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Note

DECOMPOSITION OF AMMONIUM BIFLUORIDE AND THE PROTON AFFINITY OF THE BIFLUORIDE ION

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The proton affinities of many ions of charge -1 have been determined, and typical values for the proton affinities of these ions range from -1300 to -1600 kJ mole^{-1} [1]. It has previously been shown that the proton affinities of certain anions can be determined by means of an appropriate thermochemical cycle and the measured heat of decomposition of the ammonium salt of that anion [2]. Owing to the hydrogen bonding in HF_2^-, it is expected that the proton affinity of the bifluoride ion should be lower than that of F^-. However, no quantitative estimate of this decreased proton affinity is at hand. Consequently, we have determined the proton affinity of HF_2^- by studying the decomposition of NH_4HF_2 in order to determine the effect that hydrogen bonding to HF has on the proton affinity of F^-.

EXPERIMENTAL

Reagent grade NH_4HF_2 was used without further treatment except for powdering. The decomposition was studied using a Perkin-Elmer differential scanning calorimeter model DSC-1B. Owing to the acidity of NH_4HF_2 at high temperatures, samples were heated in gold pans. Peak areas for the decomposition endotherms were measured using a planimeter, and ΔH was calculated by comparing the peak areas to those obtained using the fusion of metallic tin.

RESULTS AND DISCUSSION

The decomposition of NH_4HF_2 was observed in the range 387–495 K. The average heat of decomposition was found to be 215.6 ± 32.6 kJ mole^{-1} for several samples, although it was observed that some of the endothermic peaks had somewhat different shapes. The decomposition could take place according to

$$NH_4HF_2(s) \rightarrow NH_4F(s) + HF(g) \qquad (1)$$

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$$NH_4F(s) \rightarrow NH_3(g) + HF(g) \qquad (2)$$

However, previous studies [3] have shown that the decomposition takes places instead in a single step

$$NH_4HF_2(s) \rightarrow NH_3(g) + 2\ HF(g) \qquad (3)$$

While the decomposition of NH_4HF_2 in this study gave only a single endothermic peak, it may be that the reaction does not occur cleanly according to eqn. (3) which gives rise to a rather large standard deviation for ΔH and the irregularities in peak shape.

It has been shown that the dominant species present in HF vapor is the hexamer, $(HF)_6(g)$ [4]. Accordingly, we have assumed that the state of the HF(g) produced is that of the hexamer. Therefore, the appropriate thermochemical cycle is

$$\begin{tikzcd} NH_4HF_2(s) \arrow[r, "\Delta H_d"] \arrow[d, "U"] & NH_3(g) + 1/3\,(HF)_6(g) \\ NH_4^+(g) + HF_2^-(g) \arrow[r, "-PA_{NH_3}"] & NH_3(g) + H^+(g) + HF_2^-(g) \arrow[u, "PA_{HF_2^-}"'] \end{tikzcd}$$

where ΔH_d is the enthalpy of decomposition of NH_4HF_2, U is the lattice energy, and PA_{NH_3} and $PA_{HF_2^-}$ are the proton affinities of NH_3 and HF_2^-, respectively. Values of PA_{NH_3} of -866, -870, and -874 kJ mole^{-1} are given [1], and the mean value of -870 kJ mole^{-1} is used here. Consequently, using $U = 705$ kJ mole^{-1} [5] and $PA_{NH_3} = 870$ kJ mole^{-1} [1], the value of 215.6 kJ mole^{-1} for ΔH_d results in $PA_{HF_2^-} = -1359.4$ kJ mole^{-1}. Assuming that the uncertainty in ΔH_d gives the total uncertainty in $PA_{HF_2^-}$, the value would be -1359 ± 33 kJ mole^{-1}. It should be pointed out that if the decomposition is to produce $(HF)_2$ rather than the hexamer and if the addition of H^+ to HF_2^- also yields the dimer, the thermochemical cycle is still valid. It should also be noted that the value of $PA_{HF_2^-}$ determined in this work is comparable to those for other -1 ions [1].

The proton affinity of F^- has been determined by several workers and the reported values have been tabulated by Huheey [1]. It appears that the values of -1544 and -1548 kJ mole^{-1} are the most reliable. Thus, the proton affinity of F^- is about -1546 kJ mole^{-1} and it is considerably larger than that of HF_2^-, with the difference being about 187 kJ mole^{-1}. Hydrogen bonding of F^- to HF does reduce the proton affinity of F^- significantly. It is interesting that the reaction

$$F^- + HF \rightarrow FHF^- \qquad (4)$$

has a ΔH of -155 kJ mole^{-1} [6]. This value is, to within experimental error, about equal to the difference between the proton affinities of F^- and HF_2^-. It appears that the proton affinity of HF_2^-, which is considered as F^-

hydrogen bonded to HF, is just about equal to that of F^- reduced by the strength of the hydrogen bond to it.

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