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On the thermal stability of some ammonium salts

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Abstract

The thermal behavior of ammonium acetate, nitrate and chloride were investigated. The dependences between Eyring parameters for particular salts were determined. The dependence of Gibbs free energy of activation on decomposition temperature was calculated. The values of maximum of transformation rate were compared with energies of chemical bonds between ions.

Keywords: Kinetics of decomposition of ammonium salts; Eyring parameters; Kinetic parameters; Ammonium acetate; Ammonium nitrate; Ammonium chloride

1. Introduction

The kinetics of thermal decomposition of ammonium salts has been studied by many workers [1–13]. These compounds have a great technical importance. Therefore, their thermal stability and reactivity have fundamental significance. The thermal reactions of ammonium salts are unusually complicated. Numerous salts leave no residue on completion of decomposition. Here, there is the possibility of proton transfer and the evaporation of NH_3 molecule and other gases, several solid phase transformations and concurrent sublimation or melting. For most ammonium compounds, the first step is proton transfer. There is no detailed analysis of kinetics and thermodynamic parameters of decomposition that could give some explanation of the differences mentioned.

The thermal decomposition of selected ammonium salts were investigated by means of TG, DTG, DTA and DSC methods.

The kinetics of thermal decomposition can be adequately described by a simple equation [14]:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{R}\right)f(\alpha) \quad (1)$$

where α is the transformation degree, $f(\alpha)$ the conversion function dependent on mechanism of the reaction, T the absolute temperature (K), R the gas constant (J mol^{-1} K^{-1}), E the apparent activation energy (kJ mol^{-1}), and A the pre-exponential Arrhenius factor (min^{-1}).

The kinetics of thermal dissociation of investigated ammonium salts was followed by the integral method by applying the Coats–Redferns approximation [15,16].

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

where

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (3)$$

and q is the linear heating rate (K min^{-1}).

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This equation is frequently used to describe the kinetics of thermal decomposition of solids in general. A plot of $\ln[g(\alpha)/T^2]$ versus $1/T$ gives a straight line for the correct model relation.

The thermodynamic parameters of activation can be calculated by Eyring equation [17,18]:

$$\Delta H^* = E - RT \tag{4}$$

$$\Delta S^* = R\left(\ln\frac{hA}{k_\mathrm{B}T} - 1\right) \tag{5}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{6}$$

where ΔH^* is the enthalpy of activation (kJ mol^{-1}), ΔS^* the entropy of activation (kJ mol^{-1} K^{-1}), ΔG^* the Gibbs free enthalpy of activation (kJ mol^{-1}), h the Planck constant and k_B the Boltzmann constant.

The following statistic parameters were calculated to aid the selections of the $g(\alpha)$ function that best describes the experimental results: the regression coefficient — R and the Snedecor's variable — F.

2. Experimental

P.P.H. Polskie Odczynniki Chemiczne, Gliwice, Poland, supplied the initial salts, analytical grade, used in the present investigations.

The thermogravimetric measurements were carried out on the Hugarians derivatograph MOM — PC. The operational characteristics are as follows:

- heating rate: 2.5 K min^{-1};
- sample size: 20 mg;
- atmosphere: static air;
- temperature range: 20–500°C.

Five experiments were carried out under the same conditions. The reproducibility was good.

3. Results

The thermoanalytical curves (TG, DTG, DTA) of investigated ammonium salts are shown in Figs. 1–3 and the analysis date are summarized in Table 1.

The decomposition of ammonium acetate (Fig. 1) started at about 326 K. The double peak relating to the intermediate product was observed on DTA curve. This is in agreement with the results [2]. The TG curve shows a one continuous mass loss under the conditions of the experiments.

Physical changes of ammonium nitrate started at 325 K. The DTA curve for the salt (Fig. 2) exhibits following four phase transformations — the three changes of crystal structure and melting point at 442 K. The NH_4NO_3 decomposition begins at 455 K and occurs in one stage.

The thermal behavior of NH_4Cl is presented on Fig. 3. The endothermic DTA peak at 461 K for ammonium chloride indicates the change of crystal structure of salt. Above 473 K, the substance sublimes and after sublimation it dissociates completely in the gaseous phase into ammonia and hydrochloric acid [2].

From the mass losses observed in the TG-curves, the $\alpha(T)$ relations were estimated for particular salts.

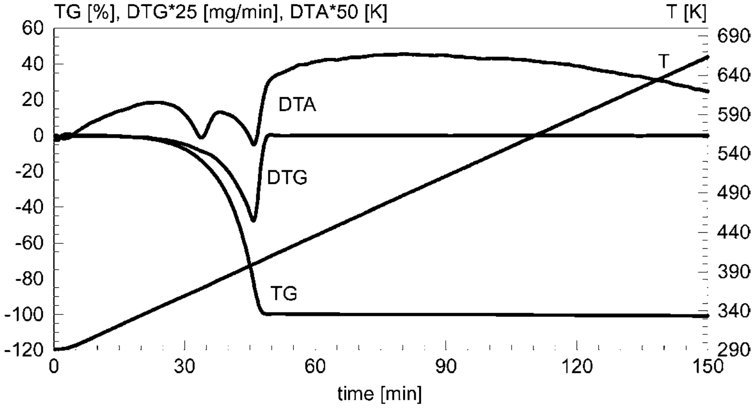

Fig. 1. DTA, DTG and TG curves of ammonium acetate.

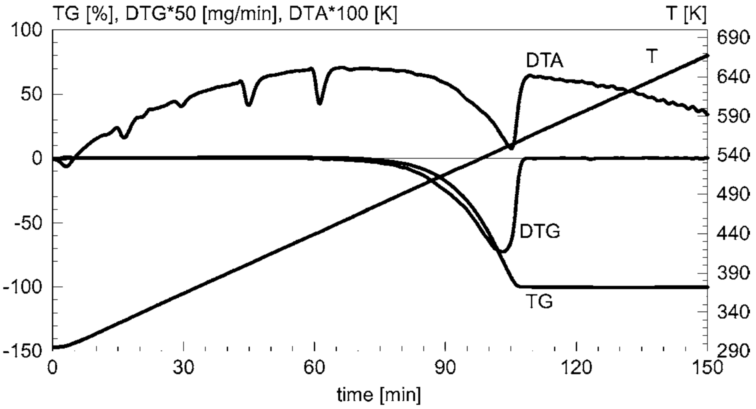

Fig. 2. DTA, DTG and TG curves of ammonium nitrate.

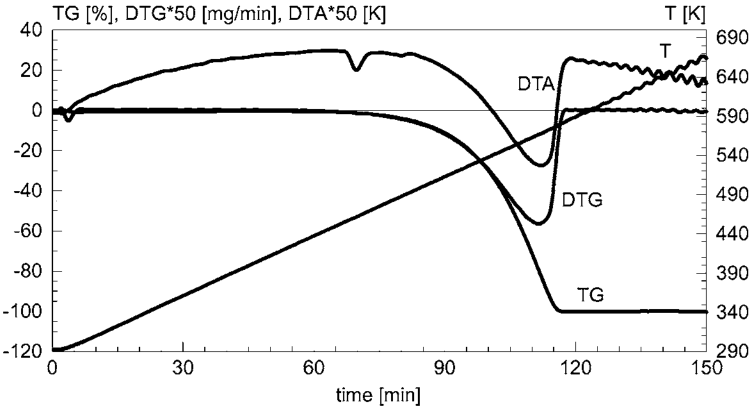

Fig. 3. DTA, DTG and TG curves of ammonium chloride.

Table 1
Thermal characteristics of ammonium salts[a]

	DTA			DTG			Change
	T_{inA} (K)	T_{mA} (K)	T_{endA} (K)	T_{inG} (K)	T_{mG} (K)	T_{endG} (K)	
CH_3COONH_4	326	369	380				D
	380	401	410	327	400	407	D
NH_4NO_3	325	329	337				Pt
	356	362	369				Pt
	396	401	410				Pt
	436	442	452				Pt
	455	553	564	449	547	558	D
NH_4Cl	454	461	469				Pt
	469	568	583	440	565	580	D

[a] Pt: phase transformation, D: decomposition.

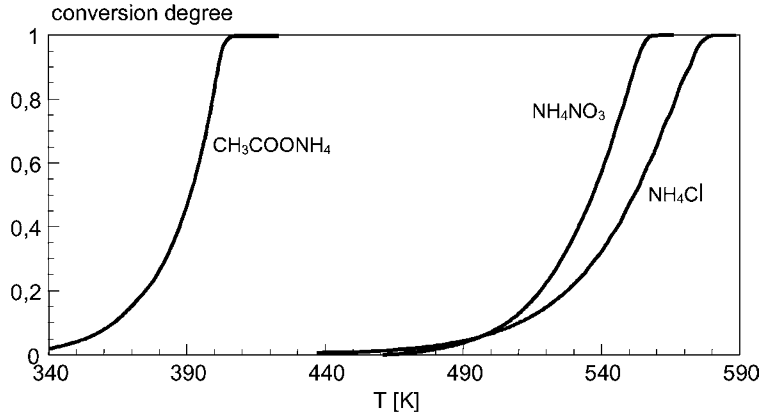

Fig. 4. The α–T curves for particular ammonium salts.

Table 2
Kinetic and thermodynamic parameters values from dynamic experiments

Salt	Model	*E* (kJ mol^{-1})	*A* (min^{-1})	ΔS^* (JK^{-1} mole^{-1})	ΔH^* (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	*R*	*F*
CH_3COONH_4	D1	133	3.64×10^{16}	27	129	118	−0.9996	142463
	D2	142	3.98×10^{17}	47	138	119	−0.9991	60525
	D3	154	9.69×10^{18}	74	151	121	−0.9946	9678
	D4	146	5.24×10^{17}	50	142	123	−0.9982	28777
	F1	81	1.06×10^{10}	−98	78	117	−0.9930	3018
	A2	38	8.54×10^{3}	−214	34	120	−0.9805	2615
	A3	23	7.03×10^{1}	−254	20	121	−0.9773	2236
	R1	63	1.95×10^{7}	−150	60	120	−0.9996	124897
	R2	71	2.83×10^{8}	−128	68	119	−0.9972	18689
	R3	74	8.36×10^{8}	−119	71	118	−0.9942	9048
NH_4NO_3	D1	232	1.99×10^{21}	115	227	164	−0.9924	9788
	D2	246	3.56×10^{22}	139	242	165	−0.9964	20773
	D3	269	3.04×10^{24}	176	264	168	−0.9987	58702
	D4	253	6.58×10^{22}	145	249	170	−0.9978	33547
	F1	145	1.79×10^{13}	−39	140	161	−0.9919	9111
	A2	68	3.32×10^{5}	−187	64	166	−0.9909	8173
	A3	43	7.58×10^{2}	−237	38	168	−0.9898	7274
	R1	112	4.33×10^{9}	−108	107	166	−0.9917	8956
	R2	124	1.07×10^{11}	−81	120	164	−0.9982	41322
	R3	130	4.40×10^{11}	−69	126	163	−0.9986	54712
NH_4Cl[a]	D1	156	2.22×10^{13}	−37	152	173	−0.9986	79276
	D2	163	6.91×10^{13}	−28	159	174	−0.9977	46434
	D3	173	2.66×10^{14}	−16	168	177	−0.9942	18667
	D4	166	5.03×10^{13}	−30	162	179	−0.9968	34505
	F1	88	1.45×10^{7}	−155	83	171	−0.9530	7310
	A2	40	2.51×10^{2}	−247	35	174	−0.9828	6193
	A3	24	6.07×10^{0}	−278	19	176	−0.9793	5132
	R1	74	3.89×10^{5}	−186	69	174	−0.9985	74549
	R2	80	1.85×10^{6}	−173	75	173	−0.9960	27179
	R3	82	3.45×10^{6}	−167	77	172	−0.9938	17433

[a] Parameters of sublimation process.

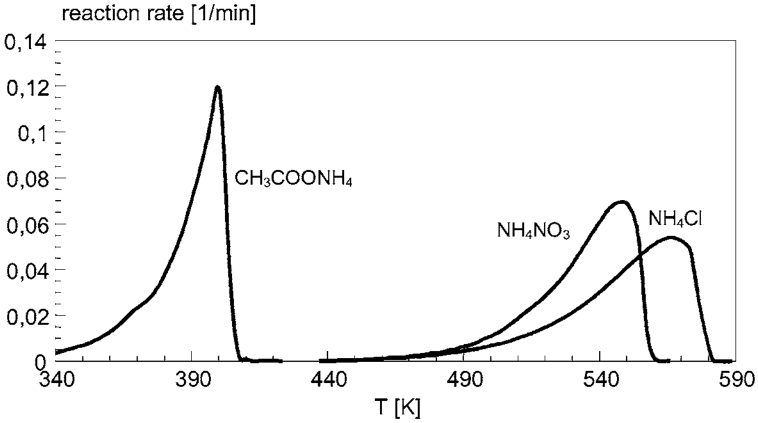

Fig. 5. Dependences of transformation rate on the decomposition temperature.

Based on the $\alpha(T)$ dependencies (Fig. 4), the $g(\alpha)$ function from Eq. (2) was calculated for the well-known kinetic models [8]. Values of kinetic, thermodynamic and statistic parameters for particular models are listed in Table 2.

From Table 2, it can be seen that the best fitting expressions for all investigated salts are diffusion models.

The dependencies of ΔH^* (J mol^{-1}) on ΔS^* (J mol^{-1} K^{-1}) derived from data for different kinetic models can be described by equations:

$$\Delta H^* = 401,\ \Delta S^* + 119800,\ \text{for}\, NH_4C_2H_3O_2$$

$$\Delta H^* = 550,\ \Delta S^* + 165700,\ \text{for}\, NH_4NO_3$$

$$\Delta H^* = 573,\ \Delta S^* + 175400,\ \text{for}\, NH_4Cl$$

Above relations allow to determinate values of Gibbs energies particular transformations (an intercept) and the temperatures at which the conversion rates are maximum — T_m (a slope).

The thermal stability (temperatures of decomposition) of the investigated ammonium salts increase with values of Gibbs free energy of activation (J mol^{-1}) of salts. The dependence is linear and can be described by the equation

$$\Delta G^* = 317,6 \quad T_m - 7726.2$$

with the value of coefficient of determination — R^2 equal to 0.9985. The results show that the equation gives the best fit of date with R^2 very close to unity. T_m is the temperatures at which weight-variant (TG) processes have maximum rate.

The dependencies of transformation rate dα/dt on temperature for particular ammonium salts are shown in Fig. 5. The values of maximum of transformation rate for $NH_4C_2H_3O_2$, NH_4NO_3 and NH_4Cl were in the ratio 1.71:1.0:0.78, respectively. In the same sequence, the stretching energies of chemical bonds between N (in NH_4^+) and anions decreased. The values of these energies calculated by means of the computer program HYPERChem were 303.2, 288.5 and 268.8 kcal mol^{-1}, respectively.

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