The Thermal Decomposition of Azodicarbonamide (1,1'-Azobisformamide)

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When azodicarbonamide is decomposed in the temperature range 165—195°, gas is evolved and a white sublimate and a white residue are formed. The gas consists of nitrogen and carbon monoxide together with a third component, which is isocyanic acid at lower and ammonia at higher temperatures. The sublimate consists of cyanuric acid, cyamelide, and urea, and the residue is a mixture of biurea, cyanuric acid, and urazole. Two main primary reactions appear to take place concurrently. In the first azodicarbonamide decomposes to form biurea, nitrogen, and isocyanic acid, and in the second to form urazole, nitrogen, isocyanic acid, and ammonia. At 171·5° the first mode of decomposition is twice as frequent as the second. Cyanuric acid, cyamelide, carbon monoxide, and urea all appear to be products of secondary reactions involving isocyanic acid. On prolonged heating at higher temperatures the biurea initially formed decomposes into urazole and ammonia. When the quantity of gas evolved is determined as a function of time, an S shaped curve is obtained with a long linear centre portion. This near constant rate of decomposition over the main part of the reaction has an activation energy of 228 kJ mol^{-1} and is accounted for by a one-dimensional propagation of the decomposition through the crystal lattice.

AZODICARBONAMIDE (AC) is used extensively in industry as a blowing agent for expanding plastics. Reed [1] reports that when the dry solid is decomposed at 190° the gas evolved amounts to 32% by weight of the products. It consists mainly of nitrogen together with a smaller but significant quantity of carbon monoxide.

A sublimate made up of cyanuric acid and a trace of cyamelide accounts for a further 27% of the products, while the remaining 41% is a solid residue of urazole and biurea.

Waki and Yamashita [2] agree with Reed that the main gaseous products are nitrogen and carbon monoxide and that cyamelide is present in the sublimate and biurea in the residue. However they claim that ammonium cyanate rather than cyanuric acid is the other

[1] R. A. Reed, *Brit. Plastics*, 1960, **33**, 468.
[2] K. Waki and T. Yamashita, *Nippon Kagaku Kaishi*, 1972, 2359.

sublimation product, and that cyanuric acid rather than urazole is to be found mixed with biurea in the residue.

The present investigation was undertaken with the object of obtaining more detailed and unambiguous data on both the products and kinetics of AC decomposition so as to resolve the conflicting claims regarding the products, and in the hope of achieving greater understanding of the reaction mechanism.

EXPERIMENTAL

Purification.—Commercial Genitron AC (Fisons) was dissolved in dimethyl sulphoxide. The saturated solution was filtered, and distilled water added slowly to the stirred solution at room temperature until fine yellow crystals of AC were obtained. The crystals were filtered off and washed with cold distilled water, alcohol, and ether. This recrystallisation procedure was then repeated twice. The final material was dried *in vacuo* and stored in the dark.

Decomposition Apparatus.—The decompositions were carried out by placing a known weight of AC (usually 0·1—0·2 g) in a 2 cm diameter tube (*ca.* 100 cm³). The tube was evacuated and the reaction started by placing the end of the tube either in an oil-bath or in an electrically heated aluminium block furnace. The temperature in both cases was controlled to $\pm 0\cdot 2°$.

T.l.c.—Merck silica gel GF_{254} plates [3] were used with dioxan–benzene–acetic acid (80 : 20 : 2, v/v) as solvent. The compounds were detected with the aid of the following solutions: A, mercuric acetate (0·25 g) in 96% (v/v) ethanol (100 cm³) and a few drops of acetic acid; B, diphenyl-carbazide (0·05 g) in 96% ethanol (100 cm³); C, sodium nitroprusside–hydrogen peroxide (no. 290 in ref. 4); and D, p-dimethylaminobenzaldehyde (2 g) in 96% ethanol (50 cm³)–concentrated hydrochloric acid (10 cm³). The solution was then diluted to 100 cm³ with 96% ethanol.

I.r. Spectra.—I.r. spectra were obtained using KBr discs for the solids and a 10 cm path length cell for the gases.

G.l.c.—A Linde molecular sieve 5A column maintained at 40° was used for preliminary gas analysis. Samples of the total gas evolved up to different times from the start of the reaction were analysed.

Quantitative Product Analysis.—Liquid nitrogen was placed around the decomposition tube and the non-condensible gas transferred to a gas burette and measured. The carbon monoxide was oxidised over heated copper oxide, and the carbon dioxide so formed separated from the nitrogen by a liquid nitrogen trap. The quantities of nitrogen and carbon dioxide were then each measured separately.

Isocyanic acid, the only constituent of the condensible gas from decomposition at 171·5°, was determined by admitting a measured excess of ammonia to the decomposition tube, removing the liquid nitrogen from around the tube to allow the ammonia and isocyanic acid to react, and then measuring the residual quantity of ammonia.

The solid products were extracted with warm water (below 50°). No attempt was made to separate the residue

and sublimate. The extract was cooled and filtered. The amount of insoluble material was determined only when the AC had decomposed completely. The filtrate and washings were combined and made up to a known volume. Urazole and cyanuric acid were determined by making up one portion of the solution with 0·1m-HCl and measuring the absorbance at 220 nm. A second portion was then made up with 0·05m-borax and the absorbance measured at 216·5 nm. Urea was determined by the colorimetric method used by Brown,[5] and biurea by the colorimetric method used by Ellis and Formaini [6] for the determination of biuret. Biurea forms a complex in a similar way to biuret with an absorption maximum at 410 nm. Urazole also forms a complex which absorbs weakly at 410 nm and a correction was applied to allow for this based on the urazole concentration already determined.

Kinetics.—In the kinetic runs the reaction tube was attached directly to the gas analysis apparatus and the evolution of the gas followed manometrically.

RESULTS AND DISCUSSION

Products.—When AC was heated in the temperature range 165—195° it was observed to decompose without melting to yield a gas, a white sublimate, and a white residue. The residue dissolved completely in warm water and t.l.c. indicated it contained three major components, biurea, urazole, and cyanuric acid. Reed [1] found biurea and urazole, but detected cyanuric acid only in the sublimate. Waki and Yamashita,[2] relying solely on an examination of the i.r. spectrum of the residue, deduced that biurea and cyanuric acid were present. They failed to detect urazole almost certainly because it has no strong i.r. absorptions [7] which do not coincide with those of biurea [7] and cyanuric acid.[8]

The mass spectrum of the residue confirmed the presence of all three compounds. Parent peaks were obtained at *m/e* 129 (cyanuric acid), 118 (biurea), and 101 (urazole). Biurea has a fragment ion peak at 101 but the ratio of the 101 to the 118 peak was far in excess of that which could be accounted for by biurea alone.

Most of the sublimate also dissolved in warm water and t.l.c. indicated that the only major components of this water soluble fraction were cyanuric acid and urea. The i.r. spectrum of the small proportion of the sublimate which did not dissolve was identical with that of cyamelide.

Reed [1] also found cyanuric acid as a major, and cyamelide as a minor, component of the sublimate, but did not detect urea. However there is no doubt that urea is present since extraction of the sublimate with hot acetone followed by recrystallisation yields a crystalline solid whose m.p., i.r. spectrum, and other properties are identical with those of pure urea.

The i.r. spectrum of the sublimate showed no sharp absorptions in the region of 2175 and 2245 cm⁻¹ as

[3] E. Stahl, ' Thin-layer Chromatography,' Academic Press, London, 1965.

[4] ' Dyeing Reagents for Thin-layer and Paper Chromatography,' E. Merck, Darmstadt, 1971.

[5] H. H. Brown, *Analyt. Chem.*, 1959, **31**, 1844.

[6] G. C. Ellis and R. L. Formaini, *J. Agric. Food Chem.*, 1955, **3**, 615.

[7] C. J. Pouchert, ' The Aldrich Library of Infrared Spectra,' Aldrich Chemical Company, 1970.

[8] W. M. Pagett, jun., and W. F. Hammer, *J. Amer. Chem. Soc.*, 1958, **80**, 803.

observed by Waki and Yamashita [2] and attributed by them to the presence of ammonium cyanate. It is possible that some ammonium cyanate is formed initially. If so, either sufficient heat is generated on its formation, or the temperature at the point at which it is formed (just outside the reaction zone) is high enough, for all of it to be rapidly converted into urea.[9]

In agreement with Waki and Yamashita,[2] no trace was found in either the residue or the sublimate of oxamide, which at one time [10] was thought to be a product of the decomposition.

Preliminary g.l.c. analysis of the gas evolved revealed that under all conditions more than 50% was nitrogen. On decomposing AC for 480 min at 171·5° the i.r. spectrum of the gas showed that carbon monoxide and isocyanic acid were also present but no ammonia or carbon dioxide. A complete analysis of both solid and gaseous products formed under these conditions is shown in Table 1. It is seen that nearly 96% by weight of the original AC is accounted for.

TABLE 1

Relative amounts of products formed on decomposing AC for 480 min at 171·5°

| | Weight % product [a] | |
Product	Experimental	Predicted
Biurea	37·3	36·6
Urazole	13·6	12·2
Urea	5·9	7·2
Cyanuric acid	11·1 ⎫	⎫
Cyamelide	4·5 ⎬ 19·2	⎬ 20·0
Isocyanic acid	3·6 ⎭	⎭
Nitrogen	16·0	15·9
Carbon monoxide	3·9	3·9
Total	95·8	95·8

[a] Relative to AC.

Effect of Temperature.—The slow polymerisation of isocyanic acid made it difficult to analyse quantitatively for the gaseous products, and for this reason only the variation of the solid products with temperature was investigated. The results are shown in Table 2.

TABLE 2

Variation of the solid products with temperature

		Weight % product [a]				
$T/°C$	$t/\min$	Biurea	Urazole	Urea	Cyanuric acid	Cyamelide
171·5	480	35·8	13·2	5·8	11·7	4·9
177·0	360	38·9	13·9	6·7	10·1	4·4
182·0	180	36·7	16·8	7·9	11·2	1·4
187·0	150	16·8	20·8	14·5	13·7	1·0
191·5	150	16·2	24·4	14·7	13·4	0·7

[a] Relative to AC.

Isocyanic acid is known to polymerise to form cyanuric acid and cyamelide, with the proportion of cyamelide decreasing as the temperature is raised.[11] Table 2 shows that the percentage of cyanuric acid increases with temperature while that of cyamelide decreases. It seems reasonable to conclude that both cyanuric acid

and cyamelide are secondary products formed as a result of the polymerisation of isocyanic acid.

Urazole Formation.—It will be observed in Table 2 that at the higher temperatures the percentage of urazole increases while that of biurea decreases. Biurea is known to decompose into urazole and ammonia at 180° and at lower temperatures in the presence of gaseous hydrogen chloride.[12] In an attempt to ascertain whether urazole is solely a secondary product arising entirely as a result of biurea decomposition, the amounts of the four water-soluble products were determined as a function of time at two temperatures. The results are shown in Table 3.

TABLE 3

Variations of the water soluble products with time

	Weight % product [a]			
$t/\min$	Biurea	Urazole	Urea	Cyanuric acid
		171·5°		
15		1·1		
30	2·0	1·7	0·7	0·4
45		2·0		1·7
60	5·0	2·7	1·9	2·2
75		3·1		3·1
90	12·1	3·9	3·1	3·5
105		4·6		4·2
120	15·4	5·2	4·1	4·4
180	23·8	8·8	4·9	8·4
240	31·8	10·7	5·1	9·8
360	34·7	12·6	5·9	11·6
480	35·8	13·2	5·8	11·7
		191·5°		
10	3·3	0·8	0·8	2·4
20	19·4	4·2	2·4	8·0
40	33·2	8·6	5·2	11·9
60	30·2	10·8	7·4	14·6
80	28·9	11·5	8·4	15·1
100	27·8	11·6	9·1	16·5
120	27·3	12·2	9·7	15·1
135	24·7	15·2	11·4	15·7
180	23·0	18·0	11·1	14·0
300	14·3	22·9	12·8	14·6
420	12·7	26·1	13·3	13·7

[a] Relative to AC.

At both temperatures urazole is formed at the very start of the reaction and at 171·5° as the reaction nears completion, no decrease occurs in the amount of biurea, as would be expected if the latter were decomposing into urazole and ammonia.

At 191·5°, however, prolonged heating beyond the time (40 min) at which the initial reaction is virtually complete, does result in a decrease in the quantity of biurea and a corresponding increase in the amount of urazole. I.r. spectra of the gaseous products after heating AC for 420 min at 191·5° revealed the presence of carbon monoxide and ammonia, and the absence of isocyanic acid. It is clear that at 191·5° a slow secondary reaction does occur in which biurea decomposes into urazole and ammonia. Sufficient ammonia is formed to convert all the isocyanic acid in the gas phase into urea and leave an excess of ammonia.
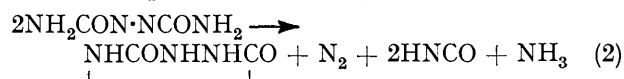
[9] J. Walker and J. K. Wood, *J. Chem. Soc.*, 1900, **77**, 21.
[10] R. A. Reed, ' The Chemistry of Modern Blowing Agents,' Plastics Progress,' Iliffe and Sons, London, 1955.
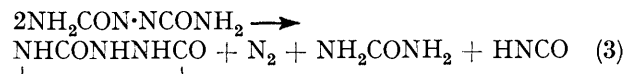
[11] E. A. Werner and W. R. Fearon, *J. Chem. Soc.*, 1920, **117**, 1356.
[12] J. Thiele and O. Stange, *Annalen*, 1894, **283**, 1.

However this secondary reaction cannot at either temperature account for the urazole formed initially, and it appears that this urazole is a primary product formed directly from AC and not from biurea. The evidence therefore points to two primary processes (1) and (2) occurring concurrently. An alternative

$$2NH_2CON\cdot NCONH_2 \longrightarrow$$
$$NH_2CONH\cdot NHCONH_2 + N_2 + 2HNCO \quad (1)$$

$$2NH_2CON\cdot NCONH_2 \longrightarrow$$
$$NHCONHNHCO + N_2 + 2HNCO + NH_3 \quad (2)$$

to reaction (2) is (3) but at the temperature at which

$$2NH_2CON\cdot NCONH_2 \longrightarrow$$
$$NHCONHNHCO + N_2 + NH_2CONH_2 + HNCO \quad (3)$$

AC decomposes, urea itself is unstable and dissociates to form ammonia and isocyanic acid [13] [reaction (4)].

$$NH_2CONH_2 \longrightarrow NH_3 + HNCO \quad (4)$$
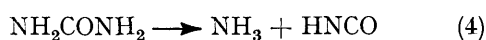
It is impossible, therefore, to distinguish between reaction (2) and the combination of reactions (3) and (4). The urea determined experimentally undoubtedly results from the recombination of ammonia and isocyanic acid in the cooler parts of the reaction tube [reaction (5)].

$$NH_3 + HNCO \longrightarrow \begin{array}{l} NH_4NCO \\ \downarrow \\ NH_2CONH_2 \end{array} \quad (5)$$
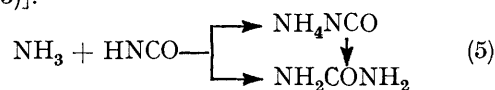
Carbon Monoxide Formation.—G.l.c. analysis of the gas evolved when AC was decomposed between 166·5 and 183° showed that at the very start of the reaction little carbon monoxide was formed and the nitrogen to carbon monoxide ratio was $>15:1$. But by the time 10% decomposition had occurred the rate of carbon monoxide formation relative to the rate of nitrogen formation had reached a maximum and the nitrogen to carbon monoxide ratio had fallen to $<3:1$. For the remaining 90% of the decomposition the rate of carbon monoxide formation fell relative to that of nitrogen formation slightly but steadily and the nitrogen to carbon monoxide ratio increased again to a final value close to $4:1$. Careful examination of Figure 7 of ref. 2 shows very similar variation of the nitrogen to carbon monoxide ratio with time at 186°.

These observations are explained if the carbon monoxide is formed as a result of the reduction of isocyanic acid by undecomposed AC [reaction (6)]. As a result

$$NH_2CON\cdot NCONH_2 + 2HNCO \longrightarrow$$
$$NH_2CONH\cdot NHCONH_2 + N_2 + 2CO \quad (6)$$

of being produced by this secondary process, carbon monoxide does not appear initially but only once appreciable isocyanic acid has been formed. Reaction (6) competes with the polymerisation of isocyanic acid to form cyanuric acid and cyamelide. As the AC decomposition proceeds, depletion of unchanged AC shifts the balance away from carbon monoxide formation and towards polymer formation so that less

carbon monoxide is formed per molecule of AC decomposed by reactions (1) and (2). Since the bulk of the nitrogen is formed by reactions (1) and (2), a steady fall occurs in the rate of carbon monoxide formation relative to that of nitrogen formation over the last 90% of the decomposition.

Relative Importance of Different Reactions.—If reactions (1), (2), (5), and (6), together with the polymerisation of isocyanic acid, are the only ones occurring, an equality should exist between the number of moles of nitrogen formed and the sum of the moles of biurea and of urazole formed. Examination of the experimental data in Table 1 reveals that the molar quantity of nitrogen formed is in fact larger than the sum of the molar quantities of biurea and urazole. This may be due to experimental error or may indicate that a small
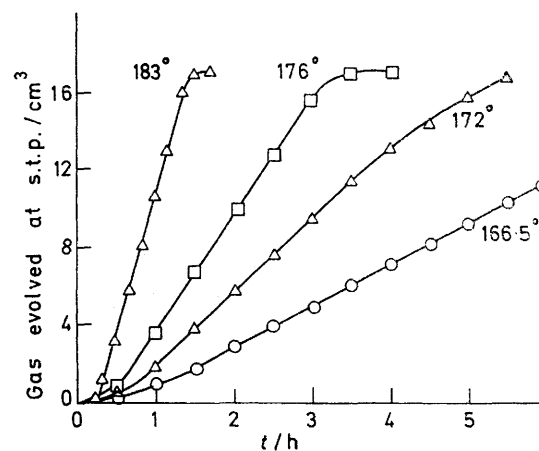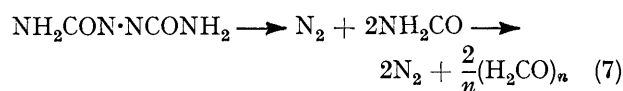

FIGURE 1   Gas evolution–time curves for the composition of AC (0·1 g) at various temperatures

percentage of AC decomposes to give nitrogen without biurea or urazole by a reaction such as (7).

$$NH_2CON\cdot NCONH_2 \longrightarrow N_2 + 2NH_2CO \longrightarrow$$
$$2N_2 + \frac{2}{n}(H_2CO)_n \quad (7)$$

If at 171·5°, 56% AC reacts by reaction (1), 28% by reaction (2), 8% by reaction (6), and 8% by reaction (7), and all the ammonia formed in (2) reacts by (5), the percentages of the products formed would be expected to be those shown in the right hand column of Table 1. The values are in reasonable agreement with the experimental percentages.

Thus reactions (1) and (2) appear to be the major primary reactions by which AC decomposes with (1) occurring twice as frequently as (2) at 171·5°. The important secondary reactions all stem from the reactivity of the isocyanic acid formed in (1) and (2), most of which polymerises, or combines with ammonia, or reacts with AC.

Kinetics.—Gas evolution–time curves for the decomposition of AC at four temperatures between 166·5 and 183° are shown in Figure 1. It will be seen that the

[13] F. J. Schiltknecht, Doctoral Dissertation, Eidgenossische Technische Hochschule, Zurich, 1963.

curves are S shaped and are characterised by long linear centre portions corresponding to almost constant rates of decomposition. A plot of the logarithms of the slopes of these linear portions against the reciprocal of the absolute temperature is found to be linear and leads to a value of 228 kJ mol^{-1} for the activation energy of the main part of the reaction. This is appreciably greater than the value of 161 kJ mol^{-1} obtained by Waki and Yamashita [2] over a slightly higher and narrower temperature range (181·5—197·3°).

will be seen that urazole and ammonia formation [reaction (2)] demand rather more atomic and molecular rearrangement than biurea formation [reaction (1)] which is probably why (2) occurs less readily than (1).

Comparison with Decomposition in Solution.—The kinetics and mechanism of the decomposition of AC in solution [16] are very different from those reported here for the solid state decomposition. In solution AC decomposes *via* isomerisation from the *trans*- to the *cis*-form. Such a decomposition pathway is blocked
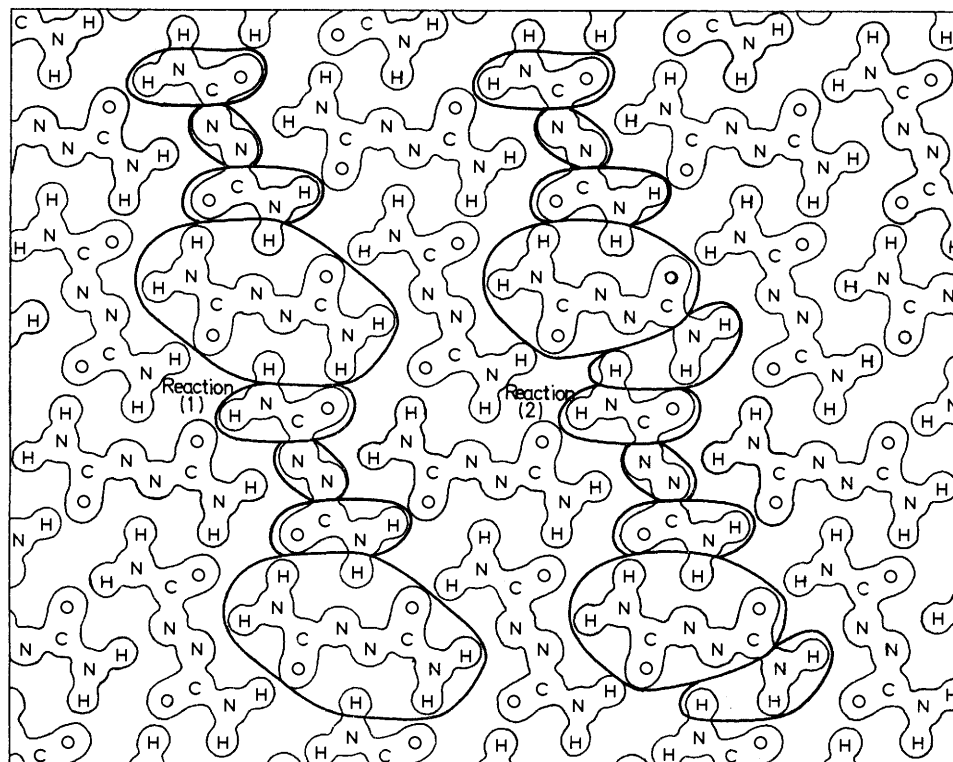

FIGURE 2   Arrangement of AC molecules in a single sheet and showing how reactions (1) and (2) may occur

The crystal structure of AC has been shown by Bryden [14] to be monoclinic. The molecules lie in sheets with each molecule hydrogen bonded to four neighbouring molecules as shown in Figure 2. The constancy of the rate of decomposition over the major part of the reaction suggests that the propagation of the decomposition through the lattice is a one-dimensional process.[15] The way in which this could occur within a given sheet and lead to decomposition according to reactions (1) and (2) is indicated in Figure 2. It

in the solid state because of the way the molecules are arranged and held in the *trans*-configuration in the crystal lattice as shown in Figure 2. Decomposition therefore occurs *via* alternative pathways [reactions (1) and (2)] and entirely different kinetics and secondary reactions result.

[14] J. Bryden, *Acta Cryst.,* 1961, **14**, 61.
[15] A. K. Galwey, ' Chemistry of Solids,' Chapman and Hall, London, 1967, p. 171.

[16] J. E. Herweh and R. M. Fantazier, *J. Org. Chem.,* 1974, **39**, 786; R. M. Fantazier and J. E. Herweh, *J. Amer. Chem. Soc.,* 1974, **96**, 1187.