661. *The Thermal Decomposition of Oxamide.*

By F. M. Tayler and L. L. Bircumshaw.

The thermal decomposition of oxamide, to cyanogen and water, has been studied in the gas phase by use of a static gasometric method, over the temperature range 320—490°. The reaction was found to be of first order and the velocity constant can be expressed by the equation $k = 10^a e^{-b}$, where $a = 10{\cdot}25 \pm 0{\cdot}31$ and $b = (41{\cdot}38 \pm 0{\cdot}94)/\boldsymbol{R}T$. The influence of concentration, surface area of the reaction vessel, and of the presence of nitrogen, cyanogen, and water was examined. The presence of nitrogen gave unusual effects.

From a study of the thermal decomposition of oxamide it was hoped to obtain information on the relative ratio of decomposition in the solid and in the gas phase. Experiment showed, however, that oxamide undergoes a polycondensation in the solid phase and that in the gas phase the decomposition was a simple dissociation into cyanogen and water.

Oxamide has a rather high melting point, 417°, and despite its polar groups it is only very slightly soluble in water. It usually forms a very fine crystalline powder and attempts to grow larger crystals tend to produce complicated branched growths. The crystals are triclinic and the structure has been examined by Misch and Van der Wyk [1] and Duke.[2] The molecules lie flat in parallel planes; in each plane the molecules are linked directly to each of their near neighbours by strong hydrogen bonds to form an infinite sheet—also strong bonding of an undefined type exists between the planes. This strong hydrogen bonding gives great cohesion in the lattice plane and would explain oxamide's high m. p., low solubility in water, and high density. The existence of intermolecular hydrogen bonding is also demonstrated by the Raman spectrum of crystalline oxamide. The band due to the N–H frequencies is at 3141 cm.$^{-1}$ and indicates strong hydrogen bonding of the C=O group and the N–H group in the *cis*-position relative to the C–N bond.

Werner and Carpenter [3] reported that when oxamide is heated to a temperature just sufficient to ensure complete volatilisation, a sublimate of ammonium cyanate, urea, and biuret is formed and ammonia, water, carbon monoxide, and hydrogen cyanide are evolved. The experimental evidence is, however, not very detailed. These authors were hoping to check the results of Williamson [4] who obtained urea by heating oxamide with mercuric oxide. This they were unable to do although they obtained urea by heating oxamide alone.

Experimental

Purification and Analysis of the Oxamide.—The material was obtained from the Ministry of Supply: it all passed through a B.S.S. 200-mesh sieve (13·5 microns), and 90% passed through a 240-mesh sieve (10 microns), this grade being used in the experiments. By the *p*-nitrobenzenediazonium chloride colour test, the material was found to contain 0·2% of ammonium ion. After two crystallisations from water this figure was reduced to 0·001%, and this product was used. The total nitrogen in the oxamide was estimated by the Kjeldahl–Gunning method, and the purity found to be 100·02 ± 0·03%.

Preliminary experiments showed that the only products of thermal decomposition were cyanogen and water. This was confirmed quantitatively. 0·5 G. samples of the oxamide were accurately weighed into a glass boat placed in the reaction tube between two gauzes. A slow stream of nitrogen was passed through the tube, and the gauzes, heated by two burners, were moved forward until the whole of the oxamide and any products of the decomposition were forced over into a U-trap cooled by liquid air. The operation took about 15 min. and the temperature of the nitrogen reached about 350°. An electrostatic precipitator was included in the system to deal with a certain amount of " smoke " which oxamide easily forms. The precipitator was then removed and a spiral absorber containing N/20-sodium hydroxide solution coupled to the trap. The nitrogen flow was adjusted so that a steady stream of bubbles passed up the spiral.

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[1] Misch and Van der Wyk, *Compt. Rend. Soc. Phys. Hist. Nat. Geneve*, 1938, **55**, 97.

[2] Ayerst and Duke, *Acta Cryst.*, 1954, **7**, 588.

[3] Werner and Carpenter, *J.*, 1918, **113**, 699.

[4] Williamson, Mémoire, Congrès Scientif. de Venise, 1847.

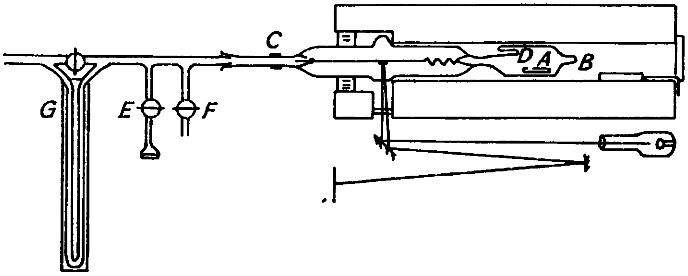
The liquid air around the trap was removed and replaced by a beaker of water; long white crystals of cyanogen could then be seen. These crystals were quickly absorbed in the alkali. Cyanogen was estimated by conductometric titration of the cyanate–cyanide with silver nitrate, Ripan-Tilici's method[5] being used. It was necessary to adjust the pH of the solution to 9·90 ± 0·02 with nitric acid before titration. The presence of any ions capable of reacting with silver nitrate masked the three breaks in the conductivity curve. In all titrations the breaks in the conductivity curve occurred at $\frac{1}{4}$ equiv. ($\frac{1}{2}$ cyanide), $\frac{1}{2}$ equiv. (total cyanide), and equiv. (total cyanide and cyanate), showing that only cyanogen was present in the gases. The oxamide in the U-tube and precipitator was estimated by determining the nitrogen content (Kjeldahl–Gunning method) of the solid collected. The analytical results are given in Table 1. The standard error of these results is 0·3% of the decomposed material and we may assume that the dehydration reaction represents the decomposition of oxamide under these conditions.

TABLE 1.

Oxamide taken (g.)	C_2N_2 found (g.)	Oxamide eq. to C_2N_2 (g.)	Oxamide found (g.)	Total oxamide (g.)	Proportion (%) Decomposed	Not decomp.	Total
0·5007	0·0142	0·0238	0·4769	0·5007	4·75	95·25	100·00
0·4999	0·0338	0·0572	0·4426	0·4998	11·45	88·53	99·98
0·5002	0·0090	0·0152	0·4853	0·5005	3·04	97·0	100·02

The kinetics of the reaction was studied by measuring the pressure rise in a sealed Pyrex glass vessel by means of a glass-spiral gauge used as a null-point instrument; air was admitted to a compensation chamber to balance the pressure due to the reactants, the pressure being read on a mercury manometer. This method was used because oxamide sublimes very readily, making it necessary to have the reaction vessel at one constant temperature with the gauge very slightly hotter. The apparatus is shown diagramatically in Fig. 1. The oxamide (6—15 mg.) was weighed into the small tube *A* and this was dropped down the side tube into the reaction vessel. The tube *A* was sealed at both ends, having a small hole in one side through which the oxamide was introduced. The reaction vessel was evacuated and sealed off at the constriction *B*. The compensation chamber was then evacuated, and the oven brought to the correct temperature. An old reaction vessel and gauge were kept inside the oven between experiments so that the correct temperature distribution could be maintained. The oven had an automatic temperature-control device.

FIG. 1.



One minute before the start of an experiment the oven current was raised to a maximum and then the disused gauge was removed. The oven was moved over the reaction vessel until the window flange of the gauge touched the " step " inside the furnace tube. The gauge unit was rotated until the light spot was on the scale zero, and the unit was then firmly clamped, at *C*, to the oven trolley. During the initial period of the reaction, the temperature of the vessel was measured with a thermocouple placed at *D*. When the reaction tube was within 5° of the experimental temperature, the oven heating voltage was decreased to its normal value, and the automatic temperature control allowed to function normally. At intervals air was " leaked " into the compensation chamber to bring the light spot back to zero and the pressure was read. Considerable control of this operation was obtained by admitting the air through a sintered-glass filter stick. If the pressure in the reaction vessel exceeded atmospheric, air could be blown in through the tap *F*. At the end of each experiment the gauge unit was opened by cracking

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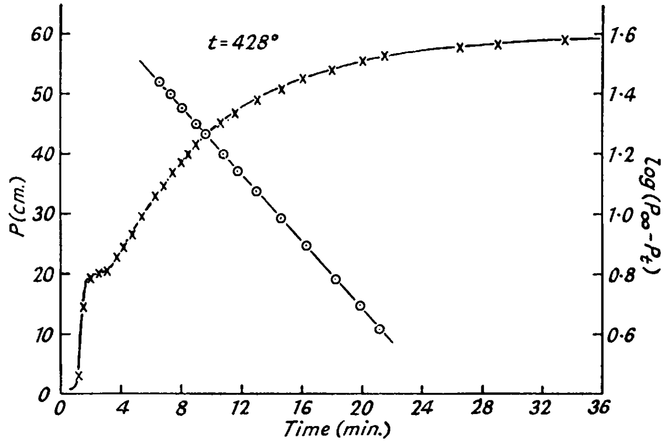
[5] Ripan-Tilici, *Z. anal. Chem.*, 1934, **99**, 415.

the end of the tube at B. In a few experiments the decomposition was carried out in an atmosphere of added inert gas; the appropriate pressure was then " leaked " into the apparatus from a storage bulb just before sealing off.

The quantity of oxamide used was usually adjusted to give a final pressure of 40—60 cm. in the 22 c.c. reaction vessel, which was found to be a suitable range for the instrument. The gauges were rather susceptible to vibration, but this was avoided by mounting the whole oven assembly on large pieces of sponge rubber. The mirror on the spiral gauge was front-silvered with aluminium by vacuum sputtering and attached to the glass spindles by fireclay cement. The time taken for the gauge unit to reach the experimental temperature was usually about 3—4 min.

An oven with a rather unusual temperature distribution was required to prevent the oxamide subliming into the spiral, which was kept a little hotter than the reaction vessel. A tubular furnace which completely enclosed the reaction vessel and gauge was constructed. The movements of the mirror were observed through a small window cemented into the side. The oven was 18 in. long with a diameter of 1·5 in. and 3 in. diameter for 3 in. from the window outwards. On this tube was laid a winding of 150 ft. of 24-gauge " Brightway " wire after the core had first been insulated with a layer of refractory cement. On top of this winding, two supplementary heaters were placed, one of 22 ft. 24-gauge over 3 in. inwards from the step, and the other 9 ft. over 2 in. at the narrow end of the tube, each winding being separate. The oven was assembled on a trolley which ran on rails so that the oven could be run over the reaction vessel at the beginning of an experiment.

FIG. 2.



The furnace was controlled by a Sunvic platinum-resistance thermometer controller type R.T.I. The platinum-resistance thermometer was placed inside the narrow end of the furnace tube. With this arrangement the furnace took 2—3 min. to reach the temperature of the experiment and then remained constant to within ±0·05°.

Experiments showed that the oxamide decomposed with a measurable velocity over the temperature range 320—490° at initial pressure of between 14 and 30 cm. In the first minute, as the reaction vessel warmed, there was no pressure rise, but suddenly the pressure increased to that equivalent to the oxamide present; it then steadied for a while but rose again as the vessel reached the reaction temperature, and then rose smoothly to reach a final value of three times the pressure of the original oxamide. The measured values of this final pressure P_∞ were within 2% of the theoretical value. There was very little formation of paracyanogen, the walls of the reaction vessel becoming slightly discoloured after 10—15 experiments.

The reaction followed a first-order law and a plot of 2·303 log $(P_\infty - P_t)$ against time gave satisfactory straight lines. One is shown for 428° in Fig. 2. For the determination of these first-order constants, however, Guggenheim's method[6] was used, in which t is plotted against log $(P_{t+\tau} - P_t)$, τ being a constant time interval greater than the half-life of the decomposing substance.

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[6] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

Influence of Temperature.—The decomposition was followed in the temperature range 300—500° and found to be of first order over the whole range. In Fig. 3 are shown the pressure-time curve and the plot of log $(P_{t+\tau} - P_t)$ against time for 425°. In Fig. 4 $\log_{10} k$ is plotted against $1/T$, and from this graph are calculated the following values: $\log_{10} A = 10{\cdot}25 \pm 0{\cdot}31$, $E = 41{\cdot}38 \pm 0{\cdot}94$ kcal.

Influence of Concentration.—Over the limited initial pressure range of 14—30 cm. the value of the rate constant is unaltered. Owing to experimental difficulties, final pressures measured had to be kept below 90 cm., and final pressures below 40 cm. meant that the errors in reading the pressures became rather large. In Table 2 are given the velocity constants at 405°, the standard deviation being ±1·3%, well below the overall experimental accuracy of ±4%. Velocity constants at 428° are also shown.

FIG. 3.

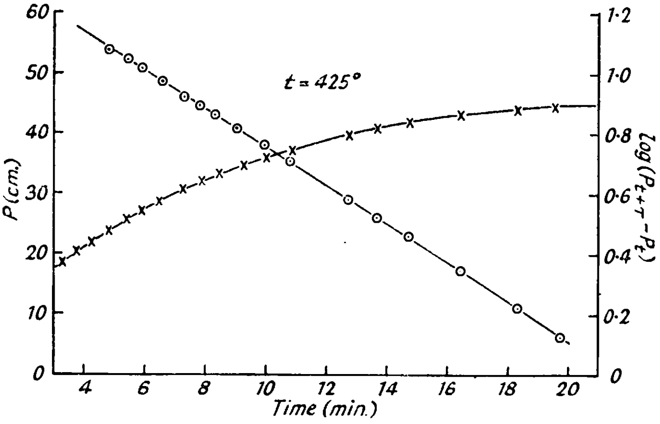


FIG. 4.

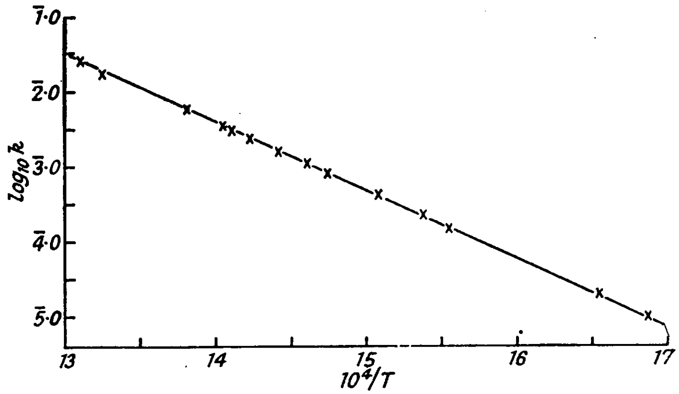


TABLE 2.

	At 405°						At 428°		
Initial oxamide press. (cm.)	16·1	19·3	21·2	21·8	25·8	26·8	13·9	20·0	23·9
$10^6 k$ (sec.$^{-1}$)	767	779	793	790	770	767	219	230	222

Effect of Increased Area of the Reaction Vessel.—A number of runs were made in which the surface area of the reaction vessel was increased by " packing " it with thin-walled Pyrex glass tubing of 1 mm. diameter. The increase in surface area was about four times that of the original area. Values of the velocity constants at various temperatures for the packed reaction vessel are given in Table 3, corresponding results in unpacked vessels being given in parentheses.

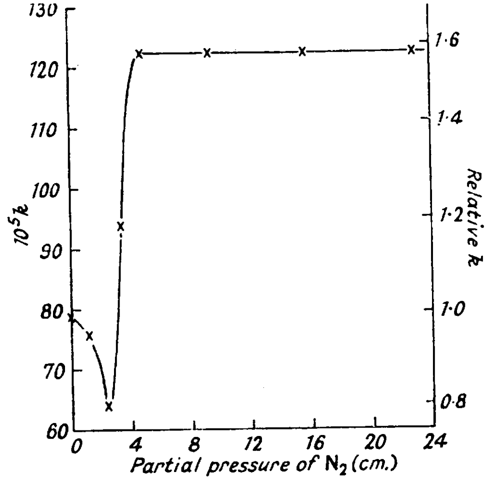
It will be seen that the velocity of the reaction over this range of temperature is unaffected by the ratio of surface to area of the reaction vessel.

TABLE 3.

Temp.	436°	430°	390°	377°	320°
10^5k (sec.$^{-1}$)	334 (333)	275 (242)	39 (39)	21 (21)	1 (1)

Effect of Added Gases.—The effect of nitrogen was first studied. It was introduced into the reaction vessel at pressures from 1·0 to 23·0 cm., the temperature of the experiment being 407° and the partial pressure of the oxamide being 20 cm. (All pressures measured at 407°.) The results are shown graphically in Fig. 5. The reaction remains of first order kinetically; excellent plots of log $(P_{t+\tau} - P_t)$ against time are obtained, and it is seen that small pressures of nitrogen lower the reaction rate slightly but larger pressures increase it appreciably. Above a certain pressure, *ca.* 4·5 cm., the rate becomes practically independent of the nitrogen pressure.

FIG. 5.



The effect of cyanogen up to partial pressures of 28 cm. was studied, the temperature and partial pressure of oxamide being as above. The results are given in Table 4. At the lower pressures cyanogen had no effect, but pressures of 20 cm. or more reduced the rate to a small extent. The reaction remained strictly of first order. Had the reverse reaction $C_2N_2 + 2H_2O \rightleftarrows (CO{\cdot}NH_2)_2$ occurred to a measurable extent the values of the function $P_{t+\tau}$ would be less than expected. The values of $(P_{t+\tau} - P_t)$ would also be lower than the expected figures and so the gradient of the plot of log $(P_{t+\tau} - P_t)$ against time would be steepened, the gradient increase becoming more noticeable as the experiment continued. This effect was not observed, so the reverse reaction was presumed not to occur.

TABLE 4.

Cyanogen pressure (cm.)	0·0	2·3	7·25	14·8	20·6	28·25
10^5k (sec.$^{-1}$)	79	79	79	79	53	57

Water vapour was studied up to a pressure of 18 cm., with the following results:

H_2O pressure (cm.)	0·0	2·3	18·4
k (sec.$^{-1}$)	0·00079	0·00079	0·00079

From these, it is assumed that under the experimental conditions outlined the addition of the products of the decomposition has little effect on the course of the reaction.

Discussion.—There is much evidence to show that many first-order gas-phase pyrolysis reactions have free-radical mechanisms, but there is little evidence to show that such a mechanism applies here. The usual tests for thermal free-radical reactions could not be applied since the gases would react with cyanogen.

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[7] Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25.

The decomposition of oxamide is apparently homogeneous, so that any chain mechanism would involve radical chains in which chain formation and termination both occur only in the gas phase or only on the walls of the reaction vessel.[7] The presence of nitrogen in the reaction vessel might be expected to increase the reaction rate with a chain mechanism, since the additional collisions would increase the effective length of the chain. The effect is observed to some extent. Nitrogen could only increase the rate if termination was on the walls, any chain mechanism must therefore involve wall initiation and termination only.

There is no obvious possible radical-chain mechanism for the decomposition of oxamide. The low value, $10^{10 \cdot 25}$, of the temperature-independent factor suggests that the rate-controlling step does not involve the breaking of a single bond to give radicals which normally requires a factor of 10^{13}.

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