The Thermal Decomposition of Biurea

By **Paul R. Russell** and **Alec N. Strachan,*** Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU

Biurea decomposes in the temperature range 230—260° to yield gas, a white sublimate, and a viscous liquid residue. The gas is mainly ammonia (*ca.* 71%), but some carbon dioxide (*ca.* 17%) and nitrogen (*ca.* 12%) are also present. The main constituent of the sublimate is urea and that of the residue urazole. The products are accounted for by four reactions involving hydrogen atom transfer, together with two subsequent reactions of isocyanic acid. The decomposition takes place in three stages, an initial small evolution of gas, an induction period, and a final stage during which most of the decomposition occurs and which is autocatalytic. Recrystallisation largely eliminates the first stage. Lowering the external gas pressure lengthens the induction period. The final stage is more reproducible than the other two. It remains acceleratory almost to the very end of the reaction and has an activation energy of 114 kJ mol^{-1}. The kinetics of the decomposition are interpreted in terms of a nucleation and growth mechanism.

BIUREA is a major product of the thermal decomposition of azodicarbonamide[1] which is used extensively in industry as a blowing agent for expanding plastics. It is therefore desirable to have knowledge of the thermal stability of biurea and of the products formed when it itself undergoes thermal decomposition. The present investigation was undertaken to obtain such knowledge, the only previous information being the finding by Thiele and Stange[2] that biurea decomposes at 200° into urazole and ammonia.

EXPERIMENTAL

Materials.—Biurea (>98%) was supplied by Kodak Ltd. This was either used directly (untreated biurea) or recrystallised by dissolving in hot water and filtering the solution into a flask immersed in an ice-bath. The rapid cooling produced material made up of very small crystals similar to the untreated biurea. The recrystallised biurea was washed with acetone and dried in a vacuum desiccator.

Procedure.—The decompositions were carried out by placing a known weight of biurea in a tube 2 cm in diameter and *ca.* 100 cm^3 in volume. The tube was evacuated and the reaction started by inserting the end of the tube in a Statim 452 aluminium heating block thermostatically controlled to $\pm 0.1°$.

The gaseous products were analysed by placing liquid nitrogen around the tube and transferring the non-condensible gas to a gas burette. I.r. examination showed that no carbon monoxide was present and hence the non-condensible gas was assumed to be all nitrogen. The i.r. spectrum of the condensible gas showed it to be a mixture of ammonia and carbon dioxide. Its total quantity could not be determined directly because when it was transferred to the gas burette and compressed solid ammonium carbamate was formed. Decompositions were therefore carried out in duplicate and in one case ammonia was determined after absorption of the carbon dioxide by soda lime, and in the other carbon dioxide determined after absorption of the ammonia by oxalic acid.

In the kinetic runs the decomposition tube was connected directly to a mercury or oil (n-butyl phthalate) manometer. The decompositions under different pressures of nitrogen were carried out using a smaller reaction tube with a volume approximately half that of the normal tube.

Chromatography.—Solvent systems and reagents described in the literature[3,4] were used to separate and identify the solid products by paper chromatography, and t.l.c. analysis was carried out using similar plates, the same solvent and solutions C and D described previously.[1]

RESULTS AND DISCUSSION

Products.—On decomposing untreated biurea at 234°, gas is evolved, a white sublimate forms on the upper sides of the decomposition tube, and a viscous liquid residue remains at the bottom. This liquid rapidly solidifies to a clear mass when the tube is removed from the heating block. Both the sublimate and residue are soluble in water, the latter dissolving very readily.

The gas evolved on heating untreated biurea (150 mg) at 234° amounts to 14 cm^3 reduced to s.t.p. and comprises 71 mole % NH_3, 17 mole % CO_2, and 12 mole % N_2.

T.l.c. shows the sublimate to contain urea and the

---

[1] A. S. Prakash, W. A. Swann, and A. N. Strachan, *J.C.S. Perkin II*, 1975, 46.

[2] J. Thiele and O. Stange, *Annalen*, 1894, **283**, 1.

[3] M. Takimoto and K. Koeda, *Kogya Kagaku Zasshi*, 1960, **63**, 797 (*Chem. Abs.*, 1962, **56**, 6,639d).

[4] R. C. R. Barreto, H. S. R. Barreto, and I. R. Pinto, *J. Chromatog.*, 1961, **6**, 416.

residue urazole. Paper chromatography and *X*-ray powder diffraction confirm urea as the major component of the sublimate but both indicate that some biurea is also present. *X*-Ray examination of the residue shows it to be amorphous. On allowing an aqueous solution of the residue to evaporate slowly a solid is obtained with a weak powder pattern in which the main reflections of urazole show up well. Paper chromatography also confirms the presence of urazole.

However pure urazole is a solid at 234°. Hence the residue being liquid cannot consist solely of urazole. Unfortunately none of the analytical techniques employed reveal the nature of the other component or components present. The absence of such knowledge prevents quantitative analysis for urazole and urea being undertaken.

Mechanism.—The crystal structure of biurea[5] shows that each of the six hydrogen atoms is hydrogen bonded to an oxygen atom in a neighbouring molecule. The movement of hydrogen atoms usually along hydrogen bonds followed by cleavage of such and other bonds can produce ammonia, nitrogen, isocyanic acid, and water as in reactions (1)—(4).

$$\text{-NH}_2 + \text{H} \longrightarrow \text{NH}_3 \qquad (1)$$

$$\text{-NH-NH-} - 2\text{H} \longrightarrow \text{-N=N-} \longrightarrow \text{N}_2 \qquad (2)$$

$$\text{-CONH}_2 - \text{H} \longrightarrow \text{HNCO} \qquad (3)$$

$$\text{-CONH}_2 + 2\text{H} \longrightarrow \text{CH=NH} + \text{H}_2\text{O} \qquad (4)$$

The fragments left as the result of (1) can form urazole and the reactions of isocyanic acid with water and ammonia [reactions (5) and (6)] account for carbon

$$\text{HNCO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{NH}_3 \qquad (5)$$

$$\text{HNCO} + \text{NH}_3 \longrightarrow \text{NH}_2\text{CONH}_2 \qquad (6)$$

dioxide and urea formation. The imides formed as a result of reaction (4) would explain why the residue is not pure urazole.

Thus processes (1)—(4) followed by secondary reactions (5) and (6) are adequate to account for all the products. The high proportion of ammonia in the gas indicates that process (1) is the major one taking place. But it is equally clear that decomposition to ammonia and urazole [reaction (7)] is far from being the sole reaction occurring.

$$\text{NH}_2\text{CONHNHCONH}_2 \longrightarrow \text{NH}_3 + \underline{\text{CONHNHCONH}} \qquad (7)$$

Kinetics.—Gas evolution–time curves for the decomposition of different sample weights of untreated biurea at 234° are shown in Figure 1. The curves indicate three stages to the reaction. At the start a small quantity of gas is evolved fairly rapidly but the evolution is not maintained. This is followed by the second stage, an induction period, when little gas is evolved. In time the third and final stage is reached when most of the decomposition occurs. This last stage is remarkable for remaining acceleratory almost to the very end.

First stage. An enlargement of the first stage at various temperatures obtained by the use of an oil manometer is shown in Figure 2. The initial acceleration of the rate is probably due to the biurea sample taking a finite time to reach the constant temperature. Once at constant temperature the rate is deceleratory. Uncertainties in the initial and final parts of the curves makes analysis of their shape impossible. But a plot of the logarithm of the slope of the linear centre section against the reciprocal of the absolute temperature is linear and leads to a value of 59 kJ mol^{-1} for the activation energy of this stage of the reaction. This is too high to be solely a heat of adsorption. Furthermore the gas evolved, although too small in amount for quantitative analysis, is shown by tests to contain ammonia. It is therefore not just desorbed air.

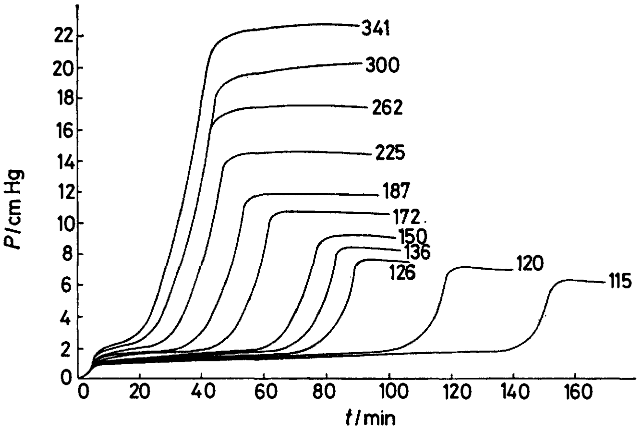

FIGURE 1 Pressure–time curves at 234° for different weights (mg) of untreated biurea

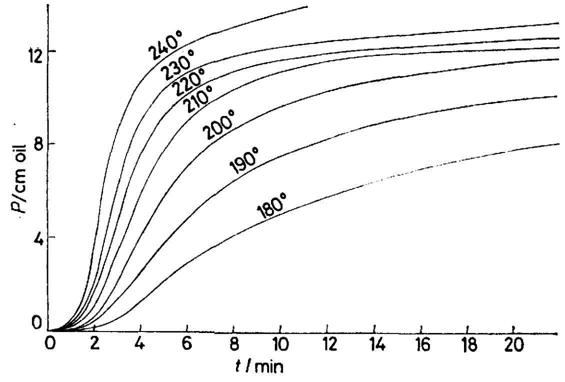

FIGURE 2 Pressure–time curves at various temperatures for the first stage of the decomposition of untreated biurea (120 mg)

Figure 3 shows that recrystallisation of the biurea reduces markedly the amount of gas evolved during this first stage. Possibly an ageing process, similar to that observed with other solids,[6] is responsible for the more pronounced initial gas evolution from untreated biurea.

Induction period. Figure 1 shows that the smaller the

---

[5] D. S. Brown and P. R. Russell, *Acta Cryst.*, 1976, **B32**, 1056.

[6] D. A. Young, ' Decomposition of Solids ', Pergamon, Oxford, 1966, pp. 45—49.

sample size, the longer is the induction period, and Figure 3, that recrystallisation lengthens the induction period. Two factors appear to be at work to produce these curious effects. The first is that a minimum pressure (*ca.* 2 cmHg) of product gas must be evolved before the third and final stage can occur. The smaller the size of the sample the greater is the proportion of the latter which must decompose, and hence the longer the time, before this critical pressure is reached. Likewise with recrystallised material, since the initial burst of gas is missing, a longer time is required as compared with aged material for enough gas to be formed to trigger the third stage. Additional evidence of the need for a critical pressure to be reached is the observation that if the product gases are pumped away periodically, the induction period can be lengthened indefinitely, with the result that the third stage never takes place.

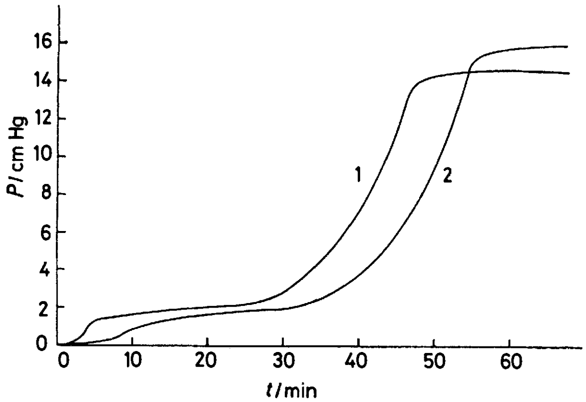

FIGURE 3 Comparison of the decomposition behaviour at 234° of the same sample weight (225 mg) of untreated biurea (1) and recrystallised biurea (2)

The second factor is that the greater the external pressure the faster does decomposition occur during the induction period. Thus the larger the sample the quicker the external pressure around it builds up and this in turn accelerates the induction processes taking place. The separate involvement of the two factors is seen more clearly in Figure 4 which shows the decomposition behaviour of a constant sample weight under different pressures of nitrogen. The third stage only occurs after roughly the same minimum pressure of product gas has been evolved in each case. But the time required for this to happen is steadily reduced as the nitrogen pressure is increased. A minimum and constant induction period is reached at nitrogen pressures of *ca.* 60 mmHg and above.

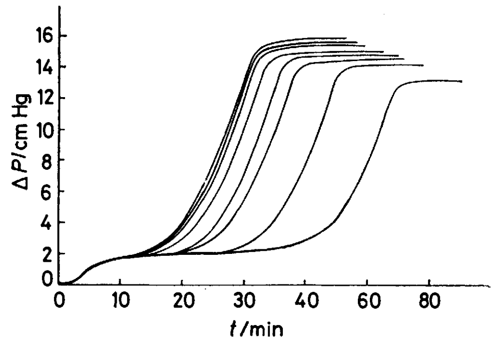

FIGURE 4 Pressure increase–time curves at 234° for samples (120 mg) of untreated biurea under different pressures of nitrogen. From right to left 0, 6, 12, 18, 24, 30, 40, and 60 mmHg. A smaller than normal reaction tube was employed for these experiments

It seems likely that the induction period corresponds to a nucleation process, but why the external pressure influences the nucleation rate and why it apparently must reach a critical value before the nuclei start to grow remains obscure.

Figure 4 shows an additional feature, namely that the longer the induction period the smaller is the final pressure of evolved gas. This effect is also discernible in the data shown in Figure 1 where, if the maximum pressure attained is divided by the sample weight, the yield of gas per gram is found to diminish as the induction period increases. The most probable cause of this trend is that sublimation of the biurea is competing with its decomposition. The longer the induction period, the more biurea sublimes and the less remains to decompose. This would also explain why some biurea is found along with the urea in the sublimate.

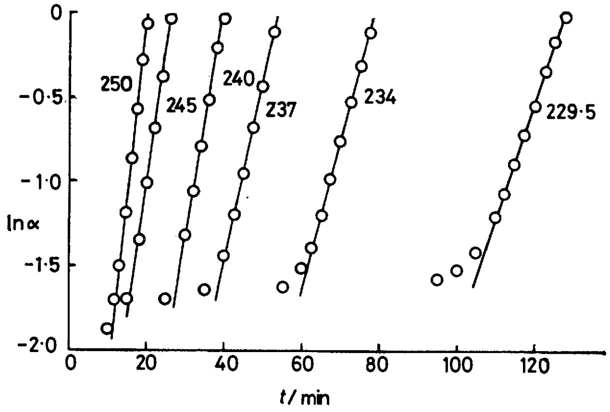

FIGURE 5 Plots of lnα *versus* time at different temperatures for samples (150 mg) of untreated biurea

Third stage. Figures 5 and 6 show that for the third and final stage of the decomposition plots of lnα *versus* time are linear, where α is the fractional decomposition as measured by $P/P_{\text{max.}}$, P being the pressure of evolved gas at time t and $P_{\text{max.}}$, the maximum pressure attained at the end of the decomposition. Thus the reaction during the last stage is autocatalytic with the rate obeying the equation $d\alpha/dt = k\alpha$, k being the autocatalytic rate constant. Integration leads to $\ln\alpha = kt +$ constant. Hence the slopes of the linear portions of the lnα *versus* time plots give values of k. The Table lists values of k at different temperatures obtained from the plots for untreated (aged) biurea shown in Figure 5 and from a similar set of plots (not shown) for recrystallised biurea. A graph of ln$k$ *versus* $1/T$, where T is the absolute temperature, is linear, and leads to a value of 114 kJ mol^{-1} for the activation energy of this final stage of the reaction.

Figure 6 shows that at a given temperature the slopes, and hence the k values, are the same regardless of the size of the sample, the size of the reaction tube, the pressure of inert gas, and whether the biurea is untreated (aged) or recrystallised. This indicates that none of these variables affect the autocatalytic rate at which this third stage, once triggered off, takes place, and illustrates how much more reproducible this stage is than either of the first two.

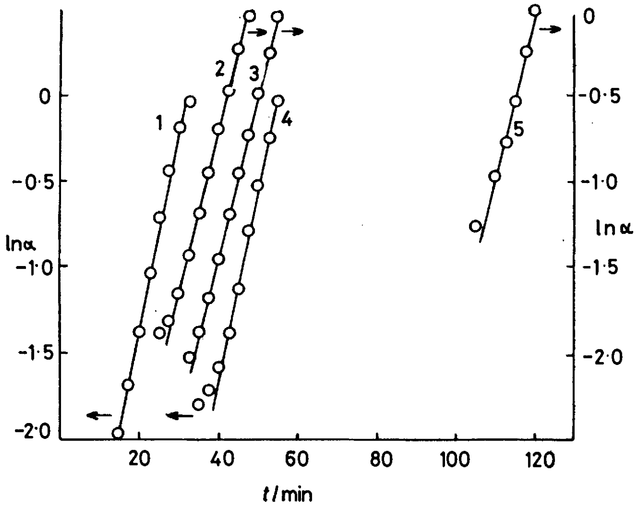

FIGURE 6 Plots of ln α *versus* time at 234° for different samples and conditions: 1, untreated biurea (120 mg) in small tube plus 60 mmHg nitrogen; 2, untreated biurea (225 mg) in normal tube; 3, recrystallized biurea (225 mg) in normal tube; 4, untreated biurea (120 mg) in small tube; 5, untreated biurea (120 mg) in normal tube

Autocatalysis in the decomposition of solids is usually explained in terms of chain branching in which growing nuclei fertilize additional potential nuclei which then grow and fertilize still more.[6] However with most solids the autocatalysis, when it occurs, is normally observed over an early stage of the decomposition and is followed by a deceleration corresponding to a contracting envelope.[6] With biurea, as can be seen from Figures 1, 3, 5, and 6, the autocatalysis lasts from $\alpha < 0.3$ to $\alpha > 0.9$, *i.e.* over the greater part of the decomposition and almost to its very end. Only in the case of one other solid has similar behaviour been observed.[7] It is unlikely that self-heating is the cause since in a differential thermal analysis apparatus the decomposition is wholly endothermic.

Values of the autocatalyst rate constant k for untreated and recrystallised biurea at different temperatures

T/°C	Untreated k/min^{-1}	Recrystallised k/min^{-1}
229.5	0.072	
234	0.087	0.095
237	0.108	
240	0.140	0.138
244		0.162
245	0.170	
250	0.202	0.225
254		0.263
260		0.354

One factor which may play a part in postponing the onset of deceleration is the formation of a liquid phase as the reaction proceeds. Some of the remaining reactant may be dissolving and decomposing faster as a result than it would have done had it remained solid. Clearly further work is required to determine more exactly the causes of the autocatalytic behaviour observed over this last stage of the decomposition.

We are grateful to Fisons Ltd. for financial support and for continuous interest and help.

[7/1084 *Received, 22nd June*, 1977]

---

[7] L. L. Bircumshaw and F. M. Tayler, *J. Chem. Soc.*, 1950, 3674.