

MASS SPECTROMETRIC IDENTIFICATION OF CADMIUM(II) CHLOROBROMIDE

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Abstract

Mass spectrometric studies above solid $\text{CdCl}_2 + \text{CdBr}_2$ mixtures in the temperature range 720–770 K have revealed the existence of "mixed halide" gaseous species of formula CdClBr . The heat of formation of CdClBr(g) from $\text{CdCl}_2(\text{g})$ and $\text{CdBr}_2(\text{g})$ has been found to be 0.4 ± 1 kcal/mol. It is reasoned that the driving force for "mixed halide" formation is associated with a decrease in molecular symmetry.

INTRODUCTION

Greiner and Jellineck¹ have measured vapour pressures of the molten $\text{CdCl}_2 + \text{CdBr}_2$ system by using a transpiration vapour pressure technique. They have ascribed apparently high CdCl_2 partial pressures to the formation of the vapour complex $\text{CdCl}_2 \cdot \text{CdBr}_2$. However, in the comparable chromium(II) and lead(II) systems,^{2,3} CrClBr and PbClBr vapour complexes are present and it seemed possible that an analogous cadmium complex is formed. A mass spectrometric investigation has been carried out to determine the vapour-phase species present in this system.

EXPERIMENTAL

An E.A.I. Quad 300 mass spectrometer was used. The sample was contained in a platinum crucible within a silver Knudsen cell as described previously.^{4,5} The advantages of using a quadrupole mass spectrometer for investigations of this sort have been discussed by Hastie.⁶ Temperatures were measured with a Pt/Pt+13% Rh thermocouple in the base of the cell. Throughout the temperature range employed, no liquid phase would be formed.⁷ Solid high-purity CdCl_2 and CdBr_2 were prepared by direct halogenation of molten cadmium metal, as outlined by Bloom *et al.*⁸

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¹ Greiner, B., and Jellineck, K., *Z. phys. Chem.*, 1933, **165**, 97.

² Schoonmaker, R. C., Friedman, A. H., and Porter, R. F., *J. chem. Phys.*, 1959, **31**, 1586.

³ Bloom, H., and Hastie, J. W., *J. phys. Chem.*, 1967, **71**, 2360.

⁴ Bloom, H., and Anthony, R. G., *Aust. J. Chem.*, 1971, **24**, 2001.

⁵ Anthony, R. G., Ph.D. Thesis, University of Tasmania, 1970.

⁶ Hastie, J. W., in "Advances in Molten Salt Chemistry." (Eds J. Braunstein, G. Mamantov, and G. P. Smith.) (Plenum Press: New York 1970.)

⁷ Landolt-Börnstein, "Zahlenwerte und Funktionen." Vol. II, Part 3, p. 137. (Springer-Verlag: Berlin 1956.)

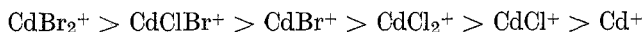
⁸ Bloom, H., Barton, J. L., and Richards, N. E., *Chem. Ind.*, 1956, 439.

RESULTS AND DISCUSSION

The mass spectra obtained did indeed indicate CdClBr(g) formation by the reaction



Ions were observed in the following order of decreasing intensity:



(about 140 : 60 : 40 : 5 : 4 : 1 at 750 K). From analogy with the $\text{PbCl}_2 + \text{PbBr}_2$ system,⁸ the following ion-precursor relationships are assumed to apply: $\text{CdBr}_2^+ \rightarrow \text{CdBr}_2$, $\text{CdClBr}^+ \rightarrow \text{CdClBr}$, $\text{CdCl}_2^+ \rightarrow \text{CdCl}_2$; CdBr^+ , CdCl^+ , Cd^+ could presumably be derived from more than one precursor. At the temperatures employed, no peaks corresponding to any other complex vapour species or to dimers were observed. Checks to ensure that the various ions were not due to second-order effects, such as ion-molecule collisions, have been discussed by Bloom and Hastie,⁹ who also reviewed similar investigations by others. Conditions in this study definitely preclude the possibility of ion-molecule interactions.

Heats of sublimation, ΔH_{sub} , of gaseous species may be determined from the slopes of linear plots of $\ln I^+T$ against $1/T$, where I^+ is the ion current and T is the absolute temperature.^{4,10} Moreover, the heat of formation, ΔH_f , of CdClBr(g) from $\text{CdCl}_2(\text{g})$ and $\text{CdBr}_2(\text{g})$ may then be determined from the following equation:

$$\Delta H_f(\text{CdClBr(g)}) = \frac{1}{2}(2\Delta H_{\text{sub}}(\text{CdClBr}) - \Delta H_{\text{sub}}(\text{CdCl}_2) - \Delta H_{\text{sub}}(\text{CdBr}_2)) \quad (2)$$

Alternatively, the same result for $\Delta H_f(\text{CdClBr(g)})$ may be determined from the slopes of linear plots of $\ln K_r$ against $1/T$ where

$$K_r = \frac{\{IT(\text{CdClBr}^+)\}^2}{IT(\text{CdCl}_2^+) \cdot IT(\text{CdBr}_2^+)} \quad (3)$$

and

$$\Delta H_f(\text{CdClBr}) = -(\text{slope}/2R)$$

The necessary plots are given in Figure 1. In calculating ion currents, the most intense peak in an ion cluster was measured. These were due to the following isotopic combinations:

Ion	<i>m/e</i>	Major contributing species
CdBr_2^+	274	$^{114}\text{Cd}^{79}\text{Br}^{81}\text{Br}$; $^{112}\text{Cd}^{81}\text{Br}^{81}\text{Br}$
CdClBr^+	228	$^{114}\text{Cd}^{35}\text{Cl}^{79}\text{Br}$; $^{112}\text{Cd}^{35}\text{Cl}^{81}\text{Br}$
CdCl_2^+	184	$^{114}\text{Cd}^{35}\text{Cl}^{35}\text{Cl}$; $^{112}\text{Cd}^{35}\text{Cl}^{37}\text{Cl}$

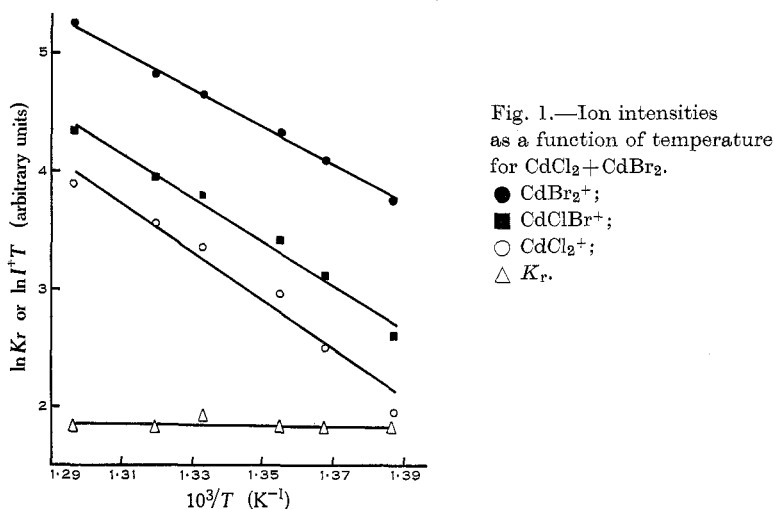
Heats of sublimation, obtained by least-squares analysis are: CdBr_2 32.0 ± 2.0 ; CdCl_2 41.2 ± 4.0 ; CdClBr 37.0 ± 3.5 kcal/mol. The values for CdBr_2 and CdCl_2 agree to within 3 kcal/mol with those given by Kubaschewski *et al.*¹¹ for the pure compounds. The least-squares calculated value for $\Delta H_f(\text{CdClBr(g)})$ was found from

⁹ Bloom, H., and Hastie, J. W., *Aust. J. Chem.*, 1966, **19**, 1003.

¹⁰ Bloom, H., and Hastie, J. W., *J. phys. Chem.*, 1968, **72**, 2706.

¹¹ Kubaschewski, O., Evans, E. L., and Alcock, C. B., "Metallurgical Thermochemistry." 4th Edn, p. 303 *et seq.* (Pergamon: Oxford 1967.)

(3) to be 0.4 ± 1 kcal/mol. (If the calculations of ΔH_f are calculated from (2) the uncertainty of measurement would be ± 7 kcal/mol.)



The measured ΔH_f of CdClBr(g), 0.4 kcal/mol, may be compared with published values^{2,3} for ΔH_f of CrClBr(g) and PbClBr(g), i.e. 0 ± 3 and 1 ± 3 kcal/mol respectively. In these mixtures, as ΔH_f is either zero or very slightly positive, it appears that one bromine atom and one chlorine atom may exchange positions with little loss in total bond strength. It is likely then that a wide range of MClBr(g) species will be formed. The driving force for "mixed halide" formation cannot be enthalpic in origin. Rather the formation of MClBr(g) species is most likely to result from a positive entropy of formation arising from a reduction in molecular symmetry. Hastie⁶ has recently proposed a similar argument to explain the formation of cationic complexes $M^+M^+X_3(g)$.

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