

Note

TG STUDIES ON THE DECOMPOSITION OF SOME AMMONIUM COMPOUNDS

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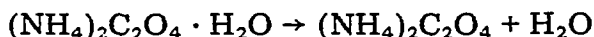
The decomposition of ammonium compounds can serve as a useful model for comparing kinetic treatments of TG data owing to the complete mass loss. Hypothetical data generated by assuming certain values for kinetic parameters seem to offer no advantage. Recently, we have begun a study of the thermal characteristics of ammonium compounds in order to determine the kinetic [1] and thermodynamic [2] parameters associated with decomposition. It was found that the decomposition of $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 gave the best fit when the first order Coats and Redfern equation [3] was used. Correlation coefficients could be used to distinguish between different orders only when mean values for several samples were used [1]. In general, correlation coefficients do not provide a reliable means of identifying a "correct" mechanistic model [4]. We have extended our study to include additional ammonium salts in an effort to determine if the characteristics of the decomposition of $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 are revealed in the decomposition of other ammonium salts. In the present paper we report the results of TG studies on $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, NH_4BF_4 , $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$.

EXPERIMENTAL

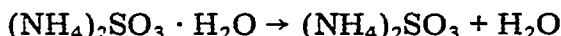
The ammonium salts used in this work, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, NH_4BF_4 , $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, were of the highest purity available and were used without further treatment. Thermogravimetric analyses were carried out using a Perkin-Elmer TGS-2 system. Procedures used were similar to those previously described [5]. In all cases a minimum of three samples were studied and kinetic parameters were determined using the Coats and Redfern equation [3] within the range $0.1 \leq \alpha \leq 0.8$. Calculations were carried out using a Texas Instruments TI-59 programmable calculator. A program was designed to enable the input of deflections of the mass curve at various temperatures and then to calculate the desired function $f(\alpha)$ for each temperature-deflection data pair depending on the order assumed. These $f(\alpha)$ values are stored and then linear regression analysis is performed without additional data entry. The value of n is then changed and a new set of $f(\alpha)$ calculated automatically until all the desired values of n are used. The deflection-temperature data are entered only once for each sample.

RESULTS AND DISCUSSION

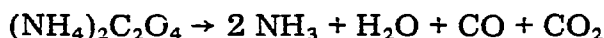
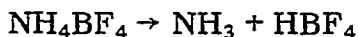
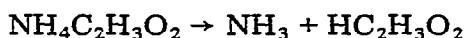
The TG curves for the ammonium salts are shown in Fig. 1. In the case of the hydrated salts the dehydration is identifiable as a separate step. Kinetic parameters for the dehydration reactions



and



were also determined. The decomposition reactions



all appear as a single step in the mass loss curves.

As was found for the decomposition of $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 [1], the correlation coefficients do not appear to change much by assuming different reaction orders. This has been investigated in the present study for the four ammonium salts studied here. Table 1 shows the correlation coefficients obtained when reaction orders of 0, 1/3, 2/3, 1 and 2 are used in the Coats and Redfern equation. In determining the individual correlation coefficients, no attempt was made to delete or smooth points to obtain a higher value.

It is readily apparent that for certain cases there is very little difference in the correlation coefficient produced by assuming different reaction orders. For example, the decomposition of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ gives $r > 0.99$ for any order from $n = 0$ to $n = 1$. In this case, the highest r value results when the zero order equation is used. Similarly, in the case of NH_4BF_4 all orders from 0 to 2 result in $r > 0.994$. Thus, any order from 0 to 2 might be deemed "acceptable" for the decomposition of NH_4BF_4 although the best fit is obtained with $n = 2/3$. It is also generally true that the value of n that results in the

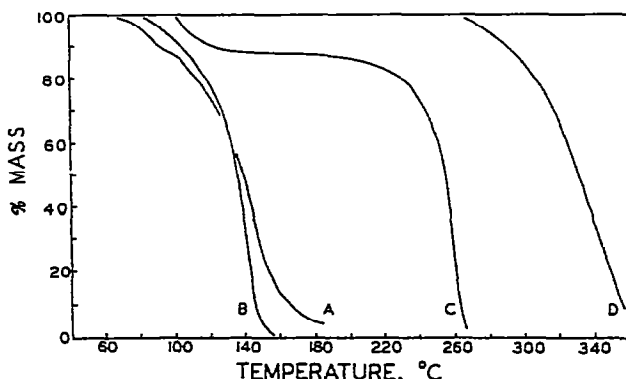


Fig. 1. TG curves for the decomposition of $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ (A), $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (B), $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (C), and NH_4BF_4 (D).

TABLE 1

Correlation coefficients for fitting various orders to the Coats and Redfern equation ^a

Compound	Correlation coefficient				
	n = 0	n = 1/3	n = 2/3	n = 1	n = 2
NH ₄ C ₂ H ₃ O ₂	0.9993 ± 0.0004 ^b	0.9980 ± 0.0009	0.9960 ± 0.0016	0.9934 ± 0.0026	0.9826 ± 0.0061
NH ₄ BF ₄	0.9987 ± 0.0014	0.9995 ± 0.0004	0.9996 ± 0.0003 ^b	0.9991 ± 0.0007	0.9944 ± 0.0023
(NH ₄) ₂ C ₂ O ₄ · H ₂ O Dehydration	0.9598 ± 0.0141	0.9648 ± 0.0114	0.9809 ± 0.0087	0.9912 ± 0.0065 ^b	0.9869 ± 0.0093
(NH ₄) ₂ C ₂ O ₄ Decomposition	0.9887 ± 0.0047 ^b	0.9855 ± 0.0058	0.9817 ± 0.0071	0.9770 ± 0.0087	0.9599 ± 0.0150
(NH ₄) ₂ SO ₃ · H ₂ O Dehydration	0.9788 ± 0.0042	0.9865 ± 0.0013	0.9922 ± 0.0017	0.9950 ± 0.0017 ^b	0.9870 ± 0.0097
(NH ₄) ₂ SO ₃ Decomposition	0.9672 ± 0.0187	0.9825 ± 0.0125	0.9930 ± 0.0076	0.9976 ± 0.0030 ^b	0.9848 ± 0.0157

^a Shown as mean value ± standard deviation.^b "Correct" order.

TABLE 2

Apparent activation energies obtained using various orders with the Coats and Redfern equation ^a

Compound	Activation energy (kJ mole ⁻¹)				
	n = 0	n = 1/3	n = 2/3	n = 1	n = 2
NH ₄ C ₂ H ₃ O ₂	58.8 ± 6.2 ^b	63.5 ± 7.1	68.7 ± 8.1	74.1 ± 9.2	92.8 ± 12.7
NH ₄ BF ₄	89.3 ± 7.6	96.4 ± 7.7	104.0 ± 7.8 ^b	112.1 ± 7.9	139.2 ± 8.0
(NH ₄) ₂ C ₂ O ₄ · H ₂ O Dehydration	74.9 ± 5.7	86.5 ± 3.5	103.4 ± 3.3	124.3 ± 3.6 ^b	211.6 ± 13.0
(NH ₄) ₂ C ₂ O ₄ Decomposition	156.8 ± 15.2 ^b	167.4 ± 19.7	177.7 ± 24.4	188.8 ± 29.6	226.9 ± 48.6
(NH ₄) ₂ SO ₃ · H ₂ O Dehydration	97.1 ± 7.7	106.0 ± 5.5	116.2 ± 2.9	128.0 ± 3.0 ^b	171.9 ± 20.2
(NH ₄) ₂ SO ₃ Decomposition	46.5 ± 6.1	54.9 ± 5.2	65.3 ± 4.6	77.8 ± 6.1 ^b	129.4 ± 22.7

^a Shown as mean value ± standard deviation.^b "Correct" values.

TABLE 3
 Logarithm of frequency factor obtained by fitting the α vs. t data to various orders of the Coats and Redfern equation ^a

Compound	ln A				
	n = 0	n = 1/3	n = 2/3	n = 1	n = 2
NH ₄ C ₂ H ₃ O ₂	16.38 ± 1.51 ^b	17.75 ± 1.57	19.20 ± 1.62	20.75 ± 1.68	25.96 ± 1.89
NH ₄ BF ₄	16.11 ± 1.60	17.62 ± 1.63	19.23 ± 1.66 ^b	20.94 ± 1.68	26.72 ± 1.71
(NH ₄) ₂ C ₂ O ₄ · H ₂ O Dehydration	21.91 ± 1.08	26.27 ± 1.06	31.69 ± 0.99	38.35 ± 0.98 ^b	65.93 ± 3.86
(NH ₄) ₂ C ₂ O ₄ Decomposition	34.55 ± 3.64 ^b	36.86 ± 4.63	39.30 ± 5.70	41.95 ± 6.92	51.01 ± 11.36
(NH ₄) ₂ SO ₃ · H ₂ O Dehydration	31.71 ± 2.43	34.81 ± 1.67	38.36 ± 0.81	42.42 ± 1.20 ^b	57.64 ± 7.22
(NH ₄) ₂ SO ₃ Decomposition	12.75 ± 1.77	15.43 ± 1.51	18.52 ± 1.40	22.38 ± 1.88 ^b	38.12 ± 6.87

^a Shown as mean value ± standard deviation.

^b "Correct" values.

highest value of r also gave the lowest standard deviation for the individual values. In other cases, such as the dehydration of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, the correlation coefficients show a much larger variation with order.

While the correlation coefficients do not show much variation with assumed reaction order, the activation energies do. The apparent activation energy values are shown in Table 2. For example, r varies from only 0.9944 to 0.9996 for the decomposition of NH_4BF_4 regardless of the order assumed. However, the apparent activation energy varies from 89.3 to 139.2 kJ mole⁻¹ depending on the value of n . For a given reaction, the higher the assumed order, the higher the apparent activation energy. Other examples produce an even more drastic change in apparent activation energy as the assumed order varies. While it is apparent that a reasonable correlation coefficient results from almost any assumed order, it is equally apparent that this situation does not exist for the activation energy. It seems that as a matter of routine several orders must be assumed and the corresponding apparent activation energy and correlation coefficient determined to have any certainty that a "correct" order and kinetic parameters have been obtained. Again, as in our previous study [1], it is obvious that it is unreliable to assign an order on the basis of a single run.

Table 3 shows the $\ln A$ values for the reactions when various orders are assumed. It is seen that a higher assumed order always results in a higher value of $\ln A$ for a given reaction.

The data presented here show that since the apparent activation energy and the pre-exponential factor vary widely and regularly with the assumed kinetic order, reliable values for these parameters will be obtained only when the "correct" order is assured. That condition will be met only when several possible orders have been tried and the highest correlation coefficient is obtained. The acceptable criterion should be that the value of r is higher than that found for any other order, not that it is higher than some arbitrary reference value, say 0.98 or so. Again, this study and our previous work [1] have shown that the "correct" order can be based only on average values for r because individual sample variations may be larger than those produced by different assumed orders.

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