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Note

A TG STUDY OF THE DECOMPOSITION OF AMMONIUM FLUORIDE AND AMMONIUM BIFLUORIDE

J.E. HOUSE, Jr. and CAROL S. RIPPON

Department of Chemistry, Illinois State University, Normal, IL 61761 (U.S.A.)

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There is a large and rapidly growing body of literature dealing with the analysis of TG curves to obtain kinetic data. A large number of numerical methods exist as well as methods derived fundamentally from rate laws. However, many of these methods are tested using hypothetical TG curves or else by the use of a model reaction, such as the dehydration of $CaC_2O_4 \cdot H_2O$, in order to show the superiority of one method over another [1]. However, we have found it equally necessary to allow for the effects of different samples in order to reveal small differences produced by the method of data treatment. Thus, sufficient data must be available to eliminate the sample-to-sample effects [2] and these are of different magnitudes depending on the type of reaction. Ammonium salts provide good examples for testing data analysis methods since there is complete mass loss [2,3]. The work reported here expands our previous results to establish kinetic parameters for the decomposition of ammonium fluoride and ammonium bifluoride.

EXPERIMENTAL

The NH_4F and NH_4HF_2 used in this work were of reagent grade and were used without further treatment.

TG studies were carried out using a Perkin-Elmer thermogravimetric system TGS-2. Procedures used were similar to those previously described [4]. The TG data were analyzed according to the method of Coats and Redfern [5] using the equations

$$\ln \ln \frac{1}{1-\alpha} - 2 \ln T = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{1}$$

when $n = 1$ and, when $n \neq 1$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)\,T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{2}$$

Kinetic orders of 0, 1/3, 2/3, 1 and 2 were tested and data analysis was carried out as previously described [3].

RESULTS AND DISCUSSION

The TG curves for the decomposition of NH_4F and NH_4HF_2 show that both decompose in a single step and there is no evidence of the conversion of NH_4HF_2 to NH_4F by loss of HF. The fluoride decomposed in the range 40—210°C and the bifluoride decomposed in the range 120—220°C. The melting point of NH_4HF_2 is 126.5°C so the decomposition of NH_4HF_2 is from the liquid state. Also, no evidence was found for the reaction

$$2\,NH_4F(s) \rightarrow NH_4HF_2(s) + NH_3(g) \qquad (3)$$

reported earlier for the decomposition of NH_4F [6]. Decomposition in a single step has characterized all the ammonium compounds that we have studied [2,3].

Kinetic parameters derived from analysis of the $f(\alpha)$ and temperature data are summarized in Table 1. In the case of NH_4F, the same correlation coefficient results when $n = 0$ and when $n = 1/3$. Also, the result when $n = 2/3$ yields almost as high a correlation coefficient. Realistically, the data do not actually differentiate between orders in the range 0—2/3. Although the correlation coefficients are nearly equal in this range, the smallest standard deviation in r values resulted with the $n = 1/3$ series of r values. This may indicate that $n = 1/3$ is the empirically "correct" order. The activation energy corresponding to this order is 47.39 ± 4.67 kJ $mole^{-1}$ although the actual activation energy could differ somewhat due to the uncertainty in the order. This E_a value is the lowest found for the decomposition of any of the ammonium compounds that we have studied [2,3]. Assuming that the rate determining step in the decomposition is the transfer of a proton from NH_4^+ to the anion, this would be expected owing to the strong hydrogen bonding to the fluoride ion. Therefore, due to the stronger hydrogen bonding, transfer of the proton to the fluoride ion should be easier than it is for other anions even though the lattice energy would be expected to be highest.

In the case of NH_4HF_2, the highest correlation coefficient ($r = 0.9998 \pm 0.0003$ was found when $n = 1/3$. However, the r value when $n = 2/3$ is almost as high so it is not possible to differentiate between the results obtained when n is in the range 0—2/3. The activation energy corresponding to the $n = 1/3$ case is 63.38 ± 4.21 kJ $mole^{-1}$. This value is higher than that for the decomposition of the fluoride and is close to that for the decomposition of $NH_4C_2H_3O_2$ [3]. This could reflect a lower tendency of the NH_4^+ ion to hydrogen bond to the HF_2^- ion [7]. A greater energy would thus be required for transfer of the proton to HF_2^- than to F^-. In neither case is the E_a value near the N—H bond enthalpy of 386 kJ $mole^{-1}$ [8] so the mechanism must involve a tunneling process rather than a direct bond breaking.

It is interesting that in the case of NH_4F and NH_4HF_2, even when average values from several samples are available, it is still not possible to unequivocally establish the order of the decomposition reactions. The decomposition of $(NH_4)_2CO_3$, NH_4HCO_3, and $(NH_4)_2SO_3$ gives the highest r when $n = 1$ [2,3]. Ammonium oxalate and $NH_4C_2H_3O_2$ give the best fit with $n = 0$, and NH_4BF_4 gives virtually identical r values when $n = 1/3$ or $n = 2/3$ [3]. It thus appears that there is not a "best" order that characterizes the decomposition

TABLE 1

Kinetic parameters [a] for the decomposition of NH_4F and NH_4HF_2

Order, n	NH_4F			NH_4HF_2		
	Corr. coeff.	E_a (kJ $mole^{-1}$)	ln A	Corr. coeff.	E_a (kJ $mole^{-1}$)	ln A
0	0.9989 ± 0.0008	43.42 ± 4.29	9.22 ± 1.14	0.9992 ± 0.0005	57.78 ± 3.75	12.20 ± 0.70
1/3	0.9989 ± 0.0004	47.39 ± 4.67	10.40 ± 1.25	0.9998 ± 0.0003	63.38 ± 4.21	14.15 ± 0.73
2/3	0.9980 ± 0.0008	51.09 ± 4.50	11.69 ± 1.37	0.9996 ± 0.0004	69.42 ± 4.76	15.82 ± 0.78
1	0.9962 ± 0.0017	56.26 ± 5.69	13.11 ± 1.62	0.9988 ± 0.0010	75.78 ± 5.45	17.59 ± 0.83
2	0.9826 ± 0.0151	71.95 ± 7.92	17.70 ± 2.11	0.9932 ± 0.0038	98.03 ± 8.12	23.57 ± 1.11

[a] Shown as mean values ± standard deviation. Eight samples of NH_4F and six samples of NH_4HF_2 were used to compute these values.

of a range of ammonium compounds and that the activation energies vary from about 45 kJ mole^{-1} for NH_4F to about 156 kJ mole^{-1} for $(NH_4)_2C_2O_4$. Clearly, no single kinetic pattern describes all these decomposition reactions.

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