

VACUUM SUBLIMATION KINETICS OF UREA NITRATE

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Urea nitrate completely sublimes in a continuously pumped vacuum at a rate dependent upon the extent of the surface area. The fraction sublimed (α) vs. time (t) curve is sigmoidal in shape with an inflection point fluctuating between 5.3 and 8.1% weight loss in the temperature range 56 to 97°.

The experimental data fit the grain burning model

$$1 - (1 - \beta)^{1/3} = k_s(t - t_0)$$
$$\beta = \alpha - \beta_0, \beta = 0 \text{ at inflection point}$$

where k_s is a sublimation rate constant, and the constants β_0 and t_0 are the respective values of α and t at the inflection point. This equation yielded an activation enthalpy of sublimation of 79 ± 5.4 kJ/mole.

Sublimation of urea nitrate was measured using a thermogravimetric method in the temperature range 56 to 97° under a continuously pumped vacuum. Four rather conclusive evidences support the conclusion that the weight loss was exclusively due to sublimation allowing a kinetic treatment of vacuum sublimation of urea nitrate. Firstly, 100% weight loss was possible. Secondly, the study was well below the lowest possible decomposition temperature of about 105°. Thirdly, a 30 mg sample was placed in a 4 mm I.D. by 20 cm long sample tube and evacuated continuously with about one-third of the tube being inserted in boiling water (94°) and the urea nitrate disappeared from the bottom of the sample cell and condensed on the walls of the upper part of the sample cell which were at room temperature. The sublimate was about 95% of the initial sample weight and on the basis of X-ray and infrared measurements it was found to be urea nitrate. Fourthly, an 8 mg sample was heated at 66° under continuous vacuum in the thermogravimetric system [1] and the residues after 8% and 69% weight loss were respectively analyzed by infrared spectroscopy. The infrared patterns of both of these residues were the same and matched exactly that of the original urea nitrate showing that no decomposition had occurred.

Experimental

Technique. A thermogravimetric system utilizing a Cahn R. G. electrobalance with a sensitivity of 0.05 μ g was used to monitor the fractional weight loss-time curve. The system was pumped continuously with a mechanical vacuum pump.

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The temperature was controlled to $\pm 0.1^\circ$ using a Thermatrol regulator* which was calibrated at the melting point of ice and the boiling point of water. The sample of urea nitrate was synthesized as a powder (10–400 μ) by IRECO Chemicals Co., Salt Lake City, Utah. A platinum sample bucket was used during the sublimation study.

Sample spreading. It was found that the sublimation rate of urea nitrate was significantly faster with the sample thinly spread in one layer as compared to the

Table 1
Sublimation rate data from Figure 2

T, °K	W ₀ , mg	k _s , min ⁻¹ × 10 ³
328.8	0.272	7.78
336.5	0.290	18.50
344.0	0.232	35.43
350.0	0.224	65.26
360.0	0.220	105.88
370.0	0.256	229.78

compact state. This was explained by the larger surface area exposed to the vacuum for the sample which was thinly spread. Because of this slight dependence of rate on spreading, the results were obtained with a uniform thinly spread sample.

Sample weight. The sublimation rate increased as sample weight was decreased but it reached a steady state for samples below 0.42 mg weight at 71°; hence samples less than this weight were used and the sample size was maintained within the limits of 0.22 to 0.29 mg (Table 1). At temperatures less than about 50° it was found that the rate of sublimation of urea nitrate increased continuously as the sample size decreased from 0.368 to 0.184 mg. Hence, data below 50° was not used in the evaluation.

Both sample spreading and sample size effects were quite clearly due to retardation of product gas diffusion effectively creating an over pressure of urea nitrate vapor which then reduced sublimation.

Results and discussion

Kinetic study. The fraction sublimed (α) as a function of time (t) for the temperature range 55.8–97° is presented in Fig. 1. The curves show an initial increase of sublimation rate to an inflection point but thereafter show a smooth decrease in rate as a function of time approaching zero residue, or total sublimation, asymptotically. This type of result fits the burning sphere model [2, 3] as given by:

$$1 - (1 - \beta)^{1/3} = k_s(t - t_0) \quad (1)$$

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where: $\beta = \alpha - \beta_0$ is the corrected fraction sublimed; $\beta = 0$ at the inflection point, i.e., at $\alpha = \beta_0$ and $t = t_0$; k_s is the sublimation rate constant and t_0 the time for initiation of sublimation, or the time at the inflection point. The correction factor, β_0 , fluctuated between $\alpha = 0.053$ to 0.081 in the temperature range studied.

The initiation of sublimation was likely due to development of fissures which increased the surface area to a maximum at or near the inflection point. Thereafter the rate of sublimation decreased according to Eq. (1) because surface area decreases-

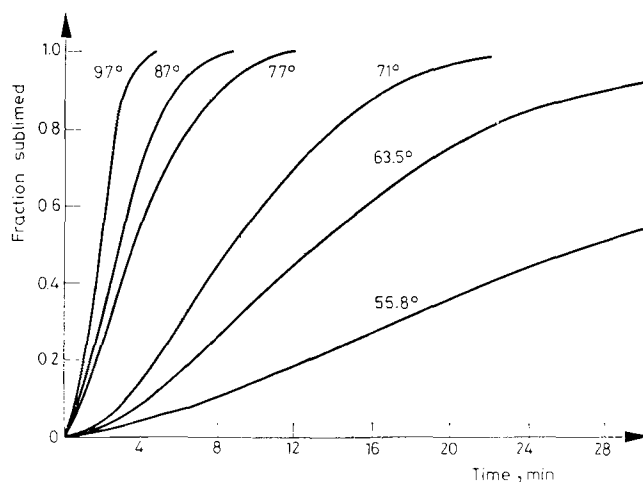


Fig. 1. Effect of temperature on sublimation of urea nitrate in a continuously pumped vacuum

ed, i.e., the sublimation could be considered as being from equiaxed particles (grains) decreasing in size and hence surface area as sublimation proceeded. The rate of sublimation is, however, not only a function of the surface area but is dependent upon the curvature of the surface. Material will sublime from surfaces having a positive radius of curvature, i.e., surface of crystalites as opposed to pores which have negative radii and hence tend to accrue matter from positive radii surfaces. Thus the surface area may not have been a maximum at the inflection point. This may represent the time at which the maximum number of sharp projections with rather small radii existed.

Treatment of the curves of Fig. 1 using Eq. (1) should be based upon weight loss after the inflection point. It was found though that the region near the inflection point was sufficiently linear that selection of β_0 to define β for the fit of Eq. (1) was not critical. The average value of β_0 is 0.067. This weight loss might have been due to the loss of water absorbed on urea nitrate, since it was found that urea nitrate absorbed water [4] as much as 6% in a flow of air saturated with water vapor in one hour at 30°. The results from Fig. 1 were plotted using Eq. (1) as shown in Fig. 2.

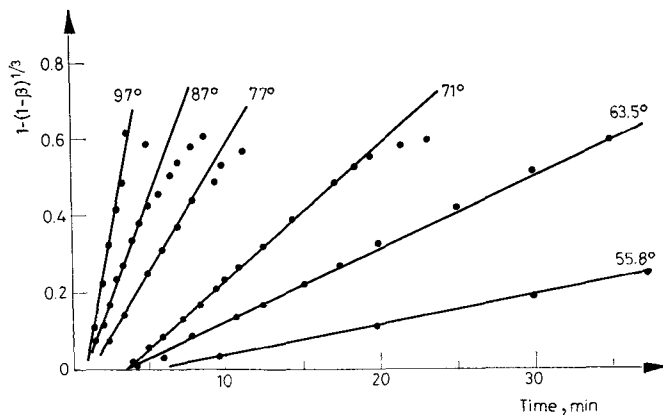


Fig. 2. Experimental plots of $1 - (1 - \beta)^{1/3}$ vs. time for sublimation of urea nitrate

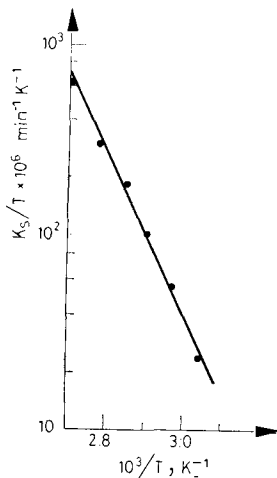


Fig. 3. Activation enthalpy plot for sublimation in continuous vacuum
 $\Delta H_s = 79.4 \pm 5.4$ kJ/mole

Equation (1) fitted the data of Fig. 1 rather well for α ranging from about 0.05 to 0.98, or for β from 0.00 to 0.93.

The sublimation reaction rate constant k_s is directly proportional to the specific rate constant k' given by the Eyring rate equation [5]

$$k' = \frac{\kappa kT}{h} \exp\left(\frac{\Delta S_s^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_s^\ddagger}{RT}\right)$$

where

$$k_s = bk' = b \left(\frac{\kappa kT}{h}\right) \exp\left(\frac{\Delta S_s^\ddagger}{R}\right) \exp\left(-\frac{\Delta H_s^\ddagger}{RT}\right)$$

or in logarithmic form

$$\log \left(\frac{k_s}{T} \right) = \log \frac{b \kappa k}{h} + \frac{\Delta S_s^\ddagger}{2.3 R} - \frac{\Delta H_s^\ddagger}{2.3 RT} \quad (2)$$

where b , κ , k , T , h , ΔS_s^\ddagger , and ΔH_s^\ddagger are, respectively: a constant which contains conversion factors, transmission coefficient (taken as unity), Boltzmann constant, absolute temperature, Planck's constant, entropy of activation of sublimation, and enthalpy of activation of sublimation.

The experimental sublimation rate constants as a function of temperature shown in Table 1 were evaluated from the linear portions of Fig. 2. Figure 3 is the plot of $\log k_s/T$ vs. $1/T$ according to Eq. (2) from which an activation enthalpy of sublimation (ΔH_s^\ddagger) of 79.4 ± 5.4 kJ/mole was calculated at 95% confidence range [6].

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RÉSUMÉ — Le nitrate d'urée se sublime complètement sous vide entretenu, à une vitesse qui dépend de la valeur de la surface. La courbe représentant la fraction sublimée (α) en fonction du temps (t) est de la forme sigmoïdale, avec un point d'inflexion fluctuant entre des pertes de poids de 5.3 à 8.1% dans l'intervalle de température allant de 56 à 97°.

Les données expérimentales peuvent être ajustées à un modèle de combustion de grain

$$1 - (1 - \beta)^{1/3} = k_s(t - t_0)$$

$$\beta = \alpha - \beta_0, \quad \beta = 0 \text{ au point d'inflexion,}$$

où k_s est une constante de vitesse de sublimation et les constantes β_0 et t_0 sont les valeurs respectives d' α et t au point d'inflexion. Cette équation donne une enthalpie d'activation de la sublimation de 79 ± 5.4 kJ/mole.

ZUSAMMENFASSUNG — In einem kontinuierlich angesaugten Vakuum sublimiert Harnstoffnitrat vollständig mit einer von der Größe der Oberfläche abhängenden Geschwindigkeit. Die Kurve der sublimierten Fraktion (α) aufgetragen gegenüber der Zeit (t) ist von sigmoider Gestalt mit einem Inflektionspunkt, welcher im Temperaturbereich von 56 bis 97° zwischen den Gewichtsverlusten von 5.3 bis 8.1% schwankt.

Die Versuchsangaben können den Kornbrennungsmodell

$$1 - (1 - \beta)^{1/3} = k_s(t - t_0)$$

angepaßt werden, wobei

$$\beta = \alpha - \beta_0, \quad \beta = 0 \text{ bei dem Inflektionspunkt,}$$

wo k_s eine Sublimationsgeschwindigkeitskonstante und β_0 und t_0 die entsprechenden Werte von α und t am Inflexionspunkt sind. Diese Gleichung ergab eine Aktivierungsenthalpie für die Sublimation von 79 ± 5.4 kJ/Mol.

Резюме — Нитрат мочевины полностью сублимируется в непрерывно поддерживаемом вакууме со скоростью зависимой от размера поверхностной площади. Кривая в координатах сублимированная фракция (α) — время (t) является σ -образной с точкой изгиба, колеблющейся между 5.3 и 8.1% потери веса в области температур от 56 до 97°. Экспериментальные данные подчиняются модели кристаллообразования

$$1 - (1 - \beta)^{1/3} = k_s (t - t_0)$$
$$\beta = \alpha - \beta_0, \quad \beta = 0 \text{ в точке изгиба}$$

и где k_s — константа скорости сублимации, а константы β_0 и t_0 — соответствующие значения α и t в точке изгиба. Это уравнение дает значение энтальпии активации процесса сублимации равное $79 + 5.4$ кдж/моль.