td>S$_{2p}$ BE (eV)</td>
<td>163.4</td>
<td>164.0</td>
</tr>
<tr>
<td>HW (eV)</td>
<td>3.05</td>
<td>4.10</td>
</tr>
<tr>
<td>PA (eV·cps)</td>
<td>608</td>
<td>919</td>
</tr>
<tr>
<td>P$_{2p}$ BE (eV)</td>
<td>134.2</td>
<td>134.2</td>
</tr>
<tr>
<td>HW (eV)</td>
<td>1.95</td>
<td>2.10</td>
</tr>
<tr>
<td>PA (eV·cps)</td>
<td>837</td>
<td>4257</td>
</tr>
</tbody>
</table>

* BE: binding energy, HW: half width, PA: peak area.
MEP changed to a NO group after heating up to 235°C. ESCA data on MEP heated at various temperatures are summarized in Table 1. Peak area ratios of O_{1s}, N_{1s} and S_{2p} to P_{2p} based on the data in Table 1 are shown in Table 2. Changes of relative peak area ratios to those of MEP based on Table 2 are shown in Fig. 4. After heating up to 190°C, the peak area ratio of S_{2p}/P_{2p} was only less than 1.0, and this result was compatible with our previous observation of SO\(_2\) evolution at temperatures of 150 to 190°C.\(^1\) After heating up to 235°C, the peak area ratios of N_{1s} and S_{2p} to P_{2p} suddenly decreased. This indicates that drastic thermal decomposition suddenly took place at temperatures of 210 to 235°C as reported previously.\(^1\) However, no significant difference in the peak area ratios of O_{1s} and N_{1s} to P_{2p} was observed between the samples heated up to 235 and 285°C, suggesting that the composition did not change to a large extent after heating up to 285°C. The values of peak area ratios of O_{1s}, N_{1s} and S_{2p} to P_{2p} of a sample were about 1, 1/3 and 1/8, respectively. This shows that when heated up to 285°C, the product changed to a complicated compound composed of mainly phosphoric acid moieties, a small amount of nitrogen and a trace amount of sulfur. These results support the first, second and third steps of the thermal decomposition mechanism of bulk MEP we proposed previously.

Then in order to determine the temperature where MEP changes to S-Me-MEP, we carried out ESCA measurement using samples heated at various temperatures for 15 min in an ESCA apparatus. The results are shown in Fig. 5. Samples heated up to 125°C gave peaks at 162.5 eV and 163.6 eV in binding energy, which were assigned to MEP and S-Me-MEP, respectively. Samples heated up to 189°C gave a clear peak at 163.8 eV in binding energy. These spectral changes suggest that MEP did not change to S-Me-MEP at a certain temperature, but that it changed to S-Me-MEP gradually at temperatures higher than about 125°C.

The results described above, led us to the conclusion that the results obtained by ESCA measurement are consistent with the thermal decomposition mechanism we proposed previously,\(^1\) and that the thermal decomposition mechanism of MEP on the sample surface is almost the same as that of bulk MEP.

We also found that the NO\(_2\) group in fenitrothion changes to a NO group when heated up to 235°C.

**ACKNOWLEDGMENTS**

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REFERENCES


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要約

ESCA によるフェニトロチオン熱分解の検討

掲出文男、辻孝三、佐々木正夫、畑岡聡正

サンプル表面の熱分解機構を明らかにするために空気中で
190, 235 および 285℃ まで加熱したフェニトロチオンを ESCA
（X 線光電子分光）分析した。190℃ まで加熱したサンプルでは
フェニトロチオンに比べて S 原子の比率が減少した。235℃ まで
加熱したサンプルでは N および S 原子の比率が減少し構成
がフェニトロチオンと大きく異なった。これらは内部報告した
結果を支持した。また ESCA 分析によりフェニトロチオンの
NO₂ 基は 235℃ まで加熱すると NO 基に変化することがわか
った。フェニトロチオンは 125℃ 以上の温度で徐々に S-メチ
ルフェニトロチオンに変化することが確認された。