

Note

KINETIC PARAMETERS AND MECHANISMS OF DECOMPOSITION FOR SOME AMMONIUM SALTS

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In previous studies, the decomposition of ammonium salts has been utilized to investigate the magnitude of sample-to-sample variations and the reliability of data analysis methods [1–5]. These compounds are useful because decomposition leads to complete mass loss. Further, we have used the measured heats of decomposition with other thermodynamic data to determine proton affinities of the anions [6–8]. Reich and Stivala have published a useful method for analyzing data from two TG runs for which the heating rates differ by a factor of two to determine the mechanism of a reaction [9]. We have tested this method for a variety of reactions to determine the extent to which the mechanism indicated depends on the input data used [10]. In the present work, we have studied the decomposition of several ammonium salts to extend that work.

EXPERIMENTAL

The compounds $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ studied in this work were of reagent grade, and they were used without further treatment.

Thermal studies were carried out using equipment and procedures that have been previously described [10]. Heating rates of 5, 10, and $20^\circ\text{C min}^{-1}$ were used. Kinetic parameters were evaluated by the methods of Coats and Redfern [11] and Reich and Stivala [12]. The Coats and Redfern method tested n values of 0, $1/3$, $2/3$, ..., 2. The procedure of Reich and Stivala was employed to determine the rate laws that gave the best representation of the data and thereby indicate probable mechanism [9].

RESULTS AND DISCUSSION

Ammonium sulfate was found to decompose in two steps

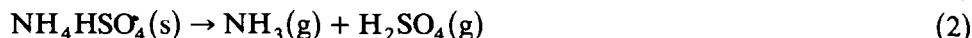


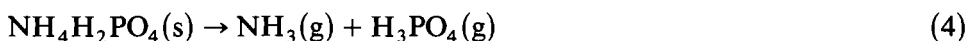
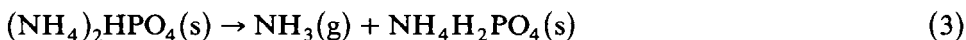
TABLE 1

Kinetic parameters for the decomposition reactions of ammonium salts

Starting compound	Heating rate (°C min ⁻¹)	Coats and Redfern method		Reich and Stivala method	
		<i>n</i>	<i>E</i> (kJ mol ⁻¹)	<i>n</i>	<i>E</i> (kJ mol ⁻¹)
(NH ₄) ₂ SO ₄ , eqn. (1)	5	1/3	153.0	0.60	162.0
	10	0	114.0	0.11	102.0
	20	0	101.0	0.10	97.9
(NH ₄) ₂ SO ₄ , eqn. (2)	5	0	111.0	0.04	110.0
	10	0	122.0	0.00	111.0
	20	0	122.0	0.08	120.0
(NH ₄) ₂ HPO ₄ , eqn. (3)	5	1/3	44.4	0.25	39.4
	10	0	45.1	0.15	47.9
	20	1	77.4	0.68	62.5
(NH ₄) ₂ HPO ₄ , eqn. (4)	5	2	177.0	2.14	213.0
	10	4/3	130.0	1.25	120.0
	20	2	107.0	2.39	139.0
(NH ₄) ₂ C ₂ O ₄ ·H ₂ O, eqn. (5)	5	1/3	71.8	0.34	70.1
	10	4/3	128.0	1.48	137.0
	20	1	72.5	1.12	76.2
Ce(NH ₄) ₄ (SO ₄) ₄ ·2H ₂ O, eqn. (7)	5	2	111.0	2.00	112.0
	10	2	169.0	5.38	355.0
Ce(NH ₄) ₄ (SO ₄) ₄ ·2H ₂ O, eqn. (8)	5	2/3	118.0	0.77	119.0
	10	2/3	139.0	0.62	135.0
Ce(NH ₄) ₄ (SO ₄) ₄ ·2H ₂ O, eqn. (9)	5	5/3	320.0	2.36	429.0
	10	1/3	183.0	0.33	180.0

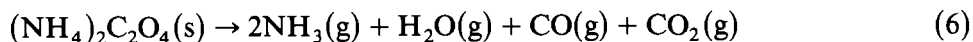
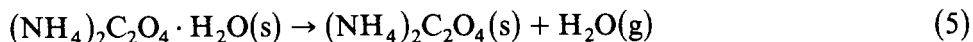
For both reactions the kinetic data are shown in Table 1. Analysis of the data for the runs at 5 and 10°C min⁻¹ indicates that the mechanism is D3 ($1 - (1 - \alpha) \wedge (1/3) \wedge 2$) for both reactions. The same mechanism is indicated by the analysis of the data from the 10 and 20°C min⁻¹ runs.

The decomposition of (NH₄)₂HPO₄ was also found to occur in two steps



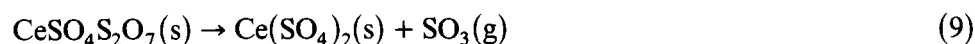
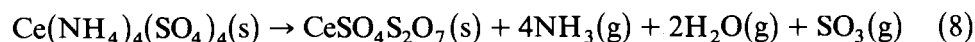
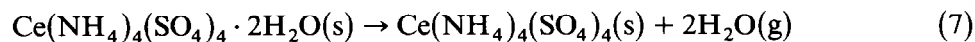
Kinetic parameters for these reactions are shown in Table 1. Data from the 5 and 10°C min⁻¹ runs taken in combination yield a best fit mechanism of D3 for the process shown in eqn. (3). For the second step in the decomposition, the data from the 5 and 10°C min⁻¹ runs indicate a D3 mechanism but the data from the 10 and 20°C min⁻¹ runs indicate a P3 $\alpha \wedge (1/2)$ mechanism. It is quite likely that the run at 20°C min⁻¹ is spurious since both the Coats and Redfern and Reich and Stivala methods yield greatly different kinetic parameters for that run than for those at 5 and 10°C min⁻¹. Consequently, the D3 mechanism seems the more probable.

The decomposition of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ occurs in two steps with the first being dehydration.



Kinetic parameters for the first reaction are shown in Table 1, but reproducible kinetic parameters could not be obtained for the second reaction. Data from runs at 5 and 10 °C min⁻¹ yield the D3 mechanism while data from the 10 and 20 °C min⁻¹ runs indicate a P3 mechanism for the dehydration reaction. In this case, all three runs yielded substantially different kinetic parameters so there is no basis for choosing between the D3 and P3 mechanisms. It again becomes clear that the mechanism indicated depends on the choice of input data [10]. Although the kinetic parameters for the second reaction were erratic, analysis of the data from the 5 and 10 °C min⁻¹ runs indicates a D3 mechanism. However, the data from 10 and 20 °C min⁻¹ runs indicate a P3 mechanism.

The decomposition of $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ was found to take place in three steps. Based on the mass losses observed, the reactions indicated are



For this compound, heating rates of 5 and 10 °C min⁻¹ were used. Analysis of the data from these runs using the Reich and Stivala algorithm indicates that the first and second steps follow a D3 mechanism. The third step gave the best fit with the P3 mechanism. Kinetic parameters for these reactions are shown in Table 1. The kinetic parameters for the second reaction [eqn. (8)] show satisfactory agreement between the 5 and 10 °C min⁻¹ runs when the results of either the Coats and Redfern or Reich and Stivala methods are considered. The results from the two data analysis methods also agree well. However, the results for the reaction shown in eqn. (7) gave very poor agreement when runs at 5 and 10 °C min⁻¹ are considered. Since the Coats and Redfern method tests values up to $n = 2$, that value gave the best fit. However, the Reich and Stivala method iterated to find $n = 5.38$, an unusually high value. The third step in the decomposition also gave kinetic parameters which were quite different for the 5 and 10 °C min⁻¹ runs. This reaction appears to be somewhat erratic and the TG curves show different shapes in this region.

The results obtained in this work show that kinetic parameters obtained by the Coats and Redfern and the Reich and Stivala methods are, in general, in satisfactory agreement. For certain reactions, the mechanism indicated by the Reich and Stivala procedure [9] shows no variation when data from several runs are used. In general, however, it appears that the assignment of

a mechanism is not unambiguous. Consideration of the kinetic parameters from several runs may help identify spurious results which may help eliminate some of the mechanisms indicated.

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