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THE COMPOSITIONS OF SODIUM AND POTASSIUM CHLORATE VAPORS

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Smyrl and Devlin¹ 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 Na^+ and 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 ± 3 kcal/mole for Na^+ and 39 ± 3 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 Searcy² 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 Na^+ ion is due mainly to the sodium chlorate monomer, NaClO_3 . The slopes of the log IT vs $1/T$ plots for 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 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°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.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 Na^+ . Markowitz et al.⁴ have reported the formation of sodium perchlorate from sodium chlorate in the melt at temperatures near 300°C, and Ritzhaupt and Devlin⁵ 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.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 $K^+/K_2ClO_3^+$ ratio varied in an unsystematic manner with temperature and no slopes could be obtained. The decomposition of $KClO_3$ to 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°K.

The most interesting aspect of the mass spectrum of potassium chlorate vapor is the complete absence of a monomer parent ion, $KClO_3^+$. In this respect potassium chlorate is unique among the alkali pseudohalides so far investigated.⁶ Berkowitz^{7,8} has pointed out that the M^+/MX^+ of alkali-halide-like compounds increases with increasing ionic character. On this basis, $KClO_3$ is the most ionic alkali pseudohalide yet observed.

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Table I. Mass spectra of sodium and potassium chlorate vapors ion intensities relative to alkali metal ion.

595°K		610°K	
Na^+	1.0	K^+	1.0
NaClO_3^+	0.02	KClO_3^+	<0.003
NaClO_4^+	<0.004	K_2ClO_3^+	0.083
$\text{Na}_2\text{ClO}_3^+$	1.2		
$\text{Na}_2\text{ClO}_4^+$	0.14		

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

	Knudsen Cell	Cell with Porous Lid
Na^+	1.4×10^3	62
$\text{Na}_2\text{ClO}_3^+$	1.1×10^3	9.8(613°K)
$\text{Na}^+/\text{Na}_2\text{ClO}_3^+$	1.3	6.3

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