KINETICS OF THERMAL DECOMPOSITION
OF AMMONIUM SALTS
OF TEREPHTHALIC AND ISOPHTHALIC ACIDS

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The decomposition of crystalline diammonium terephthalate, monoammonium terephthalate and diammonium isophthalate in a stream of inert gas was investigated using a fluid bed at atmospheric pressure in a range of $100-200°C$. Both ammonia molecules were split off of the ammonium salts simultaneously. The course of the thermal decomposition in the kinetic region was satisfactorily described by the kinetic equation $(1 - x)^{0.5} = (1 - k't)$, corresponding to reactions taking place in the interface reaction layer of a two-dimensional model. The kinetic model includes the effect of crystal size and shape on the course of decomposition.

Thermal decomposition in a stream of inert gas according to equation (*1*)

$$p\text{-}C_6H_4(COONH_4)_2 \rightarrow p\text{-}C_6H_4(COOH)_2 + 2\,NH_3 \qquad (1)$$

is a simple example of decomposition of a solid substance giving rise to a solid and to a gaseous product and represents thus a convenient method of preparing terephthalic acid with a reportedly[1] 99.5% yield. The kinetics of the decomposition of crystalline diammonium terephthalate in a stream of argon was studied by Archipova and Rafikov[2] who found that the decomposition takes place *via* consecutive splitting off of two molecules of ammonia, the monoammonium salt representing an intermediate of the reaction. The course of the decomposition was described by two different kinetic equations for the two reaction steps.

It was the objective of the present work to describe the kinetic course of thermal decomposition of crystalline ammonium salts of terephthalic and isophthalic acids in a stream of inert gas, to compare the rates of their decomposition and to explain the subsequent decomposition of diammonium terephthalate[2]. For studying the reactions we used a fluid reactor where temperature gradients are greatly reduced.

EXPERIMENTAL

Chemicals

Diammonium terephthalate was prepared by introducing ammonia into a suspension of 166 g terephthalic acid (Mobil Oil Corp., USA, purity 99·5%) in 2 liters of water at 60°C. After cooling, the crystalline product was filtered and combined with a fraction obtained by concentration of the mother liquor. After washing with water and drying at 20°C and 20 Torr, a total of 102 g (51%) diammonium terephthalate with 16·88% HN_3 (17·02% calculated) was obtained.

Monoammonium terephthalate was prepared by introducing carbon dioxide into saturated aqueous solution of diammonium terephthalate at 25°C. The precipitated product was filtered, washed with water and dried at 20°C and 20 Torr and was found to contain 9·22% NH_3 (9·30% calculated). The yield was 40%.

Diammonium isophthalate was prepared by introducing ammonia into a suspension of 83 g isophthalic acid (Amoco Chemical Corp., Chicago, USA; purity 98·5%, 1·5% *o*-phthalic acid) in 400 ml water. Under stirring and cooling, keeping the temperature below 20°C, a total of 83 g of further acid was gradually added. The solution obtained, freed of excess ammonia *in vacuo*, was filtered, and added to 3 liters absolute ethanol and the fine precipitate was left overnight at normal temperature. The crystalline product was filtered, washed with absolute ethanol and dried at 20°C and 1·5 Torr. A total of 177 g (88%) diammonium isophthalate was obtained, containing 16·83% NH_3 (calculated 17·02%). The product was free of *o*-phthalate ions.

Nitrogen used as the inert gas was a commercial product of Technoplyn (Ostrava) and contained 0·2% (v/v) of oxygen.

Procedure

The experiments were carried out in a fluid reactor of 20 mm diameter and 120 mm height under atmospheric pressure. The reactor was placed in an ultrathermostat U 10 with a methylphenylsiloxane bath and provided with a thermometer reaching to the centre of the bed. The nitrogen serving as carrier gas was preheated to the reaction temperature by passage through a copper tubing (250 cm long) and a glass spiral (130 cm long) of the reactor. The liberated ammonia removed from the reactor with the carrier gas was absorbed in 500 ml 0·1N-H_2SO_4. The rate of ammonia formation was followed by titration of samples of the absorption solution taken at given time intervals.

A typical procedure of estimating the reaction rate was the following: 1 g ammonium salt was placed into the preheated reactor and, immediately after closing, the flow of nitrogen was set at 300 liters/h. Temperature of the fluid bed was stabilized within 1—3 min and was then maintained at a constant value with an accuracy of ±0·5°C. Only at higher reaction rates was the accuracy less because of the endothermic nature of the reactions. After termination of each experiment the amount of undecomposed salt in the reactor was determined.

In the course of decomposition of diammonium terephthalate and of monoammonium terephthalate a static charge was formed by the terephthalic acid particles formed during the process which resulted in a decrease of fluidization intensity toward the end of reaction. It followed from comparative experiments with a carrier gas containing water vapour which eliminated the phenomenon that the decrease of fluidization intensity had no effect on the reaction rate.

The crystals maintained their original size during decomposition as well as after termination of the reaction.

Analytical Methods

Ammonia was determined in the samples of the adsorption solution as well as in the decomposition product by amperometric oxidimetry using the hypochlorite method[3]. For measuring the IR spectra of the products of thermal decomposition of ammonium salts we used a double-beam IR spectrophotometer Zeiss (Jena), model UR-20. The spectra were estimated in a Nujol suspension. The X-ray analysis of crystalline ammonium salts was carried out by the Debye–Scherrer method on a Mikrometa II apparatus using a Cu lamp (Cu_{K_α}).

RESULTS AND DISCUSSION

To determine suitable reaction conditions for the kinetic region of thermal decomposition we investigated the effect of nitrogen flow on the rate of decomposition of di-ammonium terephthalate. For values of 2·5, 5, 9, 12, 15, 18, 21, 30 and 90 liters/h in a solid-bed reactor containing about 1 g salt the reaction rate in the whole range depends on the flow of nitrogen and the reaction time for 197°C lies between 150 and 10 min. The rate of flow ceased to affect the rate of diammonium terephthalate decomposition at 150°C using a fluid reactor, at values above 240 liters/h.

In further tests the effect of crystal size of diammonium terephthalate on the re-action rate was investigated for the following sizes: $0·8 - 1·7 . 10^{-3}$ mm, $0·16 - 0·25$, $0·25 - 0·40$, and $0·8 - 1·0$ mm. Crystals larger than $1·0$ mm did not form a true fluid layer in view of their weight, under the given conditions. To follow the decomposition of the microcrystalline fraction $(0·8 - 1·7 . 10^{-3}$ mm) in the fluid reactor it was necessary to compress the powdery sample formed by mechanical crushing, into pellets. The pellets formed at a hydraulic pressure of 150 atm were crushed and a fraction of $0·16 - 0·25$ mm was obtained by sieving.

It is known from the literature[4,5] that a decrease in crystal size is generally accompanied by an increase of reaction rate but that over a certain limit it can result in an opposite phenomenon. In such a case we are generally dealing with an effect of diffusion on the reaction rate. To exclude the effect of diffusion in the compressed pellets the dependence of the reaction rate on the size of compressed pellets was examined for the following size fractions: $0·16 - 0·25$, $0·25 - 0·40$, $0·40 - 0·80$ and $0·80 - 1·0$ mm at 135°C. It followed from the results obtained that for pellet size of $0·16 - 0·25$ mm, compressed from diammonium terephthalate crystals of the $0·8 - 1·7 . 10^{-3}$ mm fraction, there is no effect of diffusion on the reaction rate. The resulting dependences of the reaction rate on the crystal size are shown in Fig. 1 where it may be seen that a smaller size of crystals has a favourable effect on the increase of the reaction rate of decomposition over the whole range.

On the basis of these results the kinetic measurements were done for a flow rate of 300 liters/h, comparing the rates of decomposition of microcrystalline $(0·8 - 1·7 . 10^{-3}$ mm) and crystalline sample $(0·25 - 0·40$ mm) of diammonium terephthalate at different temperatures.

Kinetic curves of thermal decomposition of diammonium terephthalate, mono-

ammonium terephthalate and diammonium isophthalate are shown in Figs 2−5. Diammonium isophthalate was decomposed below 100°C while the decomposition of diammonium terephthalate and particularly of monoammonium terephthalate was apparent only at higher temperatures. The residual amounts of bound ammonia in the thermal decomposition product of ammonium salts amounted between 100 and 200°C to $3 \cdot 3 - 0 \cdot 5$ mol % NH_3 which corresponds to a degree of decomposition of $0 \cdot 967 - 0 \cdot 995$.

It follows from Figs 2−5 that the degree of decomposition increases with increasing temperature or with prolongation of the reaction period. Thus, *e.g.*, the decomposition of both diammonium salts proceeded within 60 min at 200°C to 99·85%. It followed from the results obtained that the decomposition under the given conditions was not accompanied by dehydration and hence by formation of acid amides or nitriles. The absence of these by-products in the reaction product was supported by IR spectroscopy. Between 3400 cm^{-1} and 3200 cm^{-1} no bands corresponding to the $CONH_2$ group and at about 2200 cm^{-1} no band corresponding to the CN group were found.

The literature contains descriptions of two approaches to the kinetic analysis of decomposition of solid substances giving rise to a solid and a gaseous product. The first is based on the concept that the rate of decomposition depends on the probability of formation of crystal nuclei of the product and is represented by the equation of Avrami-Jerofjejev (nuclei growth equation)[6,7]:
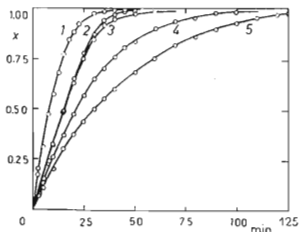
$$- \ln (1 - x) = (kt)^m , \qquad (2)$$

FIG. 1

Dependence of the Degree of Conversion of Diammonium Terephthalate at 150°C on Time and Crystal Size

1 $0 \cdot 8 - 1 \cdot 7 . 10^{-3}$ mm, *2* $0 \cdot 16 - 0 \cdot 25$ mm, *3* $0 \cdot 25 - 0 \cdot 40$ mm, *4* $0 \cdot 80 - 1 \cdot 0$ mm, *5* $1 \cdot 0$ to $1 \cdot 3$ mm.
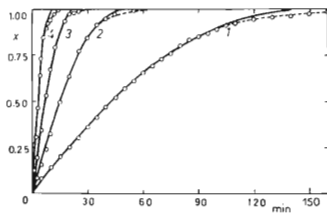

FIG. 2

Kinetic Curves of Decomposition of Diammonium Terephthalate ($0 \cdot 25 - 0 \cdot 40$ mm) at Different Temperatures

The theoretical curves were calculated from equation (6). *1* 135°C, *2* 150°C, *3* 165°C, *4* 180°C.

where x is the degree of conversion, k is a rate constant, t is time and m is a constant. The equation is frequently used[8-11] for describing allotropic and polymorphic conversions[12-16]. A special case is represented here by the Prout–Tompkins equation[17]

$$\ln (x/(1 - x)) = kt + \text{constant} \tag{3}$$

based on the concept of a chain course of the reaction and suited for describing reactions with a rapid course, in particular of reactions proceeding explosively.

The second approach assumes that the reaction rate depends on the area of the reaction interface between the decomposed and the nondecomposed substance (contracting model). Hence follows the dependence of the reaction rate on the total surface which is proportional to the surface of the nonreacted crystal and hence also the dependence of the reaction rate on shape and size of the crystals. The corresponding equation (4) for a general three-dimensional crystal has the form[18]

$$1 - x = \frac{(1 - \tau)^3 + (1 - \tau)^2 (\lambda + \eta) + (1 - \tau) \lambda\eta}{1 + (\lambda + \eta) + \lambda\eta}, \tag{4}$$

where τ is defined as kt/a, a is the principal dimension of the crystal, λ and η are constants. Equation (4) found a wide application first of all in simplified forms[7,10,11,19-22]. Thus e.g. for a cubic or a spherical crystal of the principal dimension a equation (4) is reduced to

$$(1 - x)^{1/3} = 1 - kt/a, \tag{5}$$

or, for a two-dimensional crystal of cylindrical shape of radius a to
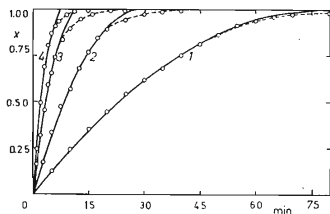
$$(1 - x)^{1/2} = 1 - kt/a. \tag{6}$$

Fig. 3

Kinetic Curves of Decomposition of Diammonium Terephthalate $(0.8 - 1.7 \cdot 10^{-3} \text{ mm})$ at Different Temperatures

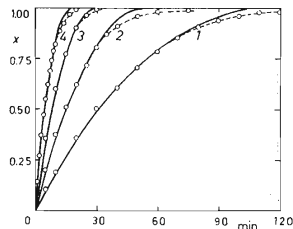The theoretical curves were calculated from equation (6). 1 135°C, 2 150°C, 3 165°C, 4 176°C.

Fig. 4

Kinetic Curves of Decomposition of Monoammonium Terephthalate $(0.25 - 0.40 \text{ mm})$ at Different Temperatures

The theoretical curves were calculated from equation (6). 1 170°C, 2 180°C, 3 191°C, 4 200°C.

When using equations (5) and (6) for describing the decomposition of solid substances the authors are satisfied with a description of the reaction up to a certain degree when $x = 0.9$ (ref.[10]), 0.8 (ref.[11]), 0.7 (ref.[21]), or even less[23].

In view of the fact that decomposition of salts (Fig. 2–5) exhibits no detectable induction period, characteristic for the formation of crystal nuclei, one can assume that the nucleation process is not kinetically significant in the present context and that equations (2) and (3) are not suitable for describing the reaction investigated.

Interpretation of the kinetic data obtained based on a concept of a reaction taking place in the reaction interface showed that thermal decomposition of ammonium salts of terephthalic and isophthalic acids is best described by a two-dimensional crystal model of cylindrical shape and by the corresponding equation (6). Agreement between the values calculated from this equation nad experimental results (Fig. 2–5) hold up to 80, or 95% conversion, respectively (Table I), over the entire range of temperatures. A much less pronounced agreement was obtained on using equation (5) based on the concept of a spherical model, in particular in the region of lower values of reaction rates.

The modified rate constants $k' = k/a$, dependent on the lattice shape and crystal size, were obtained by linearization of equation (6). Linearization of the data obtained from the decomposition of diammonium terephthalate is shown in Fig. 6 and the rate constants determined for the decomposition of di- and monoammonium terephthalate and diammonium isophthalate are in Table I. The highest rate of decomposition was found for diammonium isophthalate, somewhat lower for diammonium tere-
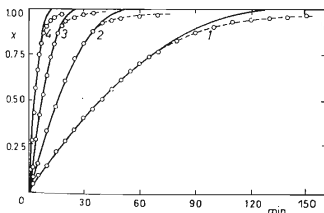

FIG. 5

Kinetic Curves of Decomposition of Diammonium Isophthalate (0·25—0·40 mm) at Different Temperatures

The theoretical curves were calculated from equation (6). 1 100°C, 2 110°C, 3 120°C, 4 130°C.
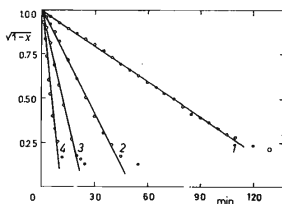

FIG. 6

Linearization of Kinetic Data of Decomposition of Diammonium Terephthalate (0·25 to 0·40) at Different Temperatures according to Equation (6).

1 135°C, 2 150°C, 3 165°C, 4 180°C.

TABLE I

Maximum Values of the Degree of Conversion (x_{max}) for the Range of Validity of Equation (6), Rate Constants (k'), Activation Energy (E) and Frequency Factors (A) for Thermal Decomposition of Ammonium Salts of Terephthalic and Isophthalic Acids

Parameter	Diammonium terephthalate		Monoammonium terephthalate	Diammonium isophthalate
	$0.25-0.40$ mm	$0.8-1.7 . 10^{-3}$ mm	$0.25-0.40$ mm	$0.25-0.40$ mm
x_{max}	$0.90-0.95$	$0.85-0.95$	$0.85-0.90$	$0.80-0.90$
$k' . 10^3$, s^{-1}	1·14 (135)	2·11 (135)	1·50 (170)	1·25 (100)
(temperature, °C)	3·28 (150)	5·83 (150)	3·19 (180)	3·11 (110)
	6·92 (165)	13·75 (165)	5·67 (191)	6·67 (120)
	15·00 (180)	21·67 (176)	9·83 (200)	13·89 (130)
E, kcal mol^{-1}	20.77 ± 0.21	20.83 ± 0.18	25.90 ± 0.15	23.72 ± 0.13
A, s^{-1}	$1.62 . 10^8$	$3.17 . 10^8$	$9.27 . 10^9$	$1.02 . 10^{11}$

phthalate and lowest for monoammonium terephthalate. The ratio of the rate constants of decomposition of diammonium terephthalate (I), monoammonium terephthalate (II) and diammonium isophthalate (III) for 150°C and a uniform size of crystals ($0.25-0.40$ mm) amounted to $k'_I : k'_{II} = 7.4 : 1$ and $k'_{III} : k'_I = 18.1 : 1$. X-Ray analysis showed that each of the ammonium salts used crystallizes in a different crystallographic system which represents one of the possible explanations for the difference in reactivities of such similar compounds as monoammonium terephthalate and diammonium terephthalate.

Values of activation energies for the decomposition of diammonium terephthalate, monoammonium terephthalate and diammonium isophthalate calculated from the Arrhenius equation are shown in Table I, the linearity of the dependence of log k' on $1/T$ demonstrating the validity of these values about $135-200$°C, and $100-130$°C, respectively.

Table I shows the rather little pronounced dependence of the frequency factor A on the increase of crystal size and hence on the specific area of the particles of the starting diammonium terephthalate.

The character of the kinetic curves of decomposition of diammonium terephthalate and diammonium isophthalate indicates that the splitting off of both ammonia molecules from the molecule of the ammonium salts takes place in a single step. This is supported also by comparing the rate of decomposition of monoammonium terephthalate and diammonium terephthalate. This conclusion is not consistent

with that of Archipova and Rafikov[2] who found that the decomposition of diammonium terephthalate take place in two consecutive steps. An explanation may be found in different reaction conditions. It follows from the above paper[2] that at 200°C and using a flow of carrier gas equal to 1·8 liters/h, the decomposition of diammonium terephthalate lasted for about 6 h, the second step being about seven times slower; at lower temperatures the reaction could not be even brought to termination. In our case the decomposition of diammonium terephthalate proceeded at the same temperature but at a flow of carrier gas of 300 liters/h within 3 min. It thus appears that the authors[2] worked under conditions nearer the equilibrium state where a reversible reaction under formation of slowly decomposing monoammonium terephthalate can take place.

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