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ISOTHERMAL DECOMPOSITION OF UREA NITRATE

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ABSTRACT

The kinetics of isothermal decomposition of urea nitrate, an organic secondary explosive with monoclinic structure and chemical formula $CO(NH_2)_2 \cdot HNO_3$, which melts with decomposition at 152°C, was studied in open air in the temperature range 106–150°C, using a gravimetric method. Gas chromatographic analysis of product gases indicate CO_2, N_2O and traces of water vapor as product gases. A pasty amorphous product on the basis of wet chemical and infrared analysis was found to be cyanourea. The weight loss–time curve exhibited an acceleratory region extending almost to the end of the main reaction (35% decomposition) and followed a three-dimensional nucleation model obeying the relation $\alpha^{1/3} = K(t-t_0)$, where α = fraction of sample reacted at time t, K = reaction rate constant, and t_0 = induction time. On the basis of this model, an enthalpy of activation of 27.6 ±1.2 kcal/mole was calculated at 95% confidence range. The rate of decomposition was slightly accelerated in He atmosphere and slightly retarded in N_2O and CO_2 atmospheres, while water vapor drastically reduced the rate. The reaction

$$3CO(NH_2)_2 \cdot HNO_3 \rightarrow CN\text{–}NH\text{–}CONH_2\,(\text{cyanourea}) + 6H_2O + 3N_2O + CO_2$$

is presented as the most likely one for decomposition of urea nitrate in open air.

INTRODUCTION

This research is concerned with the isothermal decomposition of urea nitrate below the reported melting point of 152°C. The two most common methods of studying the thermal decomposition kinetics of solids in which the fraction reacted is recorded as a function of time are the thermogravimetric method using a quartz spring[1–3] and the pressure rise method using a monometer[4–8].

Young[9] has briefly developed the kinetic theory based on the shape of the isothermal decomposition curves, while Garner[10], and Jacobs and Tompkins[11] have discussed the classification and theory of isothermal solid reactions of the form

$$A(\text{solid}) \rightarrow B(\text{solid}) + C(\text{gas(es)})$$

in which B forms at high energy sites in the lattice of A. Decomposition commences when local fluctuations provide favorable circumstances for the formation of B.

Garner[10], and Jacobs and Tompkins[11] have also described various decomposition curves. Models for reaction in which the overall kinetics is controlled by the changing area, or geometry, of the reactant is shown to be important in this paper as has been considered for various solid state reactions[9,10].

EXPERIMENTAL

A thermogravimetric technique utilizing an automatic recording balance with a sensitivity of 0.05 mg was used to monitor the fractional weight loss–time curve[12]. The sample was a powder (10–400 μ) and was synthesized by IRECO Chemicals Company, Salt Lake City, Utah. Sample spreading, and sample weight were controlled to obtain the best possible kinetic results as will be detailed later. Quartz, aluminum, and platinum bucket materials had no effect on the rate of decomposition. The temperature was controlled within ± 1.0°C. Of the products of decomposition, CN–NH–CONH$_2$ (cyanourea) was identified by infrared spectroscopy and wet chemical analysis, while CO$_2$, N$_2$O and traces of H$_2$O were identified by gas chromatography[13].

RESULTS AND DISCUSSION

Kinetic parameters

Figure 1 shows the effect of initial spreading of the sample on the fraction reacted (α) versus time (t) curve. The thinly spread sample caused a rapid increase in the initial rate and a slight but significant decrease in the final percent decomposed. Because of this small effect a compact sample was used for the majority of studies and unless otherwise indicated this was the procedure used in the kinetics study. A

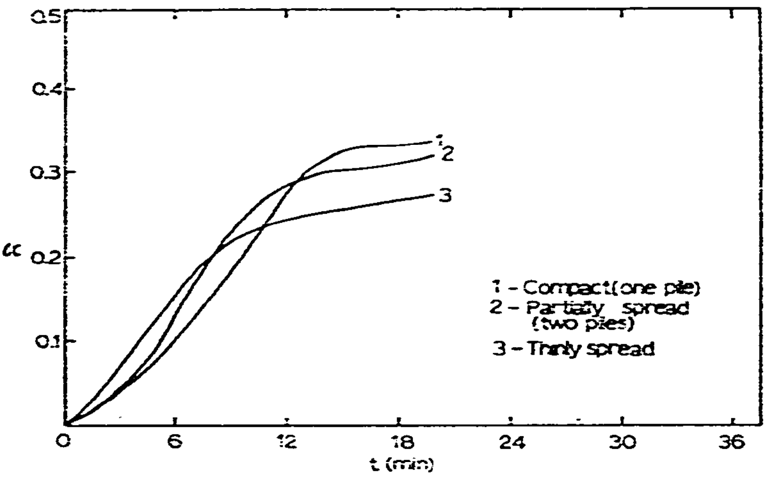


Fig. 1. Sample spreading effect on isothermal decomposition of 0.86 mg sample of urea nitrate in open air using aluminum bucket at 134°C.

cross over in the decomposition curves with variation of sample spreading was surprising and will be explained later on the basis of inhibitory gases.

Figure 2 shows that variation of initial sample weight resulted in an increase of the initial rate of decomposition as sample weight decreased. Also the shape of the decomposition curves changed slightly with reduction in sample weight indicating a change in reaction mechanism, at least in the initial or induction region. Likely product gases had an inhibitory effect causing the initial rate, and possibly even the mechanism to change as sample weight was increased; thus, the initial sample weight, W_0, was maintained rather constant in the kinetic study.

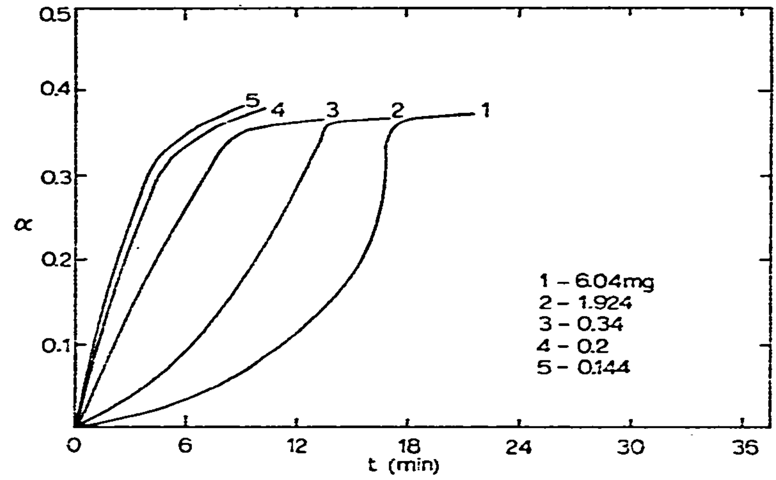


Fig. 2. Effect of sample size on the rate of isothermal decomposition of urea nitrate in open air using platinum bucket at 134 °C.

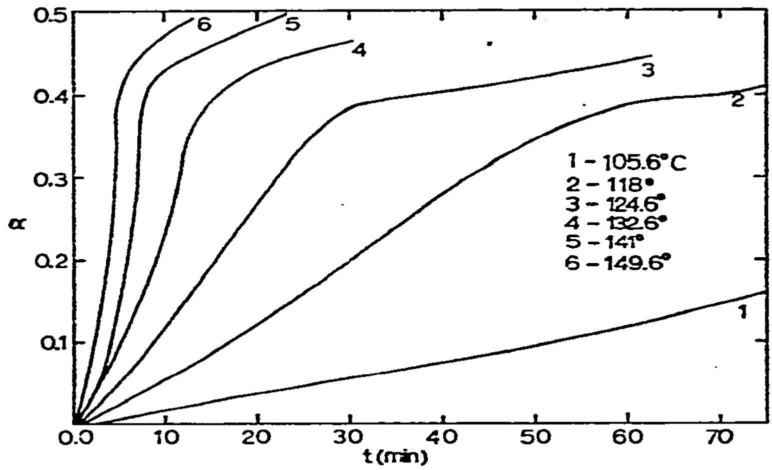


Fig. 3. Fraction reacted as a function of time during isothermal decomposition in open air using platinum bucket and 0.55 mg sample size.

Kinetic study

Plots of fraction reacted versus time for the temperature range 105.6–149.6°C in Fig. 3 show the rate increasing almost up to the end of the main reaction. This reaction follows rather well a geometric model of reaction in which the reactant interface increases in area as reaction proceeds. For the case in which the product is a sphere and the interface moves at a constant rate outward from the reaction nuclei, the expression[1]

$$\alpha^{1/3} = K(t - t_0) \qquad (1)$$

is obeyed; α, K, and t_0 are respectively fraction reacted at time t, reaction rate constant, and induction time. For uniform product spheres all initiating at time t_0 a sigmoidel curve results with the inflection point denoting the time at which the product spheres intersect each other. The curves of Fig. 3 do not show this and may be explained by a wide range in the size of the product spheres, *i.e.*, reaction nucleates at different times for various nuclei. As the smaller product spheres exist in the interstices of the larger product spheres they consume the urea nitrate in such a way that essentially all the products sphere of varying sizes impinge at the same time giving an acceleratory rate almost to the end of the main reaction.

The thermogravimetric data of Fig. 3 as plotted in Fig. 4 fits eqn (1) in the region $0.02 < \alpha < 0.35$. The positive intercept with the ordinate indicates a negative value of t_0 from eqn (1); t_0 cannot be negative but this response would occur for nucleation over an initial period which was abnormally rapid. Another possibility is the presence of some of the product nuclei at the beginning of the reaction[10]; this latter was excluded, however, because of the stability of urea nitrate at room temperature.

Experimental reaction rate constants were evaluated from the slopes of the linear portions of Fig. 4 and are given in Table 1.

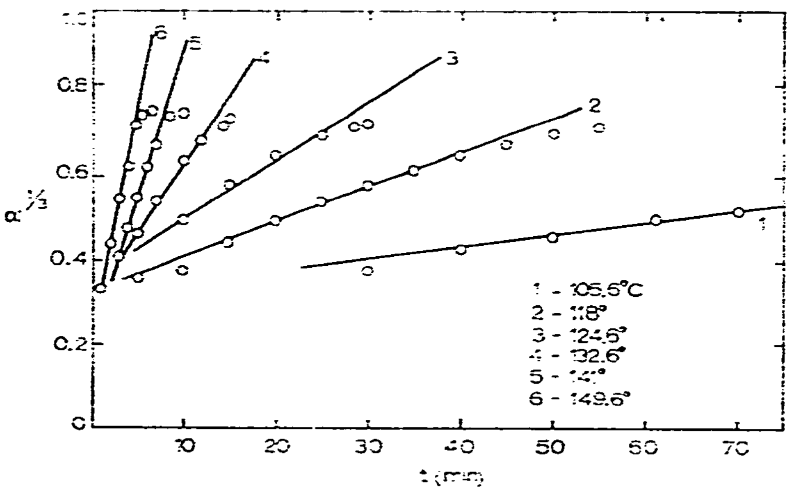


Fig. 4. Experimental plots of $\alpha^{1/3}$ versus time for isothermal decomposition in open air.

TABLE 1

RATE DATA FROM FIGURE 4

T (°K)	W_0 (mg)	K ($min^{-1} \times 10^3$)
378.6	0.542	2.50
391.0	0.556	8.72
397.6	0.542	15.76
405.6	0.560	33.33
414.0	0.562	70.00
422.6	0.555	120.00

The rate constants of Table 1 are plotted in Fig. 5 as log (K'/T) versus $1/T$ according to the Eyring absolute reaction rate theory[14] as represented by the equation

$$K' = \kappa \frac{kT}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \tag{2}$$

or in logarithmic form

$$\log \frac{K'}{T} = \left(\log \frac{\kappa kT}{h} + \frac{\Delta S^{\neq}}{2.3\,R}\right) - \frac{\Delta H^{\neq}}{2.3\,RT} \tag{3}$$

where K', κ, k, T, h, $\Delta S^{\neq}$, R, and $\Delta H^{\neq}$ are respectively specific reaction rate constant, transmission coefficient (normally assumed unity), Boltzman constant, absolute

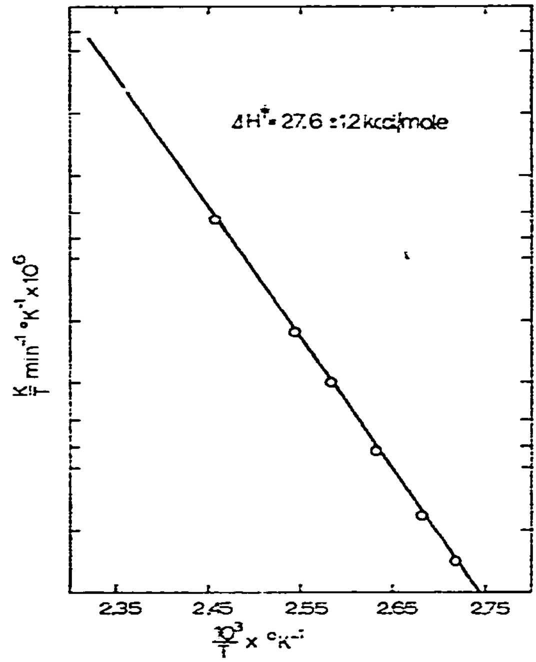
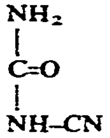


Fig. 5. Activation enthaipy plot for isothermal decomposition of urea nitrate in open air.

temperature, Planck's constant, activation entropy, molar gas constant, and activation enthalpy. The reaction rate constant K of eqn (1) is directly proportional to the specific reaction rate constant K' of eqn (2). An enthalpy of activation ($\Delta H^{\neq}$) of 27.6 ±1.2 kcal mole^{-1} was calculated at 95% confidence range[15] from Fig. 5. No attempt was made to determine $\Delta S^{\neq}$ as $K' \neq K$.

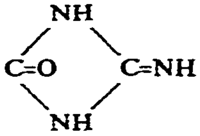
Residue and gas analysis

When urea nitrate was decomposed in a test tube in open air to $\alpha \simeq 0.35$, it was observed that a colorless liquid was produced. This material changed to a paste on cooling and was identified as cyanourea by wet chemical analysis and infrared spectroscopy. Cyanourea exists as a tautomer of the three following structures[16,17].

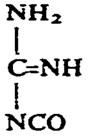


$$\begin{array}{c} NH_2 \\ | \\ C{=}O \\ | \\ NH{-}CN \end{array}$$

(I)



(II)



$$\begin{array}{c} NH_2 \\ | \\ C{=}NH \\ | \\ NCO \end{array}$$

(III)

Infrared results indicated the presence of isomers (II) and (III) only, but the relative amounts of each were not determined.

The X-ray spectrum of the residue consisted mainly of one sharp peak at $2\theta = 18°$ with a few other minor peaks which did not fit any species tabulated in the ASTM X-ray card index. The residue tended to be primarily amorphous however.

The product gases were identified chromatographically[13] as a function of time. The species N_2O and CO_2 appeared at the initiation of decomposition and maximized at the time of the maximum decomposition rate. Near the end of the decomposition ($\alpha \simeq 0.25$) some H_2O appeared. However, H_2O was relatively minor as compared to N_2O and CO_2.

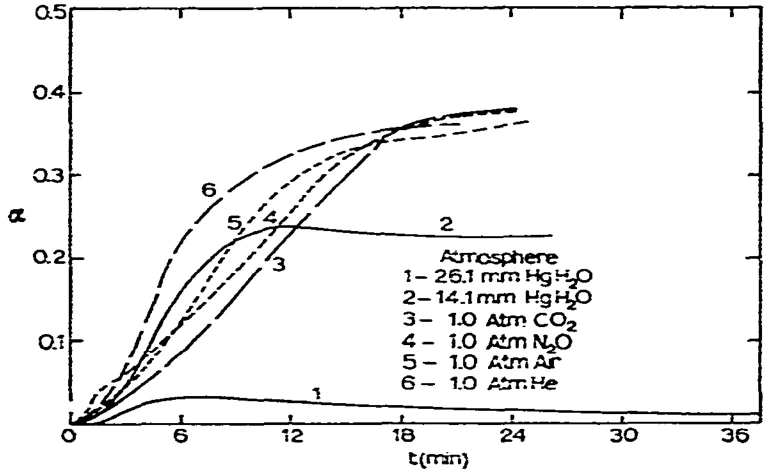


Fig. 6. Effect of static gaseous environments on decomposition using platinum bucket at 131 °C and 0.42–0.47 mg samples.

Gas environment

Figure 6 shows the effects of static gas environments on the decomposition of urea nitrate at 131 °C. Water vapor diluted to one atmosphere with helium, had a strong inhibitory effect as shown by curves 1 and 2. The weight increase at about 6–8 min was probably due to adsorption of water vapor on the reaction product.

The effect of other atmospheres on decomposition while not as dramatic as was the effect of water vapor still were significant. Comparing the gaseous atmospheres (all at about 645 mm Hg) CO_2, N_2O, and He with air, it is seen that CO_2 had the greatest inhibition of rate with N_2O also showing inhibition. Air gave a slightly reduced final fraction reacted probably due to the H_2O vapor present. Helium slightly accelerated the rate as is often found[12,13].

These results explain the "cross over" for a given size of sample as spreading was varied, as shown in Fig. 1; this is explicable on the basis of slight retardation of reaction by the gaseous products CO_2 and N_2O and reduction of the final fraction reacted due to H_2O vapor. The more open the sample the greater the influence of H_2O from air; hence, the greater the reduction in the fraction decomposed as compared to compact samples. On the other hand open spreading allowed N_2O and CO_2, the gaseous products, to diffuse out more readily and hence retarded the reaction less.

Reaction

The analytical results clearly show $CN\text{-}NH\text{-}CONH_2$ in the residue and N_2O and CO_2 as product gases; no H_2O vapor was detected during decomposition, but the reaction

$$3CO(NH_2)_2 \cdot NHO_3 \rightarrow CN\text{-}NH\text{-}CONH_2 + 6H_2O + 3N_2O + CO_2 \qquad (4)$$

is postulated for decomposition. The liquid residue consists of a mixture of cyanourea and water which changed to a paste at room temperature. Thus on the basis of the reaction solid A decomposed to solid B+gases with subsequent liquefication of B due to its hygroscopicity as has been found experimentally.

Equation (4) predicts 47.7% weight loss assuming that the H_2O produced was held by the proposed residue, cyanourea. The results of Fig. 3 show the reacted fraction reached a maximum of about 42% weight loss, in rather good agreement.

As Fig. 3 shows the amount of weight loss at the knee of the marked retardation point was directly dependent on the temperature due to some water loss as vapor at higher temperatures. Also some weight loss continued thereafter at a greatly reduced rate presumeably due to loss of water and the slow decomposition of cyanourea as has been detected by infrared and X-ray analysis; and as the residue weight at the end of the main reaction was a function of the water retained it may have included some N_2O and CO_2 as well.

REFERENCES

1 G. C. Anderson, *Ph. D. thesis*, University of Utah, 1965.
2 G. M. Thornley, *Ph. D. thesis*, University of Utah, 1965.
3 M. A. Cook and M. T. Abegg, *Ind. Eng. Chem.*, 48 (1956) 1090.

4 R. D. Farmer, *J. Chem. Soc.*, 117 (1930) 1432.

5 A. D. Yoffe, *Proc. Roy. Soc.*, A208 (1951) 188.

6 M. Mori and R. Tsuchiya, *Bull. Chem. Soc. Jap.*, 32 (1959) 67.

7 C. N. Hinshelwood, *J. Chem. Soc.*, 119 (1921) 721.

8 R. Robertson, *J. Chem. Soc.*, 119 (1921) 1.

9 D. A. Young, *Decomposition of Solids*, Pergamon Press, London, 1966.

10 W. E. Garner, in W. E. Garner (Ed.), *Chemistry of the Solid State*, Academic Press, New York, 1955, Chap. 9.

11 P. W. M. Jacobs and F. C. Tompkins, in W. E. Garner (Ed.), *Chemistry of the Solid State*, Academic Press, New York, 1955, Chap. 7.

12 D. E. Richardson, *Ph. D. Thesis*, University of Utah, 1967.

13 C. J. Chou and F. A. Olson, *Anal. Chem.*, 44 (1972) 1841.

14 S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941, Chap. 4.

15 W. Volk, *Applied Statistics for Engineers*, McGraw-Hill, New York, 1959.

16 J. S. Blair and B. E. P. Smith Jr, *J. Amer. Chem. Soc.*, 50 (1934) 907.

17 I. Heilborn and H. M. Bunbury, *Dictionary of Organic Chemistry*, Vol. I, Oxford University Press, New York, 1953, p. 629.