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A TG STUDY OF THE KINETICS OF DECOMPOSITION OF AMMONIUM CARBONATE AND AMMONIUM BICARBONATE

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ABSTRACT

The decomposition of ammonium carbonate and ammonium bicarbonate has been studied by TG. In each case, the reactions follow first order kinetics most closely. For the carbonate, the activation energy for decomposition is 85.73 ± 6.02 kJ mole^{-1}, while that of the bicarbonate is 86.19 ± 7.78 kJ mole^{-1}. Since both solids decompose to give only gaseous products, the largest possible mass loss is observed resulting in minimal experimental error. These reactions have thus served as models and have permitted an accurate assessment of the effects of equation variables on derived kinetic constants.

INTRODUCTION

The applicability of kinetic models for nonisothermal studies on solid state reactions has received a great deal of attention in recent years [1—6]. Many mathematical techniques and equations have been proposed which yield varying degrees of success. One equation that has been shown to have broad applicability is that of Coats and Redfern [7]. Comparisons between this and other equations are frequently made on the basis of some model reaction [2] or on a set of hypothetical curves [6,8]. Analysis of hypothetical curves does not necessarily prove an equation best suited for real reactions. Also, it is not possible to evaluate the magnitude of the actual variations produced by experimental data from different runs. Analysis of a model reaction such as the dehydration of $CaC_2O_4 \cdot H_2O$ involves the study of a process for which the theoretical mass loss is 13.8%. Small experimental errors are thus magnified and may thus constitute a significant fraction of the parameter being measured, leading to α values that are not accurate enough to discriminate between different kinetic treatments. This is especially true if a limited range of α is chosen. Accordingly, the decomposition of ammonium carbonate and ammonium bicarbonate has been chosen as model reactions because the decomposition leads to 100% mass loss in each case. Thus, small systematic errors have minimal effect on the kinetic analysis. Therefore, these reactions provide an extreme case in that even with α in the range 0.2—0.8 the reaction still involves a 60% mass loss from the sample.

It has been shown that regardless of the actual kinetic equation used the

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correlation coefficient may be high [6,8—11]. Thus, it may not be possible to discriminate between several kinetic models using this parameter. One objective of this study was to determine the effect on the derived kinetic parameters produced by a particular kinetic model [7] and assuming several values of the kinetic order.

Few thermal studies have been carried out on the ammonium compounds used in this work [12—14]. These studies have produced conflicting data or no data at all on the reaction parameters. Isothermal studies have been carried out by observing the gas pressure as a function of temperature [15,16]. One TG study of the decomposition of NH_4HCO_3 has been carried out yielding an activation energy of 10.6 kcal $mole^{-1}$ [17]. Consequently, a second objective of this study was to determine reliable kinetic data for the decomposition of NH_4HCO_3 and $(NH_4)_2CO_3$.

EXPERIMENTAL

Reagent-grade ammonium carbonate and ammonium bicarbonate were used without further treatment. Thermogravimetric analyses were carried out using a Perkin-Elmer thermogravimetric system Model TGS-2. Procedures used were similar to those previously described [18]. All computations were carried out using a programmable calculator, and a linear regression analysis was used to compute slopes, intercepts, and standard deviations.

RESULTS AND DISCUSSION

Much has been written about using the correct value for the order, n, in the kinetic expressions for a solid state process [1—6]. The TG curves for the decomposition of $(NH_4)_2CO_3$

$(NH_4)_2CO_3 \rightarrow 2\ NH_3 + CO_2 + H_2O$

and the decomposition of NH_4HCO_3

$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$

are shown in Fig. 1. To determine the effect of n on the kinetic analysis, the Coats and Redfern equation

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

was employed in all cases except where $n = 1$. In that case

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

was used [7]. In these equations, T is the temperature (K), R is the gas constant, n is the order, A is the pre-exponential factor, and β is the heating rate. For each run, the curves were analyzed assuming n = 0, 1/3, 1/2, 2/3, 3/4, 1 and 2 to determine exactly how much effect the order has on the derived

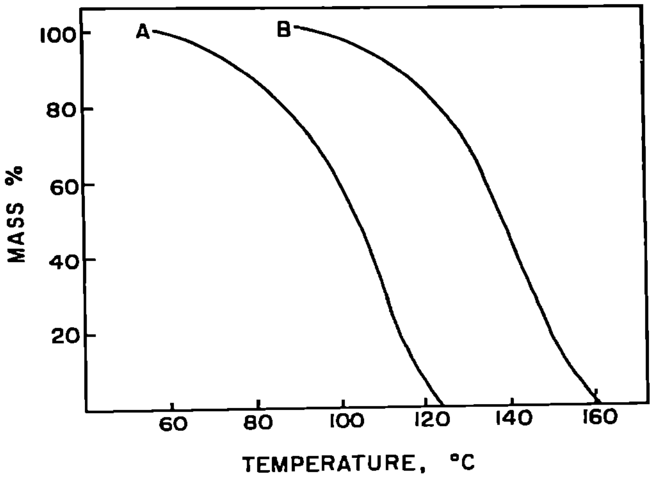

Fig. 1. TG curves for $(NH_4)_2CO_3$ (A) and NH_4HCO_3 (B).

kinetic parameters. The results of the numerical analysis of the curves in the range $0.04 \leqslant \alpha \leqslant 0.80$ are shown in Tables 1—6.

Correlation coefficients

The data shown in Tables 1—6 reveal several interesting features. First, the average correlation coefficients for several runs show that for both NH_4HCO_3 and $(NH_4)_2CO_3$ the best fit is provided by the first order equation. However, with both compounds certain individual runs gave a higher correlation coefficient for some value of n other than 1. For example, with $(NH_4)_2CO_3$, samples 2 and 4 both gave a higher correlation coefficient with $n = 2$ than with $n = 1$. However, the average value, $\bar{r}$, for five runs is 0.9978 when $n = 1$, compared with 0.9946 when $n = 2$. Therefore, a slightly better fit is provided by the first order equation than by the second order equation, but this would not necessarily appear to be so on the basis of one or two

TABLE 1

Correlation coefficients for fitting $f(\alpha)$ to the Coats and Redfern equation for the decomposition of $(NH_4)_2CO_3$

Sample	Correlation coefficient						
	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 3/4$	$n = 1$	$n = 2$
1	0.9973	0.9990	0.9995	0.9998	0.9999	0.9999	0.9951
2	0.9937	0.9956	0.9964	0.9971	0.9975	0.9983	0.9994
3	0.9923	0.9955	0.9966	0.9977	0.9981	0.9999	0.9964
4	0.9844	0.9875	0.9890	0.9903	0.9909	0.9924	0.9947
5	0.9865	0.9929	0.9955	0.9975	0.9982	0.9995	0.9875
$\bar{r}$	0.9908	0.9941	0.9954	0.9965	0.9969	0.9978	0.9946
σ	0.0053	0.0042	0.0039	0.0036	0.0035	0.0031	0.0044

TABLE 2

Activation energies for the decomposition of $(NH_4)_2CO_3$ assuming different orders of reaction

Sample	Activation energy (kJ mole^{-1})						
	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 3/4$	$n = 1$	$n = 2$
1	66.81	70.27	72.10	73.95	74.98	77.94	91.39
2	72.36	74.96	76.29	77.67	78.38	80.50	89.80
3	76.76	80.85	82.65	84.87	85.97	89.42	105.05
4	79.63	82.61	84.24	85.74	86.56	89.03	100.68
5	71.60	77.34	80.53	83.95	85.75	91.50	119.93
$\bar{E}_a$	73.43	77.20	79.16	81.24	82.32	85.68	101.37
σ	4.94	4.98	4.94	5.16	5.31	6.04	12.17

samples. Inferring a kinetic order on the basis of a limited number of runs could lead to incorrect assignment of n. It is particularly interesting to note that for NH_4HCO_3 only one value of the correlation coefficient was below 0.990 for any assumed order (sample 6 when $n = 0$). All others were between 0.990 and 1.000. In the case of $(NH_4)_2CO_3$, only four values of r were below 0.990 for five samples analyzed according to seven values for n.

It is apparent that for the compounds studied here any reasonable value for n gives a reasonably good fit to the data according to the Coats and Redfern equation. Therefore, not only might one not assign the correct order on the basis of a limited number of samples, it might not make much difference as far as getting a "linear" Coats and Redfern plot is concerned. This point should be kept in mind in reporting kinetic data obtained from TG studies regardless of the numerical procedure used to relate f(α) to the temperature. Likewise, computer optimization of TG data to give the n value of best fit appears to be unwarranted in many cases.

Activation energies

It is interesting to note that both NH_4HCO_3 and $(NH_4)_2CO_3$ give considerable variation in activation energy values between individual samples when a given order is assumed. For example, when $n = 1$ in the case of $(NH_4)_2CO_3$, the activation energy values for the samples range between 77.94 and 91.50 kJ mole^{-1}, giving a standard deviation of 6.04 kJ mole^{-1}. Two of the samples when $n = 2$ fall within that range, and three of the samples would fall within that range when $n = 1/2$. Most of the values obtained assuming $n = 2/3$ or $n = 3/4$ would also fall within that range.

The same situation is also revealed in the case of NH_4HCO_3, where the mean value from six samples is 86.19 kJ mole^{-1} with a standard deviation of 7.70 kJ mole^{-1} when $n = 1$ is used. The mean activation energies also fall within this range when $n = 1/2$, 2/3, and 3/4, and several individual values when n is assumed to be 0 and 1/3 are within this range. Only when it is assumed $n = 2$ or $n = 0$ is there much of an effect on the activation energy

TABLE 3

Values of the pre-exponential factor (A) for the decomposition of $(NH_4)_2CO_3$ assuming different orders of reaction

Sample	Pre-exponential factor						
	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 3/4$	$n = 1$	$n = 2$
1	8.388×10^{8}	2.819×10^{9}	5.381×10^{9}	1.046×10^{10}	1.470×10^{10}	4.226×10^{10}	4.828×10^{12}
2	4.062×10^{9}	1.017×10^{10}	1.632×10^{10}	2.655×10^{10}	3.409×10^{10}	7.223×10^{10}	1.920×10^{12}
3	2.202×10^{10}	9.245×10^{10}	1.755×10^{11}	3.856×10^{11}	5.654×10^{11}	1.904×10^{12}	4.634×10^{14}
4	4.648×10^{10}	1.330×10^{11}	2.294×10^{11}	4.015×10^{11}	5.354×10^{11}	1.280×10^{12}	8.014×10^{13}
5	5.542×10^{9}	4.204×10^{10}	1.297×10^{11}	4.321×10^{11}	8.145×10^{11}	6.164×10^{12}	1.328×10^{17}
$\bar{A}$	1.579×10^{10}	5.610×10^{10}	1.113×10^{11}	2.512×10^{11}	3.928×10^{11}	1.892×10^{12}	2.667×10^{16}

TABLE 4

Correlation coefficients for fitting f(α) to the Coats and Redfern equation for the decomposition of NH_4HCO_3

Sample	Correlation coefficient						
	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 3/4$	$n = 1$	$n = 2$
1	0.9939	0.9965	0.9975	0.9983	0.9986	0.9992	0.9961
2	0.9906	0.9943	0.9957	0.9968	0.9973	0.9972	0.9967
3	0.9951	0.9974	0.9982	0.9988	0.9991	0.9997	0.9981
4	0.9960	0.9980	0.9986	0.9989	0.9994	0.9999	0.9969
5	0.9924	0.9956	0.9961	0.9970	0.9974	0.9992	0.9989
6	0.9887	0.9934	0.9952	0.9967	0.9958	0.9975	0.9958
$\bar{r}$	0.9928	0.9959	0.9969	0.9978	0.9979	0.9988	0.9971
σ	0.0028	0.0018	0.0014	0.0010	0.0013	0.0011	0.0012

value. Otherwise, the value obtained may have a larger experimental error than is introduced by using an incorrect value of n. Once again it is readily apparent that subtle differences should not be inferred from a limited number of data.

Pre-exponential factors

The pre-exponential factors were calculated from the intercepts (I) of the numerical equations obtained by linear regression using the Coats and Redfern method. Since rather small differences in the intercepts result in much larger differences in A, the average values are dominated by the one or two largest values obtained. Accordingly, the standard deviations are not included since they too are large.

The data in Tables 3 and 6 show that the value of A increases regularly as

TABLE 5

Activation energies for the decomposition of NH_4HCO_3 assuming different orders of reaction

Sample	Activation energy (kJ $mole^{-1}$)						
	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 3/4$	$n = 1$	$n = 2$
1	80.03	84.86	87.44	90.15	91.49	95.78	115.23
2	67.07	71.40	74.02	76.52	77.81	80.07	100.99
3	78.63	83.02	85.32	87.70	89.52	92.65	109.24
4	65.82	69.74	71.82	73.98	75.04	76.70	93.43
5	71.25	74.96	76.90	78.90	79.93	81.33	96.98
6	69.99	75.92	79.10	82.44	86.48	90.59	114.83
$\bar{E}_a$	72.13	76.65	79.07	81.62	83.38	86.19	105.12
σ	5.92	6.11	6.24	6.36	6.72	7.70	9.31

TABLE 6

Values of the pre-exponential factor (A) for the decomposition of NH_4HCO_3 assuming different orders of reaction

Sample	Pre-exponential factor						
	$n = 0$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 3/4$	$n = 1$	$n = 2$
1	4.476×10^{9}	2.064×10^{10}	4.666×10^{10}	1.099×10^{11}	1.680×10^{11}	6.509×10^{11}	3.018×10^{14}
2	1.052×10^{8}	4.169×10^{8}	9.585×10^{8}	2.124×10^{9}	3.198×10^{9}	6.836×10^{9}	4.809×10^{12}
3	8.202×10^{9}	3.448×10^{10}	7.323×10^{10}	1.599×10^{11}	2.892×10^{11}	8.055×10^{11}	1.818×10^{14}
4	6.530×10^{7}	2.268×10^{8}	4.396×10^{8}	8.762×10^{8}	1.221×10^{9}	2.157×10^{9}	4.170×10^{11}
5	3.040×10^{8}	9.882×10^{8}	1.835×10^{9}	3.460×10^{9}	4.795×10^{9}	7.793×10^{9}	1.069×10^{12}
6	3.530×10^{8}	2.346×10^{9}	6.482×10^{9}	1.878×10^{10}	6.760×10^{10}	2.571×10^{11}	5.576×10^{14}
$\bar{A}$	2.251×10^{9}	9.850×10^{9}	2.160×10^{10}	4.917×10^{10}	8.900×10^{10}	2.884×10^{11}	1.761×10^{14}

the assumed order increases from 0 to 2. Any assumed order from 1/2 to 1 gives an A value within an order of magnitude of that obtained from the "correct" order, $n = 1$.

Mechanism of decomposition

Using the value $n = 1$, which results in the best fit for both NH_4HCO_3 and $(NH_4)_2CO_3$, it is seen that the activation energies are virtually identical. Even the pre-exponential factors are similar (2.884×10^{11} for NH_4HCO_3 and 1.892×10^{12} for $(NH_4)_2CO_3$). The fact that the average value obtained for the activation energy is the same in both cases (85.69 ± 6.02 kJ mole^{-1} for $(NH_4)_2CO_3$ and 86.19 ± 7.70 kJ mole^{-1} for NH_4HCO_3) indicates that both NH_4HCO_3 and $(NH_4)_2CO_3$ decompose by a similar mechanism. This is not unexpected since the process must involve proton transfer from NH_4^+ to either HCO_3^- or CO_3^{2-} in the lattice in either case. Such a transfer may be accomplished by a proton tunneling process without necessarily having to remove H^+ from NH_4^+, which would require a much greater energy, about 875 kJ mole^{-1}, the proton affinity of NH_3. Also, hydrogen bonding between the anion and NH_4^+ would assist the transfer of H^+ from the ammonium ion to the anion. Thus, it appears that the rate determining step simply requires that H^+ be transferred from NH_4^+ to an anion.

CONCLUSION

This study has yielded kinetic data for the decomposition of NH_4HCO_3 and $(NH_4)_2CO_3$. It has also shown that assignment of kinetic order can not be made on the basis of limited data. Other models are currently being evaluated to determine whether the small differences produced by assuming different kinetic orders are magnified when a different model is used.

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