tion of a unit smaller than those which give rise to the ulmic acids, or, which appears less likely, by the breaking away of a portion of a large unit.

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The decomposition of nitroglycerin in its early stages over the temperature range 90–135° was examined in 1909 by R. Robertson who with an apparatus devised to avoid volatilization of the ester and to avoid catalytic effects by using a current of carbon dioxide, found by a spectrophotometric method of estimation that the nitrogen was liberated for the most part, if not entirely, as nitrogen tetroxide. The logarithm of the periodical liberation of the nitrogen plotted against temperature gave a straight line. By another experimental method in which also accumulation of the products of decomposition was avoided, Roginsky obtained similar decomposition rates and extended the range of measurement to 190°. From his data and those of Robertson he found that with rise in temperature both the frequency factor and activation energy in the Arrhenius equation for the decomposition rate tended slightly to rise. In the temperature range 125–190°, however, his results could be expressed with reasonable accuracy by the equation \( k = 3 \times 10^{20} e^{-48,000/RT} \), \( k \) being the unimolecular constant for the decomposition. Roginsky noted that the decomposition rate was not greatly altered by working in dilute solution, or by the addition of phenaanthrene, anthracene, acetonaphene, benzenophene and diphenylamine.

The behavior of liquid ammonium nitrate has been examined by several investigators. Saunders found that decomposition into nitrous oxide and water occurred to the extent of 98% from 210–260° at atmospheric pressure, and, with 40 g. of material, an explosive reaction was observed near 300° leading to the formation of nitrogen, nitric oxide and nitrogen dioxide. Shah and Oza have discussed chemical aspects of the decomposition. According to Veley the decomposition rate is increased by the addition of finely divided pumice, silica, graphite, barium sulphate, and glass. Here we describe some investigations of the decomposition of these two explosives and of two compounds related to them.

The thermal decomposition of pentaerythritol tetranitrate

This was examined in the glass apparatus and the copper cans apparatus described elsewhere. As with other high explosives rapid vaporization and distillation to the cooler parts of the vessel occurred in vacuo, but this could be prevented by having an inert gas present. Nitrogen and air were used at 5 cm., 10 cm. and 76 cm., the decomposition taking place at the same rate under these different conditions. The rate also remained unchanged with further recrystallization of the sample used from acetone. The pressure-time curves over the temperature range 161–233° showed a very nearly constant rate of gas evolution for about the first half of the decomposition, after which this rate diminished in accordance with the unimolecular equation. The rate constant \( k \) for the first stages of decomposition was found from the slope of the initial straight portion of the curve and the total pressure rise in the experiment. The temperature variation of \( k \) is shown in Fig. 1. Here only the results from the glass apparatus are plotted, these being considered more reliable than those obtained over the smaller temperature range 193–222° with the copper cans apparatus, which showed some scatter about the line of Fig. 1. The straight line fitted to the points was determined by the method of least squares and gave for the initial decomposition rate the expression \( k \) (sec. \(^{-1}\)) = 10\(^{19.8} \) e\(^{-47,000/RT} \). The experimental error in activation energy was estimated to be less than 1500 cal./mol.

The unimolecular constants for the final decomposition rates were two or three times greater than those for the initial decomposition, the ratio increasing slowly with temperature.

Decomposition in solution.—In view of the extremely large value of the Arrhenius frequency factor for the pure liquid, experiments were carried out with a 5% solution of pentaerythritol tetranitrate in dicyclohexyl phthalate. This solvent had the advantages of stability and low vapour pressure and of being a solid at room temperature. The solutions, after preparation at 140° in as short a time as possible (about one minute), were rapidly cooled and subsequently handled as a solid. The decomposition was examined over the temperature range 171–238°. The general shape of the pressure-time curves was the same as that for the pure liquid apart from small effects arising from the increased time elapsing before the attainment of thermal equilibrium (about 10 sec. for 50 mg. of the mixture) and from a slight initial pressure rise due to the vapour pressure of the phthalate. Deviations from linearity in the initial part of the pressure-time curve such as would be expected to arise through retention of an appreciable proportion of the liberated gas by supersaturation, as discussed by Pedersen and Richard-son and Bailey were not observed, and for 5% solutions the volume of gas formed was many times the volume of solution. It was therefore considered justifiable to determine the rate constant for the initial stages of the decomposition in solution from the pressure-time curves as before. A small but significant
divergence from the decomposition rate of the pure liquid was noted. Thus from the Arrhenius plots at 171°, \( k \) for the pure liquid was 0.00048 sec.\(^{-1}\) compared with 0.00050 sec.\(^{-1}\) for the 5% solution; whereas the respective values at 238° were 0.49 sec.\(^{-1}\) and 0.17 sec.\(^{-1}\). Fig. 2 shows the points obtained on plotting log \( k \) against \( 1/T \) for the 5% solution. Assuming the experimental activation energy to be constant over the temperature range investigated, the rate can be represented by the Arrhenius expression

\[
k = 10^{16.1} e^{-99,900/RT}
\]

The frequency factor for the decomposition of pentaerythritol tetranitrate in dilute solution is substantially less than that for the pure liquid. The experimental data are, however, not adequate to show to what extent the decomposition rate in dilute solution can be accurately represented by the unmodified Arrhenius equation.

![Figure 2. Decomposition of pentaerythritol tetranitrate in dicyclohexyl phthalate](image)

**Products of decomposition.**—The general method described before was used. Formaldehyde present in the gases pumped off at —80° was absorbed in phenylhydrazine acetate in 50% acetic acid solution, or removed by allowing the —80° fraction to stand overnight at —80° when the formaldehyde polymerized. Nitrogen peroxide was determined by reduction to nitrogen and traces of nitric oxide with copper at a bright red heat. On account of the presence of formaldehyde or other organic vapours the gas from this treatment also contained carbon monoxide and dioxide which had to be removed. From one mol. of pentaerythritol tetranitrate decomposed at 210° for 2 minutes with nitrogen initially present at 10 cm. the products shown in Table I were obtained, together with water and formaldehyde.

**Table I**

<table>
<thead>
<tr>
<th>Product</th>
<th>Initial Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_2 )</td>
<td>3.5 mg</td>
</tr>
<tr>
<td>( \text{NO} )</td>
<td>2.1 mg</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>0.2 mg</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>0.007 mg</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>0.93 mg</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>0.28 mg</td>
</tr>
</tbody>
</table>

If the heating of the reaction bulb was continued, the nitrogen peroxide gradually disappeared by a secondary reaction, the amounts of carbon monoxide and dioxide increasing. Experiments were therefore carried out in a nitrogen stream to determine the amount of nitrogen peroxide liberated by the primary decomposition. A special decomposition apparatus was used in which the purified nitrogen, first raised to the required temperature by passage through a spiral immersed in the heating bath was led into the decomposition bulb by a sealed-in tube terminating about 1 cm. above the explosive. The gaseous products were carried away in the nitrogen stream and collected in a liquid air trap. By this means about 1.5 mol. of nitrogen peroxide could be obtained by complete decomposition of one mol. of pentaerythritol tetranitrate at 190° with a flow rate of about 1 ml./sec. The rest of the nitrogen appeared mainly as nitric oxide and nitrous oxide as in the static experiments. The flow method was also used to confirm the formation of formaldehyde in the decomposition by formation of the dimedone derivative. These results are consistent with the view that the primary step in the decomposition is the direct splitting off from the molecule of \( \text{NO}_2 \) followed either by liberation of the \( -\text{CH}_2\text{O}^- \) residue as formaldehyde or its oxidation by a neighbouring \( \text{NO}_2 \) group, leaving an \( -\text{ONO}^- \) residue from which \( \text{NO} \) could separate directly. \( \text{NO}_2 \) and \( \text{N}_2 \) could then be formed by an interaction of two \( -\text{ONO}^- \) groups and a \( -\text{CH}_2\text{O}^- \) group. The formation of hydrogen could result from the direct breakdown of a \( -\text{CH}_2\text{O}^- \) residue.

### The decomposition of nitroglycerin

A few experiments were carried out with nitroglycerin at temperatures from 200°-255°, somewhat above the range covered by Roginsky. The glass reaction vessel was used with air or nitrogen present at 5 or 10 cm. pressure to diminish vaporization of the explosive. The nitroglycerin (a few mg.) was introduced into the bulb either in a thin glass capillary or on a small piece of platinum foil. The decomposition of those samples which did not explode followed the unimolecular equation, the rate constants being in agreement to within about 30% with those calculated from Roginsky's equation already quoted. The agreement was considered satisfactory in view of the probability of considerable decomposition taking place in the gaseous phase in these experiments.

### The decomposition of ethylenediamine dinitrate

This substance is of some interest in explosives technology on account of its formation of a eutectic with ammonium nitrate melting at 106°.\(^a\) The decomposition was examined in glass reaction bulbs. In \textit{vacuo} the explosive vaporized and condensed on the cooler parts of the apparatus before undergoing appreciable decomposition. This was prevented by nitrogen at 10 cm. pressure. Identical pressure-time curves were obtained with air. The ethylenediamine dinitrate underwent an autocatalytic decomposition over the whole temperature range 230-357°, the originally colourless liquid becoming brown and forming a bulky dark brown solid residue which seemed to be polymeric in nature. The pressure-time curves showed complex features. An initial pressure increase due to partial vaporization was followed by a constant rate of gas evolution. This rate was unaltered by varying the inert gas pressure from 10 to 76 cm., and the mass used from 2 to 50 mg., and by further recrystallization of the explosive from aqueous alcohol. The portion of the decomposition over which the linear pressure-time relation persisted depended on temperature. In the range 230-270° at 10 cm. gas pressure it increased from about 10% of the decomposition to about 50%, remaining nearly constant at this value until about 240°, then diminishing with further increase of temperature until at 357° only about 10% of the decomposition occurred with the linear rate. Fig. 3 shows three pressure-time curves given by ethylenediamine dinitrate at different temperatures, the inert gas pressure in each case being 10 cm. The curve for 238° illustrates a slight delay before the linear rate is
established, a feature encountered occasionally at the lowest temperatures used and possibly due to some supersaturation effect. The linear decomposition rate extrapolated back to zero time and the final pressure rise were used to determine the reaction rate constant for the initial decomposition at various temperatures, and on plotting \( \log k \) against \( 1/T \) the points shown in Fig. 4 were obtained. Some scatter is observable, partly due to slight uncertainty in some cases in defining the initial rate with precision owing to the complications produced by the vaporization and the catalytic effects. The straight line was fitted to the points by the method of least squares and gave for the initial rate the expression

\[
k(\text{sec}^{-1}) = 10^{12.1} e^{-60,500/RT}.
\]

The possible experimental error in \( E \) was estimated to be 2500 cal./mol.

After the first linear portion of the decomposition a more markedly accelerative reaction was observed, the exact form of the pressure-time curves varying with both the quantity of the explosive used and the inert gas pressure. At 10 cm. gas pressure small quantities showed a more rapid acceleration of decomposition than larger quantities. This is illustrated in Fig. 5 where the logarithm of the half life \( (t_1) \), taken as the time elapsing before the pressure attained half its final value, is plotted against \( 1/T \) for quantities of about 3 mg. from 273-357°, and quantities of about 30 mg. from 230-309°.

The results with 3 mg. can be represented by the equation

\[
t_1(\text{sec.}) = 10^{-11.2} e^{64,000/RT},
\]

and those for 30 mg. by the equation

\[
t_1(\text{sec.}) = 10^{-10.85} e^{34,000/RT},
\]

these equations giving the two straight lines shown in the figure. An increase in mass by 10 times therefore increases the half life by a factor of 1.8 under these conditions. It is very probable from these results that the autocatalytic decomposition of the explosive involves processes with a considerably lower value of activation energy than that of the primary decomposition.

With about 30 mg. of explosive at 10 cm. gas pressure in the temperature range 230-263°, the pressure \( p \) was found to increase with time \( t \) according to the equation

\[
\log p = \log (1 + \text{const.}),
\]

this equation holding from the end of the linear part of the curve until nearly the end of the decomposition. The constant \( f \) was 0.0076 at 230°, and 0.0013 at 263°. Increasing the inert gas pressure to 76 cm. diminished the half-life for both large and small quantities (2-50 mg.) the autocatalytic nature of the decomposition becoming more pronounced. In addition, at the higher temperatures the effect of mass was reversed by the higher gas pressures, the larger quantities decomposing more quickly. It is probable that in the decomposition of ethylenediamine dinitrate catalysis by a gaseous or volatile decomposition product occurs, hence the catalytic effects become greater with increasing inert gas pressure as diffusion of the catalyst from the reaction bulb is impeded, and again autocatalysis is more pronounced with smaller quantities on account of the relatively greater area of liquid surface exposed to the action.

At both high inert gas pressures and high temperatures, however, self-heating probably occurs with the larger quantities of explosive which then decompose more quickly than small quantities despite the autocatalytic effects. The explosive became rather viscous during decomposition, probably as a result of simultaneous polymerization reactions, and the large bubbles formed at 10 cm. pressure dispersed the explosive as a froth throughout much of the vessel, the final brown residue being spread over a large area of the bulb, whereas the residue formed at atmospheric pressure was concentrated at the bottom of the bulb. Self-heating should, therefore, clearly be favoured by higher gas pressures.

**Gaseous products.**—Analyses were made of the gaseous products from ethylenediamine dinitrate decomposed at 309° for 8 minutes with nitrogen initially present to prevent vaporization.

One mol. of the explosive gave the products shown in Table II.

**Table II**

<table>
<thead>
<tr>
<th>Product</th>
<th>NO</th>
<th>N₂O</th>
<th>N₃</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.13</td>
<td>1.06</td>
<td>0.01</td>
<td>0.06</td>
<td>0.29</td>
</tr>
</tbody>
</table>

The weight of solid residue was about 40% of that of the original sample, so that even if 5 molecules of water were also eliminated, these gases do not account for all the volatile products. Organic substances are probably formed to a small extent. These results suggest the first steps in the decomposition to be the elimination of water with the transient appearance of a nitramine grouping followed by a primary nitrosamine grouping, from which NO and N₂O could be formed, or N₂ by a further internal oxidation step. Radicals thus formed could either continue breaking down to simple molecules or lead to the formation of polymeric substances. The nature of the autocatalyst formed in the decomposition is not known. The similarity of the pressure-time curves in air and nitrogen shows that it is not nitrogen peroxide, although in the presence of large partial pressures of this gas there was an acceleration of the decomposition. Autocatalytic effects persisted when the decomposition was carried out in a rapid stream of air, so that some catalyst must form in the liquid itself.

**The decomposition of ammonium nitrate**

This reaction was examined only in the glass apparatus since liquid ammonium nitrate reacts rapidly with copper. Distillation of the ammonium nitrate from the hot zone occurred very readily in vacuo and even at low gas pressures; it was reduced as far as possible by working with one atmosphere of air or nitrogen present.

A decomposition following the unimolecular equation was then observed, the rate of which was determined by the pressure-time curves over the temperature range 243-261°, using quantities varying from 2 to 123 mg. The rate did not depend on which inert gas was present, but at the higher temperatures it increased somewhat as the quantity of substance was reduced to a few milligrams. Thus at 309°, 2 mg. of the salt decomposed twice as quickly as 120 mg. This effect is
probably due to the greater proportion of the salt which vaporizes with the smaller quantities. In determining an Arrhenius expression for the decomposition rate, experiments above 300° with quantities of less than 20 mg. were therefore neglected; plotting log k against 1/T gave the points shown in Fig. 6, the straight line giving for the unimolecular constant k (sec.)\(^{-1}\) = 10\(^{13.8}\) e\(^{-40000/RT}\). The experimental error in activation energy was estimated at 2500 cal./mol. This expression gives greater values for k than those which can be computed from the figures given by Shah and Oza.\(^4\) Thus at 270° there is a discrepancy by a factor of about 20. It seems possible, however, that their measurements are complicated by distillation of most of the liquid from the hot zone to their condenser and by slow heating of the reaction vessel. The finding of Veley\(^5\) that glass accelerates the decomposition was not confirmed in experiments at 270°, using both Pyrex and soda glass crushed and ground; no change of rate was observed. In view of these discrepancies the possibility of some complicating factor in the decomposition was investigated. The effect of the area of interface between ammonium nitrate and air was examined making use of the small mobility of the liquid on clean Pyrex surfaces. A particle of ammonium nitrate striking the lower part of the glass bulb formed a globule which decomposed over a localized area provided the temperature was high enough to bring about most of the decomposition in a minute or so. It was therefore possible to compare the decomposition rate of one single globule of liquid with that of thirty globules having the same total mass. No difference was noted in several experiments at about 310°. No effect of mechanical agitation on the decomposition rate was detected using a reaction vessel fitted with a stirrer enabling quantities down to 25 mg. to be stirred at 200 revolutions per minute.

![Graph](attachment:image)

**Effect of impurities.**—Veley\(^6\) and Saunders\(^9\) found the initial decomposition rate of the liquid to be rather sensitive to impurities. No change in rate was found on recrystallizing the sample used twice from water. The effect of adding 2-5% of various substances to the liquid was investigated. A temperature of about 300° was used and the complete decomposition, which generally remained first order, was followed. The rate was not very sensitive to additions of oxides of calcium, cobalt, iron (Fe\(_2\)O\(_3\)), lead (PbO), magnesium, manganese (MnO\(_2\)), nickel and uranium, being increased by 20-60%. The rate was increased 3-4 times by addition of 2-5% of molybdic acid, ammonium molybdate, potassium chloride, potassium sulphate, ammonium sulphate, potassium persulphate and ammonium thiocyanate. Chromium compounds exerted a very marked effect on the reaction rate: at about 220° the addition of various chromates, dichromates, chromic salts and chromium trioxide increased the decomposition rate several hundred times. The effect was observed to depend on solution of the chromium in the ammonium nitrate, the catalytic efficiency of the various compounds being mainly determined by the proportion of chromium present and not by its original mode of combination, unless this made the compound insoluble when no sensible effect was observed (e.g., chromic oxide). Chromic salts were oxidized to chromates.

The view that an appreciable quantity of ammonium nitrate vaporized before decomposition at the higher temperatures was in conformity with the analytical results. At 350° with 30 mg. of salt and an initial nitrogen pressure of 10 cm., 0.33 mol. of NO\(_2\) and 0.23 mol. of N\(_2\), were obtained with each mol. of N\(_2\)O. According to Kaiser\(^10\) the decomposition products obtained in an evacuated bulb at temperatures about 100° lower give the equation 4NH\(_2\)NO\(_3\) = 2NH\(_4\) + 3NO\(_2\) + NO + N\(_2\) + 5H\(_2\)O. The formation of substantial amounts of nitrogen peroxide and nitrogen at the higher temperatures in the experiments described here is therefore to be expected if appreciable vaporization occurs. The mechanism of the reaction in the gas phase probably involves dissociation, whereas in the liquid phase the primary step is probably the formation of water by interaction of two ions.

**Discussion**

The Arrhenius frequency factor for the two nitrates is normal, but it has an extremely large value for the two nitric esters. In the case of pentaerythritol tetrinitrate, however, the large value is not maintained in dilute solution in dicyclopentanone. At increasing temperatures the decomposition rate of the pure liquid explosive becomes greater than that in dilute solution. This suggests that chain reactions of short length are involved in the pure liquid decomposition, the large values of the Arrhenius constants A and E arising from a slow increase of the chain length with temperature. If this increased from 1 at 171° to 3 at 238° the value of A would consequently increase about 10\(^4\) times. In 5% solution \(E\) is 39,500 cal./mol., identical with the value reported by Appin, Chariton and Todès\(^11\) for the decomposition of methyl nitrate in the gas phase in which they consider the primary step to be the direct elimination of nitrogen peroxide from the molecule, as seems also to be the case for pentaerythritol tetrinitrate. Even in dilute solution \(A\) for pentaerythritol tetrinitrate is \(10^5\) to \(10^{10}\) times greater than the normal value. Chain reactions might, however, persist in solutions of this concentration, or a number of degrees of freedom within the molecule might contribute to the activation energy.

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