

MEASUREMENT OF REACTION KINETICS BY A PRESSURE RISE METHOD

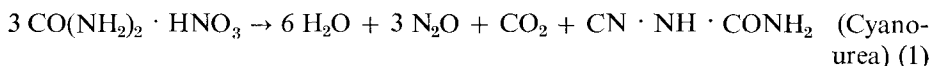
B. M. BORHAM* and F. A. OLSON

*Department of Metallurgy and Metallurgical Engineering
University of Utah, Salt Lake City, Utah 84112 U.S.A.*

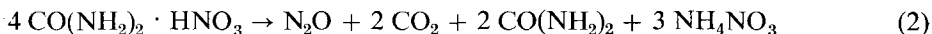
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Decomposition of urea nitrate in an initially evacuated system gave sigmoidal pressure *vs.* time curves. The experimental kinetic data fit the growing nuclei model with a measured enthalpy of activation of 142 ± 12.5 kJ/mole as compared to 115 ± 11.3 kJ/mole obtained thermogravimetrically. This higher value of ΔH^\ddagger is explained on the basis of two factors: 1) the inhibitory effect of the product gases and 2) self heating, whose extent increased ΔH^\ddagger by about 12.5 kJ/mole.

Various properties of urea nitrate have been studied by several investigators and a few have considered thermal decomposition of urea nitrate singly [1-3], its decomposition with other compounds [4-7] and others have detailed important physical properties of urea nitrate [8, 9]. In general investigators have found [1, 2] that the decomposition gases are N_2O , CO_2 , and H_2O . Ammonium nitrate, biuret, urea and cyanourea have been reported in the residue. One study [1] has reported the decomposition reaction as



while others have reported [4]



Addition of alumina (1-5%) or other salts KNO_3 , $NaNO_3$, or $BaNO_3$ (5-30%) tend to prevent decomposition and retard hygroscopicity [7]. Decomposition with ammonia accelerates the reaction and produces only urea and ammonium nitrate as reaction products [4]. Ammonium nitrate catalyzes the decomposition [5].

Thermal decomposition kinetics of solids is often measured by a thermogravimetric method [10-13] in which the fraction reacted is monitored as a function of time using quartz [10-12], or recording balances [13, 14]; or by a pressure rise method [15-18] in which the increase in the pressure due to product gases is measured as a function of time using a manometer [15-17] or other device to measure the pressure [18].

* Currently with Anaconda Copper Co., Box 27007, Tucson, AZ 85726.

The kinetic results of thermal decomposition greatly assist in explaining the mechanism of decomposition. Many mathematical expressions have been derived by various authors [10–12, 16, 19, 20, 21] to interpret simple experimental fraction reacted *vs.* time curves.

The authors used a pressure transducer [18] to measure the pressure rise due to the product gases in an initially evacuated closed system. The growing nuclei model [1, 12, 19] was used [14]

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

in which α is the fraction reacted at time t , K is the reaction rate constant, and t_0 is the induction time. The fraction reacted α is directly proportional to the quantity p/p_f where p is the pressure rise at time t , and p_f is the pressure at the inflection point of the experimental pressure *vs.* time curves (see Fig. 1). In terms of pressure, equation 3 becomes $(p/p_f)^{1/3} = K^*t$ where K^* is the reaction rate constant incorporating the aspect of induction time as just described. The experimental decomposition curves obtained by the pressure rise method were similar to those obtained by thermogravimetry [1] but some differences in the rate of reaction, activation enthalpies and mechanism were found as will be shown.

Experimental

The 10 ml pressure rise system consisted of a 2.5 ml sample cell of 4 mm I.D. by 20 cm stainless steel tubing which was attached to a pressure transducer with a short length of 3 mm I.D. steel tubing of approximately 7.5 ml volume. The latter was maintained at 80° to prevent condensation of product gases.

The urea nitrate sample was a powder (10–400 μ) and was synthesized by IRECO Chemicals Company, Salt Lake City, Utah. A 10 mg sample was used in the kinetic study. Pressure rise commenced almost immediately after the sample tube was put into the furnace and the pressure rise was measured as a function of time. It required from 20 to 30 seconds for the 10 mg samples to reach equilibrium temperature.

Results and discussion

The isothermal decomposition results for urea nitrate in the temperature range 110.6–123.1° and 129–145° are shown in Fig. 1a and 1b, respectively. The pressure *vs.* time curves are sigmoidal in shape and the reproducibility was excellent with a deviation of 2% or less. The results are rather similar to thermogravimetric results obtained previously by the authors [1]. The rate curves show acceleration of reaction almost to the end of the reaction with an inflection point just before the main reaction terminates at a pressure maximum. The pressure at the inflection point p_f was taken as the final pressure.

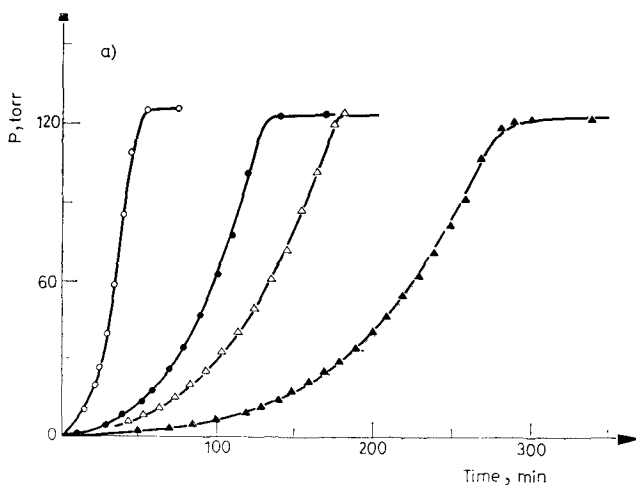


Fig. 1a. Effect of temperature on the decomposition of urea nitrate ○ 123.1° ● 116.4°, △ 114.0, ▲ 110.6°

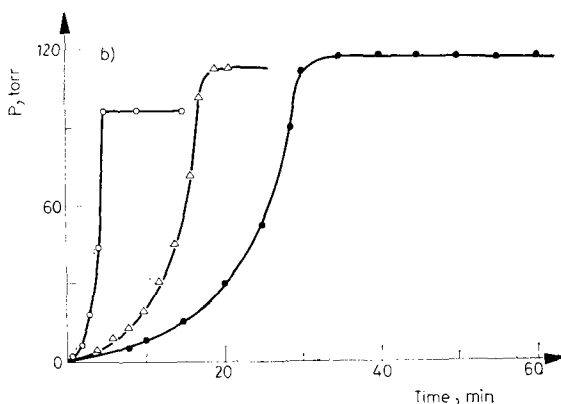


Fig. 1b. Effect of temperature on the decomposition of urea nitrate ○ 129° △ 134° ● 145°

The average percent of decomposition is not precisely known. Using the weight difference of cell with initial sample and cell with residue a lower limit of 34% weight loss results. On the basis of moles of gas produced and using the stoichiometry of Eq. 1 but with all of the water remaining in the residue an upper limit of about 50% weight loss is obtained. With the thermogravimetric results, 38.5% [1] decomposition was found. Percent decomposition is probably about the same as with the thermogravimetric results.

The effect of temperature is quite pronounced. With a reaction temperature of 110.6° the pressure changed from approximately 0.2 p_f at $t = 70$ min to 0.4 p_f at $t = 210$ minutes but at 145° the pressure was 0.2 p_f at 3 minutes and 0.4 p_f at

4 minutes. The maximum pressure decreased from 124 torr at 110.6° to 96.6 torr at 145°. This decrease in the maximum pressure p_{\max} at higher temperatures (see Table 1) was likely due to two related factors: 1) the marked increase in the rate of production of water vapor at the higher temperature and 2) the retention of larger amounts of H₂O within the samples at the higher temperature since there was much less time for diffusion of H₂O from the sample. The product gases N₂O, CO₂, and H₂O vapor were identified chromatographically as a function of time. The amount of H₂O was relatively small as compared to N₂O and CO₂ and it was noticed that

Table 1
Reaction rate data in an initially evacuated system

T, K	p_{\max} , torr	K^* , $\text{min}^{-1} \times 10^3$
383.6	124.1	2.94
387.0	123.4	4.71
389.4	124.1	6.50
396.1	125.5	16.40
402.0	116.9	23.84
407.0	114.1	40.00
418.0	96.6	140.00

H₂O appeared only as the reaction neared termination at about 0.8 p_f . The effects of N₂O and CO₂ on retardation of reaction rate were also significant but quite less dramatic than the retardation by water vapor.

The remaining material in the sample cell, after the maximum pressure was reached, had a pasty appearance and was identified as cyanourea by wet chemical analysis and infrared spectroscopy. The X-ray spectrum of the residue consisted mainly of one sharp peak at $2\theta = 18^\circ$ with a few other minor peaks. This spectrum was not similar to that of urea nitrate and did not fit any species tabulated in the ASTM X-ray card file. Cyanourea is a hygroscopic material and is unstable at 100° as has been determined by infrared and X-ray techniques. It was found previously [1] for urea nitrate that the decomposition reaction continued beyond 0.34 fraction reacted at a much slower rate due to the slow decomposition of cyanourea and presumably due to loss of water but this aspect of decomposition was not studied further.

Reaction 1 predicts 48% weight loss assuming that the H₂O produced was retained by cyanourea. It has been found thermogravimetrically [1] that a maximum weight loss of about 42% was reached which suggests that the experimental results of this study are in rather good agreement with Eq. 1.

The pressure rise data fits the growing product nuclei model as given by Eq. 3 with α being replaced by p/p_f and K by K^* . Pressure rise results in Fig. 1a and 1b were plotted as $(p/p_f)^{1/3}$ vs. t as shown in Fig. 2a and 2b, respectively. The positive intercept with the $(p/p_f)^{1/3}$ ordinate of Fig. 2a and 2b, denotes that t_0 of Eq. (3) has

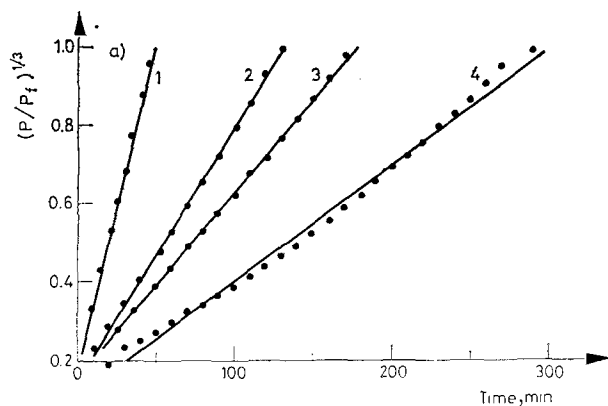


Fig. 2a. Experimental plots of $(p/p_t)^{1/3}$ vs. time from Figure 1a. 1—123.1°, 2—116.4°, 3—114.0°
4 — 110.0°

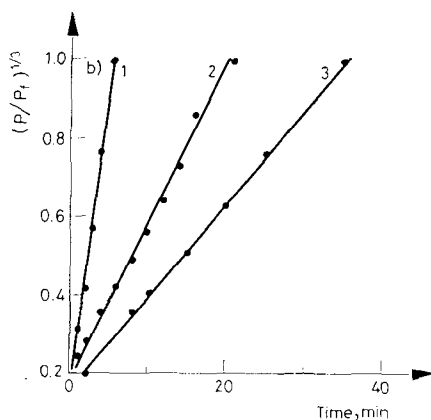


Fig. 2b. Experimental plots of $(p/p_t)^{1/3}$ vs. time from Figure 1b. 1 — 145°, 2 — 134°, 3 — 129°

a negative value; t_0 cannot be negative but this response would occur if some of the product nuclei were present at the beginning of the reaction and/or if nucleation occurs at an abnormally rapid rate [20, 21]. The first reason for negative t_0 was excluded because of urea nitrate stability at room temperature. Hence, it is deduced that nucleation is abnormally rapid [1]. The experimental rate constant was evaluated from the linear portions of Fig. 2a and 2b using the Eyring rate equation [22] to determine the enthalpy of activation ΔH^\ddagger . The reaction rate constant K^* is directly proportional to the specific rate constant k ,

$$K^* = ak' = a \left(\frac{\kappa kT}{h} \right) \exp \left(\frac{\Delta S^\ddagger}{R} \right) \exp \left(-\frac{\Delta H^\ddagger}{RT} \right) \quad (4)$$

or in logarithmic form

$$\log \frac{K^*}{T} = \log \frac{a \kappa k}{h} + \frac{\Delta S^\ddagger}{2.3 R} - \frac{\Delta H^\ddagger}{2.3 RT} \quad (5)$$

where a , κ , k , T , h , ΔS^\ddagger , and ΔH^\ddagger are respectively a constant which may contain conversion factors, transmission coefficient (taken as unity), Boltzmann constant, absolute temperature, Planck's constant, entropy of activation, and enthalpy of activation.

Table 1 shows the rate data as a function of temperature from which $\log \frac{K^*}{T}$ vs. $\frac{1}{T}$ was plotted as shown in Fig. 3 to yield $\Delta H^\ddagger = 142 \pm 12.5$ kJ/mole at 95% confidence range [23]. This measured value of ΔH^\ddagger in a closed initially evacuated system was greater than that obtained for decomposition in open air [1], 115 ± 11.3 kJ/mole. This difference was due to two factors, one of which would result in a larger ΔH^\ddagger value, the other would only appear to give a larger value.

The first factor is inhibitory product gases (1); the second is self heating [24] due to the use of a larger sample in the pressure rise study, 10 mg as compared to 0.5 mg for the thermogravimetric study [1]. Both factors are important in this case. With respect to the first factor the poisonous effect of product gases with a larger sample, especially H_2O , causes the reaction to follow a path of higher activation enthalpy as compared to decomposition in open air. This aspect was clearly shown experimentally during the isothermal decomposition of urea nitrate using a thermogravimetric method [1]. With respect to the second factor self heating probably ranged from a few degrees for the low temperature experiments to about 15° for the

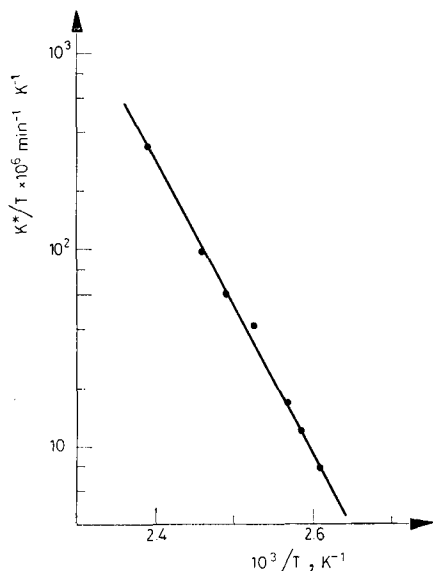


Fig. 3. Activation enthalpy plot $\Delta H = 142 \pm 12.5$ kJ/mole

higher temperature ones on the basis of DTA results obtained for urea nitrate measured in open air [24]. Self heating of this extent could cause a higher measured ΔH^* value of about 12.5 kJ/mole as has been found by the DTA results [24]. Thus the true ΔH^* value is probably about 130 kJ/mole. This is just slightly greater than the ΔH^* value of 117 kJ/mole as obtained thermogravimetrically for decomposition of urea nitrate in open air with no retardation of reaction due to inhibitory gases.

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RÉSUMÉ — La décomposition du nitrate d'urée dans un système initialement mis sous vide, donne des courbes sigmoïdales de pression en fonction du temps. Les données cinétiques expérimentales peuvent être ajustées à un modèle de grossissement de germes, avec une enthalpie d'activation mesurée de 142 ± 12.5 kJ/mole, comparée à 115 ± 11.3 kJ/mole obtenue par thermogravimétrie. Cette valeur plus élevée de ΔH^* s'explique sur la base de deux facteurs: 1) l'effet inhibiteur des gaz produits et 2) phénomène d'autoéchauffement qui augmente la valeur de ΔH^* d'environ 12.5 kJ/mole.

ZUSAMMENFASSUNG — Die Zersetzung von Harnstoffnitrat in einem anfanglich evakuierten System ergab sigmoide Druck—Zeit Kurven. Die kinetischen Versuchangaben können einem Kernwachstums-Modell einer gemessenen Aktivierungsenthalpie von $142 \pm 12,5$ kJ/mol angepaßt werden, im Vergleich zu den auf thermogravimetrischen Weg ermittelten Wert von $115 \pm 11,3$ kJ/Mol. Dieser hohe Wert von ΔH , wird auf Grund zweier Faktoren erklärt: 1) der Hemmungseffekt der Produktgase und 2) Selbsterhitzung, deren Ausmaß ΔH^* um etwa 12.5 kJ/Mol erhöhte.

Резюме — Разложение нитрата мочевины в первоначально откачанной системе дает σ образную кривую в координатах давления время. Экспериментальные данные по кинетике подчиняются модели роста зародышей кристаллов, а измеренная энтальпия активации составляла $142 \pm 12,5$ кдж/моль по сравнению со значением $115 \pm 11,3$ кдж/моль, полученным термогравиметрическим методом. Это более высокое значение ΔH^* объяснено двумя факторами: 1) подавляющим влиянием газообразных продуктов и 2) саморазогревом, вклад которого составляет около 12.5 кдж/моль.