228. *The Heat of Nitrolysis of Hexamine in Nitric Acid.*

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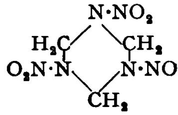
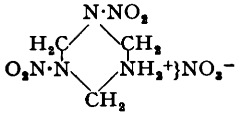
When hexamine is added to concentrated nitric acid, comparison of the rate of heat evolution with the rate of production of cyclonite (I) indicates the presence of an intermediate in the reaction. Nitrolysis with formation of two nitramino-groups occurs rapidly and the slow step is the conversion of this intermediate into cyclonite.

THE final product of the action of nitric acid on hexamine or its dinitrate at 0° is 1 : 3 : 5-trinitro-1 : 3 : 5-triaza*cyclo*hexane (hexahydro-1 : 3 : 5-trinitro-*s*-triazine; cyclonite; RDX) (I) (Henning, G.P. 104 280/1899; Herz, U.S.P. 1 402 695/1922; Hale, *J. Amer. Chem. Soc.*, 1925, **47**, 2754). At the time our investigations were carried out, no products other than (I) had been isolated from the nitrolysis mixture and no kinetic study of the reaction had been reported. By following the rates at which heat was evolved and supplementing these with rates at which (I) was produced, some insight into the mechanism of the reaction was obtained. A brief reference to the present results has already been made by Lamberton (*Quart. Reviews*, 1951, **5**, 95).

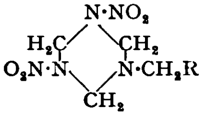
It was by no means certain at the time that hexamine and hexamine dinitrate followed the same reaction course, so hexamine was chosen for the rate studies, despite the disadvantage that a large temperature rise took place on its addition to nitric acid. In order to minimize this and the possible effects of reaction products (*e.g.*, water) on the rates, systems with the smallest practicable ratio of hexamine to nitric acid were studied. A lower limit on this ratio is placed by difficulties in the quantitative isolation of (I) from the mixture, which increase the smaller the ratio.



(I)



(II)



(III)

$$NO_2{\cdot}NH{\cdot}CH_2{\cdot}N(NO_2){\cdot}CH_2{\cdot}NH_2,HNO_3$$

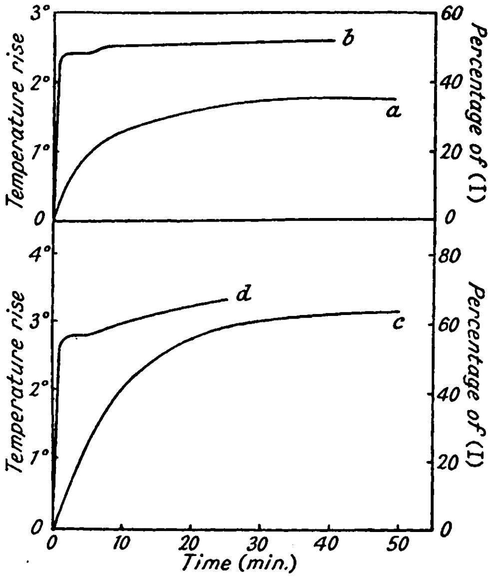
(IV)

Results.—Rate of production of (I). The rates of formation of (I) are rapid at 20°, but become slower as the temperature and the concentration of acid are decreased. Fig. 1(*a*) shows the rate at which (I) is produced in 85% acid at 20°. Fig. 2 shows how the rate depends on acid concentration at 0°, and Fig. 3 how the rate is altered by the presence of potassium nitrate in 99·6% acid at —35·5°.

Rate of heat evolution. On addition of hexamine to nitrous-free nitric acid (80—100%), evolution of heat took place in two stages: a rapid evolution complete in less than one minute, followed by a slower evolution complete in times ranging from 5 minutes for 100% acid to one hour for 85% acid. The turning point, marking the end of the first rapid evolution, was readily identifiable for 99% and weaker acids. For any particular acid concentration, the turning point became more distinct as the temperature was reduced until, at —35·5°, the second stage was completely suppressed and only the first stage remained. Fig. 4 shows some typical examples for 20°, 0°, and —35·5°.

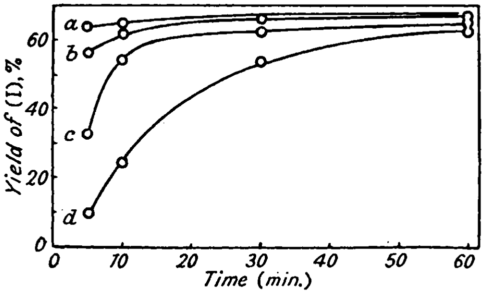
The amount of heat evolved at —35·5° per mole of hexamine in the first stage has been plotted against the acid concentration in Fig 5(*b*). A similar plot for 20° is not so curved

FIG. 1.



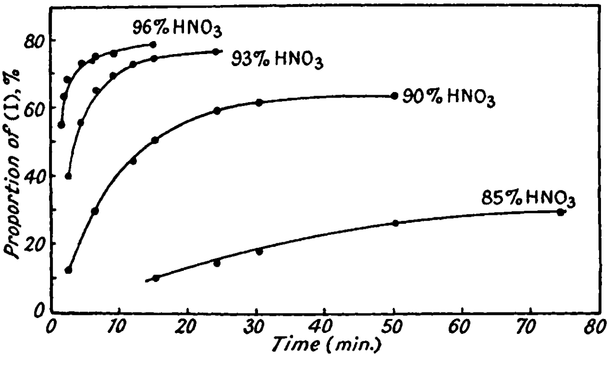
(*a*) *Rate of production of* (I) *in* 85% HNO_3 *at* 20°;
(*b*) *temperature rise in* 85% HNO_3 *at* 20°;
(*c*) *rate of production of* (I) *in* 90% HNO_3 *at* 0°;
(*d*) *temperature rise in* 90% HNO_3 *at* 0°.

FIG. 3. *Yield of* (I) *as a function of time* (*not corrected for solubility*) *in* 99·6% *acid at* —35·5°.



(*a*) *No added* KNO_3; (*b*) 5% KNO_3 *added*; (*c*) 10% KNO_3 *added*; (*d*) 15% KNO_3 *added.*

FIG. 2. *Rates of production of* (I) *in* 96%, 93%, 90%, *and* 85% HNO_3 *at* 0°.

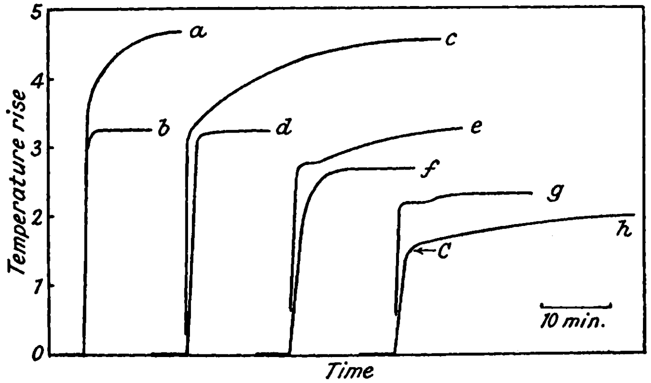


and is almost a straight line. On use of hexamine dinitrate, a curve [Fig. 5(*c*)] is obtained, which lies parallel to that for hexamine.

The total heat evolved in the first and second stages together at 20° is shown in Fig. 5(*a*).

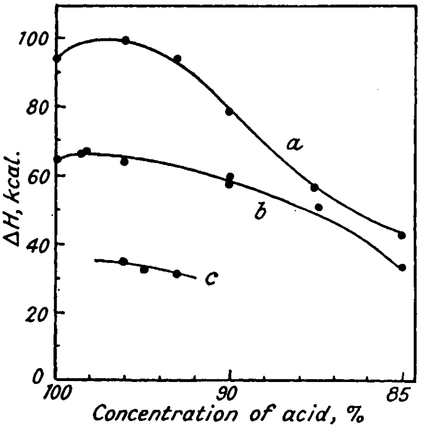
Discussion.—Comparison of the rates of heat evolution and of the production of (I) (Fig. 1) shows that the latter is not associated with the first stage: this stage must indicate the formation of a precursor of (I), and Fig. 1 suggests the conditions favourable to the isolation of this precursor. Experiments directed to the isolation and characterisation of the precursor have already been reported (Vroom and Winkler, *Canadian J. Res.*, 1950, **28,** 701; Dunning and Dunning, *J.*, 1950, 2920, 2925, 2928; Burman, Meen, and Wright, *Canadian J. Chem.*, 1951, **29,** 767). Vroom and Winkler have isolated 3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane nitrate (II) and Dunning and Dunning have isolated a series of compounds, *e.g.*, 1-ethoxymethyl-3 : 5-dinitro-1 : 3 : 5-triaza*cyclo*hexane (III; R = OEt) from the reaction mixture. These observations, together with the rate of heat evolution, indicate that the nitrolysis of hexamine to form a precursor with a ring containing two nitramino-groups and one amino-group, occurs rapidly. The slow step in the kinetics is the formation of the third nitramino-group giving (I).

FIG. 4. *Temperature rise as a function of time when hexamine is added to nitric acid.*



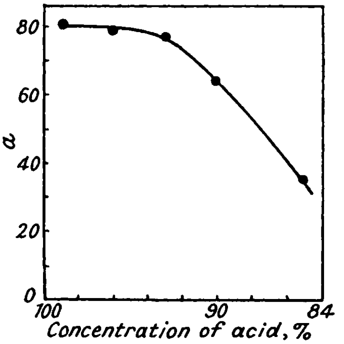
(*a*) 100% *Acid at* 20°; (*b*) 100% *acid at* —35·5°; (*c*) 96% *acid at* 20°; (*d*) 96% *acid at* —35·5°; (*e*) 90% *acid at* 0°; (*f*) 90% *acid at* —35·5°; (*g*) 85% *acid at* 20°; (*h*) 85% *acid at* —35·5°.

FIG. 5.



(*a*) *Total heat evolved per mole of hexamine at* 20° *as a function of acid concentration*; (*b*) *heat evolved in first stage at* —35·5° (*hexamine*); (*c*) *heat evolved in first stage at* —35·5° *for hexamine dinitrate.*

FIG. 6. *Value of* a *as a function of acid concentration.*



At —35·5° in 85% acid, the first stage of the heat evolution has itself become slower [Fig. 4(*h*)] and there is some indication of a resolution into a still earlier reaction. The amount of heat evolved in this earlier reaction (to point *C* in Fig. 4) is *ca.* 29 kcal., which is sufficiently close to the heat of formation of the dinitrate from hexamine and nitric acid (31 kcal.) to suggest that this earlier reaction is the formation of hexamine dinitrate in solution.

Our results indicate that the production x of (I) at 0° in 96, 93, 90, and 85% acids can be expressed empirically as a function of the time t by

$$x = a(1 - e^{-t/\tau}) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where a and τ are constants depending on the strength of the acid (see table). Such an expression would result if the precursor were formed in amount a and underwent a first-order reaction to (I), or if the precursor were formed in constant yield (*ca.* 100%) and underwent first-order reactions, not only to (I), but to by-products A, B . . . as well :

Rate of production of (I)

Acid strength : Time, min.	99%	96%	93%	90%	85%
1·5	—	55·7	—	—	—
2·0	—	64·0	—	—	—
2·5	66·9	68·7	40·9	13·3	—
4·5	—	74·1	56·2	—	—
6·5	70·2	75·3	65·8	30·5	—
9·0	—	—	70·1	—	—
12·0	74·6	74·7	73·4	45·5	—
15·0	—	—	75·1	51·4	10·3
24·0	80·9	79·2	77·2	59·9	14·9
30·0	—	—	—	62·0	18·3
50·0	80·5	—	—	63·9	26·2
74·0	—	—	—	—	29·17
100·0	—	—	—	—	33·0
120·0	—	—	—	—	32·6
a	80·7	79·2	77·2	64·5	35·5
τ^{-1}	—	0·69	0·24	0·12	0·025
k_1	—	0·55	0·18	0·077	0·009

$$\text{Precursor} \begin{array}{l} \xrightarrow{k_1} \text{(I)} \\ \xrightarrow{k_2} \text{A} \\ \xrightarrow{k_3} \text{B} \end{array} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

The isolation of (IV) by Dunning and Dunning (*loc. cit.*) suggests that the by-products may be linear compounds. The heat evolved in the first stage shows a regular decrease with decreasing acid concentration (Fig. 5). This decrease could be explained as due to the varying heats of dilution of the acid with the reaction products, implying that the amount of precursor formed in each case is the same. On the other hand, the sharp decline in the value of a (Fig. 6) for acid concentrations between 90 and 85% suggest that in the lower acid strengths, some of the precursor is being destroyed by side reactions, giving products other than (I) (see 2).

If A is the amount of precursor initially formed and x, y, and z the amounts of (I), A, B, respectively, then

$$\begin{aligned} dx/dt &= k_1(A - x - y - z) \\ dy/dt &= k_2(A - x - y - z) \\ dz/dt &= k_3(A - x - y - z) \end{aligned}$$

whence

$$x = k_1A(1 - e^{-\Sigma kt})/\Sigma k \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Comparison of (3) with (1) gives Σk equal to τ^{-1}, and $k_1A/\Sigma k$ equal to a, from which k_1, the velocity constant for the conversion of precursor into (I), may be estimated (see table).

The following equilibria exist in nitric acid,

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

$$H_2O + HNO_3 \rightleftharpoons H_3O^+ + NO_3^-$$

and possibly

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$

(Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15; Gillespie, Hughes, and Ingold, *J.*, 1950, 2552; Ingold and Millen, *J.*, 1950, 2612). The addition of water or potassium nitrate would suppress the dissociation into NO_2^+ and $H_2NO_3^+$. If one or both of these ions were the active agents in the nitrolysis, this would account for the rapid diminution of k_1 with decreasing acid concentration and for the effect of potassium nitrate on the rate of production (see Fig. 3). Since the addition of a small quantity of sulphuric acid to the nitric acid results in a reduced yield of (I), this may indicate that $H_2NO_3^+$, and not NO_2^+, is the nitrolytic agent concerned in the production of (I), though the loss in yield may be due to hydrolytic side reactions, enhanced by an increase in H_3O^+.

EXPERIMENTAL

Heat Evolution.—A cylindrical Dewar vessel formed the calorimeter, the inner portion being made from very thin " calorimeter " glass. The width of the short neck was half that of the main part of the vessel. Two lengthwise strips were left unsilvered so that the time of dissolution and any gas evolution during the reaction could be observed. The vacuum jacket was baked out *in vacuo*, gettered with cooled charcoal, and sealed off. Radiation losses were minimized by completely immersing the stoppered calorimeter in suitable temperature baths (20°, 0°, −35·5°) contained in larger Dewar flasks. Changes of temperature were observed with a standardised thermometer, readable to 0·01°. Through the stopper passed a stirrer driven by a motor, a funnel for inserting the hexamine, and a small hand-stirrer. The latter was constructed of thin glass tubing, and through the bottom ran a spiral nichrome wire by means of which electrical energy could be introduced into the calorimeter. The calorimeter constant was determined at 20° and Miscenko's values (Landolt–Börnstein " Tabellen," IIb, p. 1657) for the specific heats of the various concentrations of nitric acid were used. At −35·5°, the thermal capacities of the calorimeter and of the acid contained in it were determined for each experiment.

The appropriate acid (150 c.c.) was pipetted into the calorimeter. When the temperature had reached constancy, hexamine (0·714 g.) or hexamine dinitrate (1·3566 g.) was dropped in. Temperature readings were taken every 10 seconds for 10 minutes and then at suitable intervals until the temperature was again stationary.

In the experiments at 20°, it was found that the second part of the heat evolution was sensitive to the nitrous acid content, though the first portion was not affected. The nitrous acid was destroyed by adding a small quantity of urea (0·6 g. per 200 g. of acid) to the acid and leaving the whole overnight; the results obtained were then reproducible and, for 96% and 85% concentrations, agreed with those obtained with carefully distilled and carefully diluted acids. The effect of nitrous acid at −35° was not noticeable, and treatment with urea was not necessary.

Rate of Production of (I).—In investigating the effect of acid concentration on rates, there are several points to consider. The nitrolysis produces water, besides other products, and this will affect the acid concentration in the later stages of the reaction. Prof. H. D. Springall and Dr. E. Roberts (private communication) have measured the amount of water produced by means of the Karl Fischer reagent and this corresponds to 3 moles of water per mole of hexamine. However, the rate of production of (I) is followed by diluting the acid and allowing (I) to crystallise. Some of (I) remains in solution and difficulties of quantitative isolation become serious if the hexamine : acid ratio is reduced too far. The ratio chosen was 1 : 100 (w/w); at this ratio, the water produced by the nitrolysis would decrease the acid concentration by 0·4%. The effect which the basic hexamine has upon the acid dissociation in the early stages is also reduced by choosing a low ratio. Further control tests on (I) showed that, over the periods of the nitrolyses, there was no significant destruction of (I) in the different acids.

A quantity of 99% acid was divided into about 30 portions of 200 g., each portion being used for a single measurement. The procedure is described for the 99% series and the 85% series. In the former, 99% acid (200 g.) was cooled to a predetermined extent below 0° and finely crushed hexamine (2 g.) was added at once to the vigorously stirred acid in a thin-walled flask; the temperature rose rapidly (<30 sec.) to 0°. The mixture was immediately placed in a thermostat at 0°, and after the appropriate time intervals, it was poured into water (1000 c.c.), and more water (200 c.c. exactly) added as washings from the reaction vessel. After being stirred, the diluted mixture was transferred to a thermostat at 20° and left for 24 hours. The crystalline precipitate was collected on a sintered filter and washed with 5 c.c. of ice-cold water. The filter was heated in an air-oven at 100°, cooled, the contents damped with water, and the filter reheated. After cooling, the contents were washed with 5 c.c. of ice-cold water. This procedure hydrolyses any linear compounds, but has no effect on (I). The filter was then weighed.

For the 85% series, the 99% acid (200 g.) was divided into two portions; one portion (170 g.) was diluted with water (30 g.) and used for the nitrolysis, the other (30 g.) being added to the water (1000 c.c.) to be used later as the diluent of the reaction mixture. The procedure was then the same as for the 99% acid. This method ensures that the concentration of the nitric acid in the resultant diluted reaction mixture is exactly the same for all the series of determinations and hence any correction for solubility of (I) in the diluted mixtures is always the same.

The solubility of (I) in the diluted mixture was determined by carrying through the procedure for the nitrolysis, but using (I) instead of hexamine, and determining the amount recovered. The loss was found to correspond to 7·0% on the yield.

The yields of (I) plus 7% constitute the amount produced; these are illustrated in Fig. 2. From the gradients of the curves, a value for the yield a at infinite time (zero rate) was obtained. By use of these final values of a, log $(a - x)$ was plotted against time and, for all acid concentrations except 99%, good straight lines were obtained, the gradients of which gave the time constant τ. The values of a and τ^{-1} are given in the table, and the curves drawn in Fig. 2 correspond to these values.

The authors are indebted to Dr. E. Roberts, of the Ministry of Supply, for many helpful discussions.

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[*Received, August* 31*st*, 1951.]