**Vapor Complexation In The Crcl$_3$-Acl (A=Cs,Li) System**

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The vaporization of $CrCl_3$ has been studied over the past years and relative references can be found elsewhere[1]. Thermodynamic functions of vaporization and vapor pressures have been measured and critically evaluated. Monomeric trigonal planar species $CrCl_3(g)$ are formed but the simultaneous appearance of $CrCl_4(g)$ and $CrCl_2(s)$ has been argued to exist [2]. At elevated temperatures many molten binary halide systems are know to enhance their "apparent" volatility by forming gaseous complex molecules which have been useful in a variety of application [3,4]. Many trivalent rare earth halides increase their volatility by reacting with alkali halides and forming vapor molecules with a predominant stoichiometry 1:1 (i.e $ALnX_4$)[4].

In the present work high temperature electronic absorption spectroscopy is used in the temperature range 800-1300 K in order to study the vapors over solid $CrCl_3$ and molten $CrCl_3$-ACl (A= Cs,Li) mixtures. A reverse optics Perkin Elmer Model L-900 spectrophotometer equipped with fiber optics and a three zone cylindrical kanthal furnace capable of handling optical cells up to 10 cm have been used for measuring the spectra.

Figure 1 shows typical vapor spectra over solid $CrCl_3$ and over molten $CrCl_3$-CsCl. Measurements of spectra over $CrCl_3(s)$ in the temperature range 800-1300 K have shown no bands due to $Cl_2(g)$ and/or $CrCl_4(g)$. Bands were seen at temperatures above 950 K and their position remained unchanged with temperature. These bands (Fig. 1a) were assigned to monomeric $CrCl_3(g)$. The 750 nm band with molar absorptivity $\varepsilon \approx 20$ lit.mol$^{-1}$.cm$^{-1}$ is presumably a Cr(III) d←d transition of the trigonal $CrCl_3(g)$ and the 385 nm band a change transfer (CT) transition of the same species.

Spectra of the $CrCl_3$/CsCl vapor complex could be measured even at temperatures below 950 K indicating an "apparent" vapor pressure enhancement of the $CrCl_3(s)$. A d←d Cr (III) broad band near 800 nm with $\varepsilon \approx 21$ lit.mol$^{-1}$.cm$^{-1}$ and a high intensity band CT band near 375 nm were observed. These bands are assigned to the $CsCrCl_4$ vapors species. Temperature dependent measurements in cells having no solid or liquid phases present show both the $CrCl_3(g)$ and $CsCrCl_4(g)$ bands which indicates that these vapor species are in equilibrium: $CsCrCl_4(g) \leftrightarrows CrCl_3(g)+CsCl(g)$.

The data permit the estimation of the volatility enhancement of the $CrCl_3$ due to the comparison reaction. Values above 10 were measured at temperature below 1000 K.

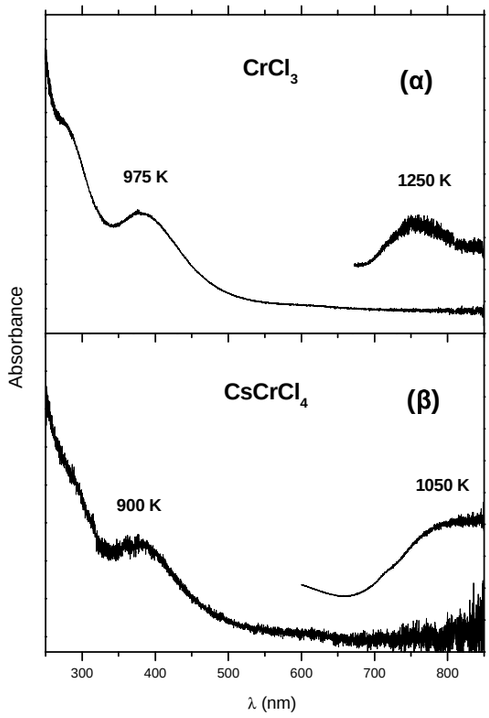


**Fig. 1.** Electronic absorption spectra of $CrCl_3$ and $CsCrCl_4$ vapor species

**References**

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