THE COMPOSITIONS OF SODIUM AND POTASSIUM CHLORATE VAPORS

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THE COMPOSITIONS OF SODIUM AND POTASSIUM CHLORATE VAPORS

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Smyrl and Devlin\textsuperscript{1} have reported the vibrational spectra of
matrix-isolated alkali chlorate vapors. They found some evidence for
the existence of dimeric species, but concluded that, with the possible
exception of $(\text{KClO}_3)_2$, dimer concentrations were quite low. The present
study was undertaken to determine the composition of sodium and
potassium chlorates by high-temperature mass spectrometry.

Mass spectra of sodium and potassium chlorate vapors are shown
in Table I. They were obtained on an Atlas CH4 mass spectrometer
using the Knudsen effusion technique. Turning first to the data for
sodium chlorate, the most obvious feature is the presence of a large
amount of $\text{Na}_2\text{ClO}_3^+$ ion corresponding to the sodium perchlorate dimer
$\text{Na}_2(\text{ClO}_3)_2^+$. Both $\text{Na}^+$ and $\text{NaClO}_3^+$ could in principle also be dimer
fragment ions. Plots of $\log IT$, where $I$ is the ion intensity and
$T$ the temperature, versus $1/T$ gave a value of $41\pm3$ kcal/mole
for $\text{Na}^+$ and $39\pm3$ kcal/mole for $\text{Na}_2\text{ClO}_3^+$. The two values are close
enough to suggest that both ions could come from the same precursor.

To resolve this problem, a technique recently described by Mohazzabi
and Searcy\textsuperscript{2} was used. In this technique, the mass spectrum obtained
using a standard Knudsen effusion cell is compared with that produced
when a cell with a porous alumina lid is used. The porous effusion
barrier effectively reduces the pressure of the effusing gas and
thus, in a mixture of monomer and dimer, shifts the equilibrium to the monomer. The experiment with sodium chlorate was carried out on a Nuclide Analysis Associates mass spectrometer. The results are shown in Table II. It is seen that the $\text{Na}^+ / \text{Na}_2\text{ClO}_3^+$ ion ratio increases from 1.3 in a standard Knudsen experiment to 6.3 in a porous lid experiment. This is a result to be expected if the $\text{Na}^+$ ion is due mainly to the sodium chlorate monomer, $\text{NaClO}_3$. The slopes of the log IT vs 1/T plots for $\text{Na}^+$ and $\text{Na}_2\text{ClO}_3^+$ thus give the heats of vaporization of monomer and dimer in the vapor. We ascribe the entire $\text{Na}^+$ ion intensity to the monomer and assume an ionization cross section ratio of 2:1 for dimer and monomer. On this basis we obtain a minimum dimer concentration of about 30% in the sodium chlorate vapor near 600$^\circ$K. The difference of this result from that obtained by Smyrl and Devlin probably reflects the fact that the evaporation in their experiment was not carried out under equilibrium conditions.\footnote{3}

A notable feature of the mass spectrum of sodium chlorate is the presence of a significant amount of sodium perchlorate dimer ions, $\text{Na}_2\text{ClO}_4^+$, showing the existence in the vapor of sodium perchlorate dimer $\text{Na}_2(\text{ClO}_4)_2$. No evidence for the perchlorate monomer was found; probably, like the chlorate monomer, it fragments mainly to $\text{Na}^+$. Markowitz et al.\footnote{4} have reported the formation of sodium perchlorate from sodium chlorate in the melt at temperatures near 300$^\circ$C, and Ritzhaupt and Devlin\footnote{5} have recently reported matrix isolation spectra of alkali perchlorates.
In the potassium chlorate mass spectrum, no evidence for perchlorate molecules was observed. This result is in agreement with results of Markowitz et al.\textsuperscript{4} who found that sodium chlorate at 300°C produced 0.49\% perchlorate in 2 days, while potassium chlorate at 370°C produced only 0.065 perchlorate in 2 days. For reasons which are not clear, the $\text{K}^+ / \text{K}_2\text{ClO}_3^+$ ratio varied in an unsystematic manner with temperature and no slopes could be obtained. The decomposition of $\text{KClO}_3$ to $\text{KCl}$ may be one reason for the erratic results. To estimate the amount of dimer in the vapor we proceed in the same manner as for sodium chlorate. In this way we calculate a minimum of 4\% dimer at 610°C.

The most interesting aspect of the mass spectrum of potassium chlorate vapor is the complete absence of an monomer parent ion, $\text{KClO}_3^+$. In this respect potassium chlorate is unique among the alkali pseudohalides so far investigated.\textsuperscript{6} Berkowitz\textsuperscript{7,8} has pointed out that the $\text{M}^+ / \text{MX}^+$ of alkali-halide-like compounds increases with increasing ionic character. On this basis, $\text{KClO}_3$ is the most ionic alkali pseudohalide yet observed.

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REFERENCES

3. J. P. Devlin, private communication.
Table I. Mass spectra of sodium and potassium chlorate vapors ion intensities relative to alkali metal ion.

<table>
<thead>
<tr>
<th></th>
<th>595°K</th>
<th>610°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Na}^+$</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>$\text{K}^+$</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>$\text{NaClO}_3^+$</td>
<td>0.02</td>
<td>$\text{KClO}_3^+$</td>
</tr>
<tr>
<td>$\text{NaClO}_4^+$</td>
<td>&lt;0.004</td>
<td>$\text{K}_2\text{ClO}_3^+$</td>
</tr>
<tr>
<td>$\text{Na}_2\text{ClO}_3^+$</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>$\text{Na}_2\text{ClO}_4^+$</td>
<td>0.14</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Porous lid experiment 610°K; ion intensities in arbitrary units.

<table>
<thead>
<tr>
<th></th>
<th>Knudsen Cell</th>
<th>Cell with Porous Lid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Na}^+$</td>
<td>$1.4 \times 10^3$</td>
<td>62</td>
</tr>
<tr>
<td>$\text{Na}_2\text{ClO}_3^+$</td>
<td>$1.1 \times 10^3$</td>
<td>9.8 (613°K)</td>
</tr>
<tr>
<td>$\text{Na}^+/\text{Na}_2\text{ClO}_3^+$</td>
<td>1.3</td>
<td>6.3</td>
</tr>
</tbody>
</table>
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