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Kinetics of the Thermal Decomposition of *N*-Nitro-compounds

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Results primarily on nitramines are summarised. Analysis of modern views indicates that a non-chain radical mechanism with rupture of the N-NO_2 bond in the rate-determining stage is the most soundly based. Kinetic parameters of the thermal decomposition of *N*-nitro-compounds are systematised. The kinetic role of phase constitution is discussed, and prospects for future research are considered. A list of 108 references is included.

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I. INTRODUCTION

The problem of the thermal stability of nitro-compounds is closely connected with those of the explosives industry. Their molecules contain relatively unstable chemical bonds, which are responsible for their great reactivity (and consequent danger involved in handling them under storage conditions and in technical operations).

For a long time estimates of the thermal stability of nitro-compounds were usually empirical in character, although attempts at a kinetic investigation of their thermal decomposition were made as early as the 1920s.[1,2] However, systematic kinetic studies began only with the founding of the Institute of Chemical Physics of the USSR Academy of Sciences in 1931, and these isolated the problem of the thermal decomposition of nitro-compounds as a separate branch of science having immense practical application. A considerable role in establishing this line of research was played by Roginskii, Apin, and Andreev[3-5]. Results obtained during the first few years were surveyed in Semenov's monograph[6].

The present Review is devoted to the kinetics of the thermal decomposition of *N*-nitro-compounds, which include such well known explosives as hexogen, octogen, tetryl, and dina. Reviews on this topic have not been published hitherto.

II. DECOMPOSITION IN THE GAS PHASE

The thermal decomposition of nitro-compounds comprises very many steps, and for the large majority the detailed mechanism remains obscure. Investigators have hitherto concentrated their efforts on elucidating and describing kinetically the primary rate-determining stages, especially as these mainly govern the thermal stability. The extraordinary complexity of the mechanism of pyrolysis led to early studies being made under relatively simple conditions—in the gas phase—uncomplicated by the surrounding medium, with any contribution by secondary reactions reduced to a minimum. The first attempt at such an investigation was made by Flournoy[7] on dimethylnitramine, after which other dialkylnitramines were examined. The main results can be summarised as follows.

Dialkylnitramines decompose in the gas phase with slight autocatalysis. In this respect they differ from most nitro-compounds of other classes—nitro-ethers, aliphatic and aromatic nitro-compounds—which decompose unimolecularly in the gas phase: i.e. the rate of the process is controlled by a single stage. Homolytic rupture of the N–NO_2 bond must be regarded as the first step in the breakdown of nitramines, since the energy of dissociation of this bond was found to coincide, within the limits of experimental error, with the activation energy of the reaction[8-11]. An important point in connection with the mechanism of the gas-phase thermolysis of nitramines is that analysis of the products from dimethylnitramine showed[7] a high yield (80 mole %) of dimethylnitrosamine. The general mechanism of the gas-phase decomposition of dialkylnitramines can be represented by the equations (for dimethylnitramine as example)

$$(CH_3)_2NNO_2 \rightleftarrows (CH_3)_2N + \dot{N}O_2$$
$$(CH_3)_2NNO_2 + NO_2 \rightarrow NO + \text{Oxidation products}$$
$$(CH_3)_2\dot{N} + NO \rightarrow (CH_3)_2NNO$$
$$(CH_3)_2NNO + NO_2 \rightarrow \text{Oxidation products}$$

A noteworthy feature is the reversibility of the first step, which was proved by the introduction of additives capable of reacting rapidly with nitrogen dioxide (to form inactive products) and thereby removing it from the sphere of reaction. Such additives (e.g. formaldehyde) were found[9,12] to accelerate decomposition, but only to a certain limit: on attainment of a certain concentration of additive (corresponding to complete removal of nitrogen dioxide) the kinetics were unaffected by further addition.

Two important conclusions follow from the reversibility of the first stage in the decomposition of nitramines. Firstly, the relatively low chemical activity of dialkylamino-radicals is confirmed. Secondly, the use as inhibitors of substances capable of reacting readily with oxides of nitrogen, a method widely applied to stabilise nitro-compounds, may produce directly contrary effects on nitramines.

An interesting feature of the above mechanism is the tendency to undergo oxidation by nitrogen dioxide, which is characteristic of nitramines in general. Since other classes of nitro-compounds did not in most cases react so readily with nitrogen dioxide, it may be supposed (although the reactions of nitramines with this compound have never been studied) that the reaction centre in the nitramine molecule is the amino-nitrogen atom, which is attacked by an oxygen atom of the nitrogen dioxide.

Table 1 gives activation parameters for the first stage (rupture of the N–NO_2 bond) in the thermal decomposition of dialkylnitramines. The paucity of experimental results does not permit correlation analysis of the kinetic data. However, Table 1 reveals closely similar activation parameters for the

decomposition of all the compounds. Since the activation energy is equal, within the limits of experimental error, to the energy of dissociation of the $N-NO_2$ bond, it is easy to calculate enthalpies of formation of dialkylamino-radicals from those of the corresponding *N*-nitro-compounds. This gave a value 19.8 kcal mole^{-1} for the enthalpy of formation of the diethylamino-radical[12].

Table 1. Activation parameters for thermal decomposition of dialkylnitramines in the gas phase†.

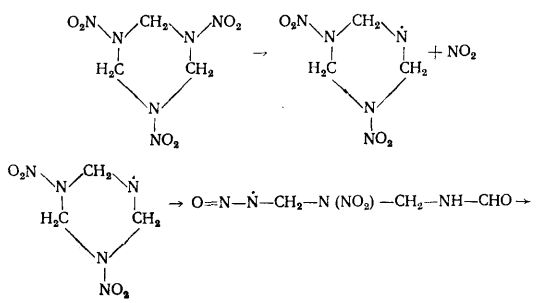
Nitramine	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Dimethylnitramine	180—240	38.9	$10^{13.7}$	[9]
Diethylnitramine	180—240	41.6	$10^{15.1}$	[12]
N-Nitropiperidine	200—240	42.1	$10^{14.8}$	[12]
N-Nitromorpholine	210—245	38.9	$10^{13.6}$	[12]

† ΔT = temperature range of measurements; E_a = activation energy; A = pre-exponential factor.

Several studies have been made of the gas-phase decomposition of the relatively non-volatile cyclic nitramines—hexogen (RDX) (1,3,5-trinitro-1,3,5-triazacyclohexane) and octogen (HMX) (1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclooctane)—whose vapour pressures at temperatures convenient for kinetic measurements are extremely low. Nevertheless, a portion does evaporate when these compounds undergo decomposition in a condensed phase (liquid or solid), and special experiments have shown[13-17] that the gas-phase process may make a contribution, sometimes very substantial, to the total rate of decomposition.

An extremely important discovery for understanding the mechanism of the gas-phase decomposition of cyclic nitramines has been the intermediate formation of nitrogen dioxide[14,16,18], which can reasonably be interpreted in terms of the above mechanism for dialkylnitramines, with rupture of the $N-NO_2$ bond as the first stage[14,17]. Among the decomposition products of hexogen have been detected not only nitrogen dioxide but also nitrogen, nitrous and nitric oxides, carbon monoxide and dioxide, water, formaldehyde, hydrogen cyanide, ammonia, formic acid, hydroxymethylformamide, 1,2-dihydro-1,3,5-triazine, trimethylamine nitrate, and a polymer $(CH_2N-CHO)_n$.[13,14,16,18]. Mass-spectrometric detection of still other compounds has been reported[18], but they could not be identified unambiguously (in all the above studies decomposition took place in both gaseous and condensed phases).

A scheme suggested[17] for the gas-phase decomposition of hexogen



$\rightarrow O_2N-\dot{N}-CH_2-NH-CHO + N_2 + CH_2O$,
$O_2N-\dot{N}-CH_2-NH-CHO \rightarrow N_2O + \dot{C}HOH-NH-CHO$,
$\dot{C}HOH-NH-CHO \rightarrow CH_2OH-NH-CHO$,
$CH_2O + NO_2 \rightarrow CO + CO_2 + NO + H_2O$,
$CH_2OH-NH-CHO \rightarrow$ Polymerisation products,
$CH_2OH-NH-CHO \rightarrow CH_2(NH-CHO)_2 + H_2O + CH_2O$,
$CH_2OH-NH-CHO + CH_2O \rightarrow (CH_2)_3N + CO_2 + H_2O$,

shows good agreement with the composition of the pyrolysis products, but cannot be regarded as strictly proved. In particular, ring fission may occur in the first stage[18] giving formaldehyde, but this suggestion was not accompanied by a detailed scheme, and no clear distinction was made between processes taking place in gaseous and condensed phases.

If nevertheless we take the mechanism with rupture of the $N-NO_2$ bond as the most probable for gas-phase pyrolysis, we must expect that the activation parameters for the decomposition of hexogen will be closely similar to those for the above dialkylnitramines (Table 1). However, the activation energy and the pre-exponential factor has been given respectively as[15] 34.1 kcal mole^{-1} and 3.14×10^{13} s^{-1}, and also[19,20] as 30.0 and $10^{11.7}$. It is difficult to explain the discrepancy in these values and their appreciable departure from those for the pyrolysis of dialkylnitramines. Only two comments must be made: papers on the gas-phase pyrolysis of hexogen do not indicate whether any heterogeneous contribution to the kinetics (wall effect) is excluded; furthermore, the technique[15] of differential scanning calorimetry measured the kinetics in the later stages, after 96.5% conversion, i.e. in the presence of a large quantity of decomposition products, the influence of which on hexogen has not been specially studied.

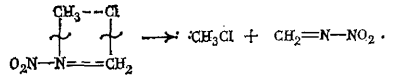
Clarity is introduced into this problem by a study[21] in which the activation energy and the pre-exponential factor for the gas-phase decomposition of hexogen have been found to be 35.0 kcal mole^{-1} and $10^{13.5}$ s^{-1}, almost the same as in Ref. 15. However, this work shows[21] that the reaction is inhibited by nitric oxide, from which it may be suggested that the above activation parameters represent not simply the primary decomposition step but a totality including secondary reactions. For the inhibited decomposition of hexogen the activation energy is 40.4 kcal mole^{-1} and the pre-exponential factor $10^{15.58}$ s^{-1},[21] values in excellent agreement with those in Table 1. They can be regarded as a strong argument in support of a mechanism of the gas-phase pyrolysis of hexogen involving rupture of an $N-NO_2$ bond as primary step.

From a detailed analysis of possible schemes for the decomposition of octogen based on published information it has been concluded[22] that the primary step is most probably homolytic rupture of an $N-NO_2$ bond, for which the activation energy and the pre-exponential factor were estimated as 46.2 kcal mole^{-1} and $10^{16.2}$ s^{-1}. The Reviewers regard these values merely as tentative, for implausible postulates had to be used[22] in their estimation. Thus the energy of dissociation of an $N-NO_2$ bond in octogen was determined from data for dimethylnitramine, but the pre-exponential factor was calculated from data for nitromethane and dinitrogen tetroxide. Other workers[19,20] give completely different parameters—32.0 kcal mole^{-1} and $10^{13.4}$ s^{-1}—for the gas-phase pyrolysis of octogen. As with hexogen, we find it difficult to explain such a marked scatter in values obtained by different workers.

In conclusion it is relevant to mention a short paper[23] expressing the interesting idea that the kinetics of the thermal decomposition of nitramines should depend on the geometrical configuration of the nitramino-group. Inspection of the experimental results shows that, if this group is

planar (dialkylnitramines, etc.), the activation parameters should be 40.9 kcal mole^{-1} and $10^{14.1}$ s^{-1}; but if it is pyramidal (hexogen, etc.) 37.8 kcal mole^{-1} and $10^{14.1}$ s^{-1}. This aspect merits further study and in particular quantum-chemical calculations.

We have been considering the thermal decomposition of compounds containing no reactive functional group other than nitramino. An investigation[24] of the pyrolysis of methylchloromethylnitramine $CH_3N(NO_2)CH_2Cl$ has shown that introduction of the chlorine atom has lowered significantly the thermal stability of dimethylnitramine and appreciably changed the kinetics of thermolysis, which is now definitely autocatalytic. The reaction is influenced appreciably by the addition of nitric oxide and inert gases (nitrogen, neon), which suggests[24] the presence of chain processes. It is significant that chloromethane and hydrogen chloride were detected among the decomposition products, and special experiments showed that the latter was the autocatalyst. Chloromethane may be formed in a unimolecular primary stage involving production of a cyclic activated complex:



This hypothesis is supported by the low pre-exponential factor $10^{10.5}$ s^{-1} of the first stage, whose activation energy is 30.7 kcal mole^{-1}.

III. DECOMPOSITION IN THE LIQUID PHASE

At the present time we are still far from having a general kinetic picture of the liquid-phase decomposition of nitramines. Moreover, there is no single nitramine whose mechanism of liquid-phase decomposition could be regarded as reliably established, although dozens of papers have appeared on this topic. It therefore appears advisable to discuss published results for each compound separately.

1. Hexogen

The thermal decomposition of hexogen (1,3,5-trinitro-1,3,5-triazacyclohexane, m.p. 205 °C) has been studied especially intensively during recent years, although Robertson's pioneering work was undertaken as early as the 1940s.[25,26] Essentially two main lines of attack—analysis of decomposition products and measurement of kinetic parameters—have been adopted in all investigations aimed at elucidating the mechanism and measuring the thermal stability of hexogen (this applies to all nitro-compounds). Unfortunately, neither of these approaches, despite their undoubted usefulness, provides an unambiguous interpretation of the reaction mechanism, mainly because kinetic investigations provide information only on the rate-determining steps—and then for not very complicated molecules—whereas the final products are mostly formed as a result of diverse secondary reactions. It is therefore to be expected that future progress in this field will involve the use of modern methods for identifying and studying intermediate reactive species (electron spin resonance, chemical polarisation of nuclei, spin traps).

The above work[25,26] detected the formation of nitric and nitrous oxides, nitrogen, hydrogen, carbon monoxide and dioxide, water, and formaldehyde. Table 2 gives as example the quantitative composition of the decomposition products. These are formed in somewhat different proportions when decomposition is conducted in solution in dicyclohexyl phthalate and trinitrotoluene.

The paper[14] first reporting the detection of nitrogen dioxide is extremely important: unlike the substances in Table 2, this may be a primary reaction product. Subsequently other products have been detected—hydrogen cyanide[14], hydroxymethylformaldehyde[16], formic acid, ammonia, trimethylamine nitrate[17], 1,2-dihydro-1,3,5-triazine, vinylnitramine (the peak in the mass spectrum having $m/e = 88$, which has been attributed to the structures $(CH_2)_2NNO_2$, $CH_2:CHNHNO_2$, and $CH_3CH:NNO_2$),[18] and also several other compounds, for which the empirical formulae

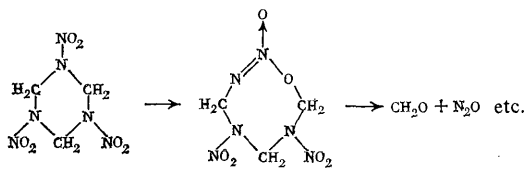
$$C_2H_4N, \quad C_2H_4N_2, \quad CH_2N_2O_2, \quad C_3N_3H_4, \quad C_3N_3H_5, \quad C_2H_4N_3O_2,$$
$$CH_2N_3O_4, \quad C_3H_4N_4O_2, \quad C_2H_4N_4O_3, \quad C_2H_4N_4O_4$$

have been proposed[27] on the basis of the mass spectra (we must repeat here that in most cases the decomposition was studied under two-phase conditions, with simultaneous occurrence of gas-phase and liquid-phase reactions).

Table 2. Products of the liquid-phase decomposition of hexogen (moles mole^{-1} hexogen).[26]

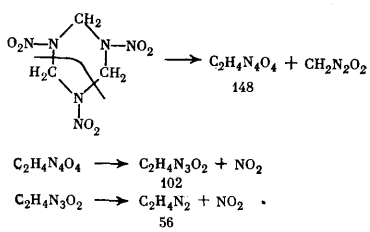
Temp.	NO	N_2O	N_2	H_2	CO	CO_2
225° C	0.54	0.98	1.16	0.09	0.40	0.48
267° C	0.75	0.76	1.03	0.06	0.29	0.44

The first ideas on the mechanism of the liquid-phase decomposition of hexogen were expressed by Robertson[26,14]:

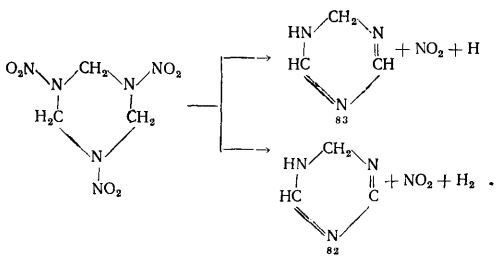


This scheme provides a reasonable explanation of the appearance of formaldehyde and nitrous oxide, but excludes the possibility of rupture of an N–NO_2 bond in the first stage, since nitrogen dioxide was not found. Although this product has since been detected[14,18,27], its kinetic behaviour with variation in the volume of the reaction vessel and in the weight of starting material differs from that of nitrous oxide and carbon dioxide[14]. From this it was concluded[14] that these products are formed under different conditions—nitrogen dioxide in gas-phase decomposition, but nitrous oxide and carbon dioxide in the liquid-phase reaction.

One of the possible mechanisms based on mass-spectrometric analysis of the decomposition products[27] involves cleavage of the ring (the numerals below the formulae indicate the masses of the ions detected in the mass spectrum):



However, these workers[27] assume a mechanism with separation of nitrogen dioxide without ring fission:



A similar mechanism was based by other workers[18] on the detection of 1,2-dihydro-1,3,5-triazine, although they examined the decomposition of hexogen only in gaseous and solid phases.

Before considering the mechanism of the liquid-phase decomposition of hexogen we note that the thermal stability was assessed qualitatively by differential thermal analysis[28]. The first kinetic investigation, showing a first-order reaction, was made by Robertson[26], who determined the kinetic parameters. However, later workers have obtained different results: thus over the range of degrees of conversion 10–80% the order appears[29] to be 1.36. A still more complicated picture has been observed[15], with an order of reaction 0.84 at degrees of conversion of 20.7–77%, followed by a sharp decrease, and then an increase to 0.94 at 96.5% conversion. Such complicated behaviour can be partly explained by the above two-phase character of the process, but the most important factor is most probably the complexity of the reaction itself, so that changes in experimental conditions lead to appreciable differences in kinetic behaviour. We may also mention the view[30] that the thermal decomposition of hexogen is autocatalytic.

Table 3. Activation parameters for the thermal decomposition of hexogen in the melt.

Method*	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Manometric	213—299	47.5±2.0	$10^{18.5}$	[26]
DSC	—	67.4±3.0	—	[31]
DTA	—	—	$10^{18.2}$	[32]
GChr	—	48.7	$1.7 \cdot 10^{19}$	[14]
DSC	206—252	48.2—53.0 **	($10^{18.8}$—$10^{20.3}$ **)	[29]
DSC	210—261	45.2±0.4	—	[33]
DSC	—	43.1	$2.44 \cdot 10^{16}$	[15]
DSC (isothermal)	204—225	41±1	—	[34]
DSC (non-isothermal)	—	42±3	—	[34]

*DSC = differential scanning calorimetry; DTA = differential thermal analysis; GChr = gas chromatography.
**Depending on choice of formula for calculation.

Table 3 shows quite good agreement among values obtained by different workers for the activation parameters of the liquid-phase decomposition of hexogen. With regard to the divergence shown by Ref.31, it may be noted that values given in this paper for other substances also differ appreciably from general published values. Furthermore, the temperature range of the measurements is not indicated[31], so that it is not very clear whether a hexogen melt was actually studied (this applies also to measurements under non-isothermal conditions in Ref.34).

The thermal decomposition of liquid hexogen is obviously complicated, and is accompanied by the formation of reactive intermediate species responsible for diverse secondary processes. It therefore appears quite natural to investigate the decomposition in solution, when bi- and ter-molecular secondary reactions are slowed down in comparison with the unimolecular decomposition of the initial compound.

Table 4. Activation parameters for the thermal decomposition of hexogen in solution.

Solvent	c*, %	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Dicyclohexyl phthalate	2—5	201—280	41.0	$10^{15.46}$	[26]
Trotyl	2—5	194.5—281	41.5	$10^{15.55}$	[26]
Convalex-10**	20	—	48.4	—	[31]
Trotyl	—	166—184	36.9±2.9	$10^{13.9\pm1.4}$	[36]
Benzophenone	—	—	37.8	$10^{14.5}$	[36]
m-Dinitrobenzene	—	160—200	39.7	$10^{14.3}$	[35]

*c = concentration of solution.
**Polyphenyl ether.

Appreciable autocatalysis is observed in dilute solution[26,35], in contrast to the melt. The induction period becomes shorter with rise in temperature, and completely disappears above 250 °C. The reaction is slower in solution than in the melt. Activation parameters in solution, determined from the initial portions of the kinetic curves on the assumption that a first-order equation is obeyed here, show good agreement among various workers (Table 4) with the exception of Ref.31. Another worker[36] did not observe autocatalysis in the thermal decomposition of hexogen: a first-order equation was satisfied throughout. The probable reason is that the experiments were conducted in relatively concentrated solutions, as first order is observed in the melt. It must therefore be expected that the induction period will become shorter with increase in concentration. This worker[36] noted also that products of the decomposition of hexogen are able to decompose trinitrotoluene. In this respect the latter is not the optimum solvent, although Table 4 shows that this does not affect the overall kinetic results.

The autocatalytic character of the thermal decomposition of hexogen in solution is most simply explained as above for the gas-phase breakdown of dimethylnitramine: on the hypothesis of a series of consecutive reactions. With rise in temperature the induction period may gradually diminish, and then completely disappear, as was observed by Robertson above 250 °C.[26]

An appreciable similarity in kinetic behaviour is evident between hexogen in solution and dimethylnitramine—the simplest secondary nitramine—in the gas phase, with slight acceleration and similar activation parameters (we have already noted a difference of 3 kcal mole^{-1} in the activation energies for the decomposition of these two compounds[23], attributed to a difference in the geometrical configuration of the nitamino-groups; however, this difference has little significance for our discussion, as the determination of activation energy in such experiments usually involves an error of 1–2 kcal mole^{-1}). Since the main features of the

mechanism of the decomposition of dimethylnitramine—primarily rupture of the $N-NO_2$ bond as the rate-determining stage—have been quite reliably established, the mechanism of the pyrolysis of hexogen in the liquid phase can reasonably be interpreted on the same basis, especially as such a hypothesis is supported by analysis of the decomposition products[18,27]. The increase in the rate of decomposition with solution concentration, passing to the melt in the limit, can reasonably be explained by an increasing contribution to the overall kinetics by bi- and ter-molecular secondary reactions, as noted above. The kinetic parameters (in particular those in Table 3) must then be regarded as overall values, not representing any particular elementary stage, which incidentally is supported by the high pre-exponential factors uncharacteristic of truly unimolecular reactions.

Robertson[26] suggested a chain mechanism for the thermal decomposition of hexogen in the melt. However, his experimental results[26] indicate that the length of the chain would be 1.31 and 2.96 at 205 and 273 °C respectively. Therefore we can hardly regard this as a chain process, and it is simpler to apply the concept of successive stages, which are eliminated with dilution of the solution.

As already stated, ideas on alternative mechanisms for the decomposition of hexogen assume in effect ring cleavage either following[26] or in the absence of[27] rearrangement. In the Reviewers' opinion, however, the composition of the products can provide only an indirect argument in support of these mechanisms, for they may be entirely formed in secondary stages, perhaps after rupture of an $N-NO_2$ bond. Furthermore, ring fission in primary stages will be expected to have activation parameters differing substantially from those for a mechanism with rupture of this bond. Nevertheless, as already stated, the decomposition of hexogen in solution is kinetically similar to that of dimethylnitramine in the gas phase.

Thus, of the two possibilities for the liquid-phase decomposition of hexogen, we prefer the radical mechanism with rupture of an $N-NO_2$ bond. In our view it is consistent with all the available experimental facts, whereas mechanisms involving ring fission show poor agreement with kinetic data for decomposition in solution. On the other hand, the choice between different mechanisms cannot be regarded as finally settled, since there is no direct evidence to prove or disprove a particular mechanism. In particular, the increase in reaction velocity on passing to the melt can be explained by a change in mechanism, with the possibility of bimolecular interaction between hexogen molecules in the melt. This aspect has been considered by Stals[37] in terms of quantum chemistry (applied to the decomposition of solid hexogen).

2. Octogen

Octogen (1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclo-octane) resembles hexogen, so that it is not surprising that it behaves similarly on thermal decomposition, although quantitatively it is more thermostable: according to differential thermal analysis[28] octogen and hexogen undergo intense decomposition at 260 and 215 °C respectively. The decomposition of octogen has been studied also by differential scanning calorimetry[29]: this paper gave degrees of decomposition corresponding to the maximum on the scanning curve as a function of rate of heating, but the kinetic parameters had not been calculated.

The first detailed kinetic investigation of the thermal decomposition of octogen was reported by Robertson in the paper already mentioned[26]: he found a first-order reaction, and traced an analogy between hexogen and octogen. Table 5 collects existing data on the liquid-phase decomposition of the latter. Another study[15] by differential scanning calorimetry indicated an order of 0.6 at degrees of decomposition of 15.5–97.7%, but the experimental method was such that reaction took place in both gas and liquid phases. In Table 5 such large activation energies as 228 kcal mole^{-1} [31] are improbable and uncharacteristic not only of nitramines but also of nitro-compounds in general. The remaining very few values show quite good mutual agreement.

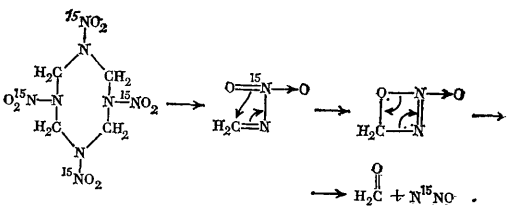
Table 5. Activation parameters for the thermal decomposition of octogen in the melt.

Method	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Manometric	271–314	52.7	$10^{19.7}$	[26]
–	—	52.7	—	[31] *
–	—	59.0	—	[31] **
DSC	—	228±24	—	[31]
DSC	—	—	$10^{18.1}$—$10^{18.9}$ ***	[32]
DSC	271–285	51.3	$6.4 \cdot 10^{18}$	[38]
DSC	—	44±10	—	[34]

*Unpublished results of Johnston, quoted in Ref.31.
**Unpublished results of Lind, quoted in Ref.31.
***Depending on method of calculation.

As with hexogen, useful information can be obtained from decomposition in solution. In Convalex-10 (a polyphenyl ether) the activation energy was 50.3 kcal mole^{-1}.[31] A more detailed investigation[35] in *m*-dinitrobenzene solution established the slightly autocatalytic character of decomposition (as with hexogen in solution and dimethylnitramine in the gas phase). The activation energy and the pre-exponential factor were respectively 44.9 kcal mole^{-1} and 10^{16} s^{-1}.

The composition of the gaseous decomposition products from octogen was about the same as from hexogen[26]. The isotopic composition of the gaseous products from octogen labelled with nitrogen-15 in the nitro-group was the same ($^{14}N^{15}NO$, ^{15}NO, $^{14}N^{15}N$, $HC^{14}N$) below and above the melting point (over the range 230–285 °C).[39] It has thus been reliably established that nitric oxide is formed only from a nitro-group, nitrogen and nitrous oxide from a nitro-group and a nitrogen atom of the ring, and hydrogen cyanide only from a cyclic nitrogen atom. From these results it was concluded[39] that the decomposition of octogen does not involve rupture of $N-NO_2$ bonds and perhaps involves the stages



Although this scheme appears reasonable from our point of view and supports a reaction mechanism involving ring cleavage in the rate-determining stage, we nevertheless consider that it does not disprove, and moreover does not even contradict, a radical mechanism with $N-NO_2$ bond rupture in the first step. Indeed, nitrogen dioxide may attack another octogen molecule at an amino-nitrogen atom (a similar scheme has been given above for dimethylnitramine), and nitrous oxide and nitrogen having the observed isotopic composition could be formed by a series of secondary processes. Oxidation by nitrogen dioxide of formaldehyde resulting from the decomposition of octogen yields not nitrous oxide[39] but nitric oxide[40], which would of course have the isotopic composition ^{15}NO.

As with hexogen, an unambiguous interpretation of the mechanism of the liquid-phase decomposition of octogen is at present impossible. However, in view of the close analogy between these nitramines (similar structure, behaviour on thermal decomposition both in the melt and in solution, and composition of reaction products), we are inclined to support a radical mechanism with rupture of an $N-NO_2$ bond in the first stage, especially as it is indicated also by a thorough analysis[22] of possible decomposition schemes (though this was undertaken for gas-phase pyrolysis). The greater activation energy of decomposition of octogen than of hexogen can be explained (in terms of the ideas in Ref. 23) by differences in stability of $N-NO_2$ bonds depending on the geometrical configuration of the nitramino-group (planar, pyramidal, etc.).

3. Dinitropiperazine and Dinitroimidazolidine

Information on the thermal decomposition of other cyclic nitramines has appeared quite recently[40,41]. The kinetics of the decomposition of *NN'*-dinitropiperazine and *NN'*-dinitroimidazolidine (1,3-dinitro-1,3-diazacyclopentane) are fairly complicated: in the melt slight autocatalysis was observed by one group of investigators[40], but not by the other group[41], who worked at higher temperatures. On the other hand, the latter observed[41] that the ratio of the initial weight taken to the volume of the reaction vessel m/V influenced the kinetics, as also in solution did the concentration or at constant concentration this ratio. Thus, although as with other compounds data obtained in dilute solution are most convenient to interpret, there is no certainty that the rate constants obtained represent solely the primary step in decomposition.

Table 6. Activation parameters for the thermal decomposition of *NN'*-dinitropiperazine and *NN'*-dinitroimidazolidine in the liquid phase[40,41].

Nitramine	State	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}
NN'-Dinitropiperazine	melt	216—250	47.4	$10^{17.3}$
NN'-Dinitropiperazine	soln.	130—245	45.8	$5.68 \cdot 10^{15}$
NN'-Dinitroimidazolidine	melt	135—200	37.1	$8 \cdot 10^{13}$
NN'-Dinitroimidazolidine	soln.	120—210	37.9	$9.53 \cdot 10^{13}$

Activation parameters determined by the two groups over different temperature ranges sometimes differed appreciably, but quite satisfactory agreement was obtained when both sets of results[40,41] were included in a single Arrhenius plot (Table 6). Furthermore, varying the solvent (*m*-dinitrobenzene, 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene) has no appreciable influence on the kinetics. Both groups interpret the results, as with hexogen and octogen, in terms of a radical mechanism involving rupture of an $N-NO_2$ bond in the first step. Comparison of the results in Table 6 for reactions in solution shows that activation parameters for the thermolysis of dinitropiperazine and dinitroimidazolidine are identical, within the limits of experimental error, with those for octogen and hexogen respectively.

Several general conclusions can be drawn from all these results on the influence of certain factors on the thermal stability of cyclic nitramines. Change in size of ring or number of nitro-groups apparently does not affect thermal stability directly. Indeed, octogen and dinitropiperazine are respectively eight- and six-membered rings containing four and two nitro-groups: and the less thermostable pair hexogen and dinitroimidazolidine are six- and five-membered rings with three and two nitro-groups. Nor does the distance between the nitramino-groups play an appreciable part: in octogen and dinitropiperazine they are separated by one and two methylene groups respectively, but the difference in activation energy in solution does not exceed 1 kcal mole^{-1}. With respect to thermal stability it is obviously most significant that change in molecular structure (ring size or number of nitramino-groups) entails a change in strength of the $N-NO_2$ bond perhaps owing to the above change in geometrical configuration of the nitramino-group[23].

The most interesting result of an analysis[40] of the gaseous products of the thermal decomposition of dinitropiperazine and dinitroimidazolidine is that nitrous oxide is not produced from the former in solution. Thus it is not necessarily a product of the thermal decomposition of cyclic nitramines.

4. Tetryl and its Analogues

Tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline), together with trotyl and nitroglycerin, was for many years a kind of model substance, from which the principal laws governing the thermal decomposition of explosives were elucidated. Thus Knowles[42], who was apparently the first to regard thermal decomposition as a method for assessing the chemical stability of explosives, worked with tetryl.

Investigation of the thermal decomposition of tetryl by differential thermal analysis showed[28] that it is less thermostable than many other explosives, including those considered above. Together with thermogravimetry these results indicate a two-stage reaction: at 162 °C the heat curve shows a sharp exothermic peak, which is followed at about 200 °C by a less marked second peak. Other workers[43] have observed exothermic peaks at 160 and 230 °C. Under somewhat different experimental conditions the same peaks have been observed[44] at 197 and 293 °C. Qualitative results have been published for the thermal decomposition of a mixture of 30% of tetryl and 70% of trotyl[45,46].

The first kinetic investigations of the thermal decomposition of tetryl have now become classics[1,2]. The reaction exhibits clearly developed autocatalysis, effected by picric acid formed in the reaction. It has since been established[47] that the rate of the liquid-phase decomposition comprises the rate of the first-order non-catalytic decomposition and that of a second-order autocatalytic reaction (first order with respect to tetryl and to the catalyst). This paper noted that calculation of catalytic rate constants must take into account the decrease in volume of the condensed compound during the reaction, as

such decrease causes an additional increase in catalyst (picric acid) concentration.

Table 7 compares results obtained for the thermal decomposition of tetryl by various workers, some of whom did not separate the stages and found gross values for the activation parameters (Table 8). All the results show good agreement: activation energies for the non-catalytic reaction lie in the range $E_a = 37.5 \pm 2.5$ kcal mole^{-1}, and the pre-exponential factors $A = 10^{14.5 \pm 1.5}$ s^{-1}; for the catalytic reaction $E_a = 37 \pm 1.5$ kcal mole^{-1} and $A = 10^{15 \pm 0.5}$ s^{-1}. Some values in Table 8 are exceptions: apart from the absence of separation of catalytic from non-catalytic stages, Roginskii's miscalculations[3,54] were based on extremely limited experimental results[1,2]; we have already noted that values in Ref. 31 show poor agreement with those obtained by other authors; and the results in Ref. 33 were obtained over a temperature range of only 4 deg.

Table 7. Activation parameters for the thermal decomposition of tetryl in the melt.

Method	ΔT, °C	Non-catalytic		Autocatalytic		Ref.
		E_a, kcal mole^{-1}	A, s^{-1}	E_a, kcal mole^{-1}	A, s^{-1}	
Manometric	211—260	38.4	$10^{15.4}$	—	—	[48]
Gravimetric	131.9—163.7	34.9	$10^{12.9}$	—	—	[49]
Calorimetric	130—155	36.0	$10^{13.8}$ *	38.0	$10^{15.6}$ *	[47]
Manometric	140—160	35.2	$10^{13.5}$	37	—	[48]
Manometric	140.3—164.9	40	10^{16}	35.5	$10^{14.5}$	[51]
Manometric**	150—175	35.9	$10^{13.5}$	—	—	[52, 53]

*Converted from values measured in min^{-1}.
**Experiments conducted in dinitrobenzene solution.

Table 8. Activation parameters for the thermal decomposition of tetryl in the melt.

Method	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Gas analysis	129.9—138.6	60.0	$10^{27.5}$	[3.52] *
Gas analysis	140—150	55.5	$10^{24.5}$	[3.53] **
Gas analysis	150—175	35	—	[42]
DSC	—	54.9	—	[30]
DSC***	—	33.5	—	[31]
DSC	—	—	$10^{15.2}$—$10^{15.5}$	[31]
DSC	170—174	58	—	[32]

*Calculated from experimental results in Ref. 1.
**Calculated from experimental results in Ref. 2.
***Experiments conducted in solution in Convalex-10.

The above mean activation parameters for the liquid-phase decomposition of tetryl agree in general with those for the other nitramines discussed, although tetryl decomposes more rapidly and has a lower activation energy, which may have several causes. Tetryl is an aromatic nitramine, and the trinitrophenyl group may influence the electronic structure of the nitramino-group, enhancing its reactivity. Furthermore, the rate of the non-catalytic stage increases with the m/V ratio[50], which implies that the reaction is catalysed not only by the condensed product (picric acid) but also by gaseous products. The activation parameters also depend on this ratio: with increase in m/V from 0.80 to 35.35 mg cm^{-3} the activation energy of the non-catalytic stage increases from 35.2 to 42.2 kcal mole^{-1}, and the pre-exponential factor from $10^{13.5}$ to $10^{17.5}$ s^{-1}.[50] Thus this rate constant is not a true but an effective value, which includes a contribution by reactions involving gaseous products. Hence the activation parameters in Table 7 (and in general those of the other nitramines considered) represent only to a first approximation the primary stage of decomposition (the data from Ref. 50 in Table 7 apply to $m/V = 0.80$ mg cm^{-3}).

Several analyses have been made of the gaseous products of the thermal decomposition of tetryl[50,51,43]. Some workers detected nitrogen dioxide, nitric oxide, and carbon dioxide and monoxide[48,49]; others found methane together with nitrogen dioxide, nitric oxide, and nitrogen[43]; methyl nitrite and nitrate are also formed[53]. During decomposition the concentrations of nitrogen dioxide and nitric oxide pass through a maximum[50]. Together with the above tendency of nitramines to be oxidised by nitrogen dioxide, this suggests that such oxidation is responsible for the dependence of the rate of the non-catalytic stage on the m/V ratio.

Gaseous decomposition products are mostly formed in secondary stages, so that their analysis gives little information on the mechanism of the initial stages. In this respect condensed decomposition products have the greatest interest. One of them (picric acid) has been known for a long time[1,2]. Other condensed products—2,4,6-trinitroanisole and *N*-methyl-2,4,6-trinitroaniline—have also been found[51]. These conclusions have since been confirmed[55,56], together with the detection of small quantities of 2,4,6-trinitroaniline, 1,3,5-trinitrobenzene, *N*-methyl-*N*,2,4-trinitroaniline, and perhaps *N*,2,4,6-tetranitroaniline.

Table 9. Kinetics of the thermal decomposition of 2,6-$(NO_2)_2$-4-$R^1C_6H_2N(NO_2)R^2$ in dinitrobenzene solution[52,53].

R^1	R^2	ΔT, °C	10^5k, s^{-1} (at 160 °C)	E_a, kcal mole^{-1}	A, s^{-1}
OCH_3	CH_3	145—165	$1.78 \cdot 10$	32.1	$10^{12.44}$
CH_3	CH_3	150—170	$1.5 \cdot 10$	34.2	$10^{13.42}$
Cl	CH_3	145—165	9.6	33.7	$10^{13.11}$
Br	CH_3	155—175	9.2	33.8	$10^{13.41}$
NO_2	CH_3	150—175	5.5	35.9	$10^{13.50}$
NO_2	C_2H_5	144—165	$3.7 \cdot 10$	33.3	$10^{13.90}$
NO_2	n-C_3H_7	135—155	$6.6 \cdot 10$	32.7	$10^{13.30}$
NO_2	iso-C_4H_9	130—150	$1.75 \cdot 10^2$	33.5	$10^{14.16}$

The above close similarity between the activation parameters of the thermal decomposition of tetryl and other nitramines suggests identity of the first stage in their decomposition—rupture of an N—NO_2 bond—which is consistent with the formation of *N*-methyl-2,4,6-trinitroaniline among the decomposition products. This compound may be formed by detachment of a hydrogen atom from an adjacent molecule by an *N*-methyl-2,4-6-trinitrophenylamino-radical produced in the first stage. Additional evidence supporting rupture of an N—NO_2 bond in the first stage of decomposition was obtained by Stepanov et al.[52,53], who made a kinetic investigation of tetryl and several of its analogues of general formula 2,6-$(NO_2)_2$-4-$R^1C_6H_2N(NO_2)R^2$. With variation of R^1 the results (first five lines in Table 9) conform well to the correlation

$$\lg k = -(0.488 \pm 0.026)\sigma - (3.898 \pm 0.011)$$
$$(r = 0.996,\ S_y = 0.016,\ n = 5).$$

A different relation is satisfied with variation of R^2 (last four lines):

$$\lg k = -(7.825\pm0.240)\sigma^* - (0.556\pm0.032)E_s - (4.259\pm0.017)\ (r=0.999,\ r_1=0.961,\ r_2=0.849,\ S_y=0.025,\ n=4).$$

Thus increase in electron density on the amino-nitrogen atom of the nitramino-group increases the rate of thermal decomposition. Examination of possible decomposition schemes also led to the conclusion[52,53] that a radical scheme is most consistent with the kinetic data and the correlation analysis. From this and the published composition of the products the following mechanism was proposed[52] for the decomposition of tetryl [Ar = 2,4,6-$(NO_2)_3C_6H_2$]:

$$\begin{aligned}
&ArN(CH_3)NO_2 \rightarrow Ar\dot{N}CH_3 + \cdot NO_2\ ,\\
&Ar\dot{N}CH_3 + NO_2 \rightarrow ArN(CH_3)\dot{O} + NO\ ,\\
&Ar\dot{N}CH_3 + NO \rightarrow ArN(CH_3)NO\ ,\\
&ArN(CH_3)NO \rightarrow ArON{=}NCH_3\ ,\\
&ArON{=}NCH_3 \rightarrow ArOCH_3 + N_2\ ,\\
&ArN(CH_3)\dot{O} \rightarrow Ar\dot{N}H + CH_2O\ ,\\
&Ar\dot{N}H + NO \rightarrow ArNHNO\ ,\\
&ArNHNO \rightarrow ArN{=}NOH\ ,\\
&ArN{=}NOH \rightarrow ArOH + N_2\ ,\\
&CH_2O + NO_2 \rightarrow CO + CO_2 + H_2O + NO\ ,\\
&ArOCH_3 \xrightarrow{\text{hydrolysis}} ArOH\ .
\end{aligned}$$

Here we may refer again to the possible formation of $ArNHCH_3$ from $ArN(CH_3)\cdot$ by acceptance of a hydrogen atom from some molecule. Similarly $ArN(H)\cdot$ can accept hydrogen to form $ArNH_2$. Picric acid can be obtained by the hydrolysis not only of trinitroanisole but also of tetryl itself[42].

The nature of the autocatalysis has remained largely obscure. Decomposition of tetryl is accelerated not only by picric acid but also by sulphuric acid[1], whereas nitric and acetic acids have no catalytic effect, apparently because of their volatility. It was suggested[2] that picric acid acts as a protic catalyst; other workers[51] assumed that protonation occurs at the amino-nitrogen atom, but gave no evidence of the mechanism of catalysis. Moreover, it remains obscure why the thermal decomposition of tetryl but not of other nitramines is so strongly autocatalytic.

5. Substituted Dialkylnitramines

The present subsection examines the liquid-phase decomposition of compounds of general formula $R^1N(NO_2)R^2$, where R^1 and R^2 are substituted alkyl groups.

The kinetics of the thermal decomposition of bis-2,2-dinitropropylnitramine in 5% solution in *m*-dinitrobenzene at 145–196.2 °C is similar[57] to that of the gas-phase pyrolysis of dimethylnitramine, with slight autocatalysis and activation parameters characteristic of the nitramines already discussed: the activation energy is 39.7 ± 1.4 kcal $mole^{-1}$, and the pre-exponential factor $10^{15.7\pm0.7}$ s^{-1}. Hence it may be supposed that decomposition of this compound resembles that of the other nitramines, having a radical mechanism with primary rupture of an $N-NO_2$ bond.

Similar results have been obtained[58] for the thermal decomposition of *N*-nitro-γ-azavaleric acid at 180–220 °C. Appreciable autocatalysis was observed; for the initial stage the activation energy and the pre-exponential factor were respectively 42.08 kcal $mole^{-1}$ and $10^{14.72}$ s^{-1}. The decomposition products included acrylic acid, nitrosomethane, *N*-methylmethyleneimine, carbon monoxide and dioxide, water, nitrogen, and nitric and nitrous oxides. The kinetic parameters again indicate rupture of an $N-NO_2$ bond in the first stage, and the scheme

$$\begin{aligned}
&CH_3N(NO_2)CH_2CH_2COOH \rightarrow CH_3\dot{N}CH_2CH_2COOH + NO_2\ ,\\
&CH_3\dot{N}CH_2CH_2COOH \rightarrow CH_3\dot{N}H + CH_2{=}CHCOOH\ ,\\
&CH_3\dot{N}CH_2CH_2COOH \rightarrow CH_2{=}NCH_3 + \dot{C}H_2COOH\ ,\\
&CH_3N(NO_2)CH_2CH_2COOH + A \rightarrow CH_3N(NO_2)CH_2\dot{C}HCOOH\ ,\\
&CH_3N(NO_2)CH_2\dot{C}HCOOH \rightarrow CH_3\dot{N}NO_2 + CH_2{=}CHCOOH\ ,
\end{aligned}$$

was suggested to explain the composition of the products, where A is a hydrogen acceptor, e.g. NO_2. The remaining gaseous decomposition products may be formed by the oxidation of $CH_3N(H)\cdot$ and $\cdot CH_2COOH$ with nitrogen dioxide and by the breakdown of $CH_3N(NO_2)\cdot$.

The decomposition of many nitramino-carboxylic acids and their salts has been studied[59] by differential thermal analysis, thermal stability being assessed from the temperature corresponding to an exothermic peak. Although kinetic parameters were not determined, qualitative relations could be established between thermal stability and molecular structure. It was found in particular that the stability increases with the length of the aliphatic chain and with the p*K* of the acid. Thermal stability is influenced also by the position of the nitramino-group in the molecule.

Table 10. Kinetics of the thermal decomposition of $R^1N(NO_2)R^2$ in dibutyl phthalate solution[53].

R^1	R^2	Δ*T*, °C	10^5k, s^{-1} (at 210 °C)	E_a, kcal $mole^{-1}$	*A*, s^{-1}
CH_3	$(CH_2)_2COOCH_3$	200–230	2.89	40.4	$10^{13.77}$
CH_3	$(CH_2)_2CN$	190–230	2.57	41.9	$10^{14.43}$
CH_3	CH_2OCH_3	190–230	2.34	40.9	$10^{13.89}$
$(CH_2)_2COOCH_3$	$(CH_2)_2COOCH_3$	210–250	1.78	40.7	$10^{13.70}$
$(CH_2)_2CN$	$(CH_2)_2CN$	210–250	1.46	41.3	$10^{13.92}$
CH_3	$(CH_2)_2COOH$	200–230	3.40	40.8	$10^{14.03}$
$(CH_2)_2COOH$	$(CH_2)_2COOH$	200–240	4.05	40.8	$10^{14.07}$

A systematic investigation of the decomposition of several substituted dialkylnitramines in 5% solution in dibutyl phthalate has shown[53] that variation in the substituents has very little effect on the kinetics (Table 10), which is characteristic of the thermal decomposition of nitramines in general. Nevertheless, a correlation was obtained between structure and reactivity (except for the last two examples whose decomposition kinetics were apparently influenced by ionisation of the carboxyls):

$$\lg k = -(0.495\pm0.02)\ (\sigma^*_{R^1}+\sigma^*_{R^2}) - (4.34\pm0.01)\ (r=0.982,\ S_y=0.028,\ n=6).$$

As in the tetryl series the values of the activation parameters and the sign of the constant ρ* again support rupture of an $N-NO_2$ bond in the first stage.

Manometric and derivatographic methods have been used[60] for a kinetic study of the thermal decomposition of ferrocenylmethylnitramines $FcCH_2N(NO_2)R$ (where Fc = ferrocenyl and $R = CNCH_2CH_2$, $CH_3C(NO_2)_2CH_2CH_2$, $FcCH_2$) in 2% solution in dibutyl phthalate. The second of these compounds follows a first-order law up to 50% decomposition, but the other two show slight autocatalysis. Table 11 lists the kinetic parameters of the initial stages calculated on the assumption that they are described by a first-order equation. The activation parameters for decomposition of the latter two compounds are closely similar to those for other nitramines,

from which it was concluded[60] that they decompose with rupture of an N–NO_2 bond in the first stage. The cyanoethyl compound decomposes appreciably more rapidly, which is attributed[60] to a different mechanism: the first stage involves rupture not of an N–N but of a C–N bond.

Table 11. Kinetics of the thermal decomposition of $FcCH_2N(NO_2)R$.[60]

R	ΔT, °C	10^4k, s^{-1} (at 170 °C)	E_a, kcal $mole^{-1}$	A, s^{-1}
CH_2CH_2CN	160–180	1.29	42.9	$10^{17.26}$
$CH_2CH_2C(NO_2)_2CH_3$	180–200	$6.30\cdot10^{-2}$	36.8	$10^{12.96}$
$FcCH_2$	190–200	$3.16\cdot10^{-2}$	38.5	$10^{13.49}$

In the Reviewers' opinion, however, there are insufficient grounds for such a conclusion, and it is more reasonable to suppose that the cyanoethyl derivative, like the other nitramines, breaks down with rupture of the N–NO_2 bond as the rate-determining stage. This view can be supported by the absence of obvious differences between cyanoethyl and the other two substituents that could cause such a sharp change in reaction mechanism. The cyanoethyl derivative decomposes with slight autocatalysis, so that the observed rate constant evidently does not characterise solely the first step. In view of the narrow temperature range of the measurements, the observed activation parameters may therefore differ markedly from those representing the primary step. Furthermore, the value $E_a = 42.9$ kcal $mole^{-1}$ in Table 11 is closely similar to those given above for other nitramines.

Derivatographic investigation of ferrocenylmethylnitramines[60] revealed several exothermic peaks, indicating that decomposition involved a series of consecutive reactions, but their nature was not studied.

Study of the decomposition of 2,4,6-trinitro-2,4,6-triazaheptamethylene diacetate by differential scanning calorimetry[33] gave the activation energy 53 ± 5 kcal $mole^{-1}$. The fewness of the experimental results makes any interpretation of this value difficult.

6. Dina

Dina (nitraminodiethyl dinitrate) contains different reactive functional groups—nitrimino and two nitrato—each of which can influence the kinetics of thermal decomposition in its own way.

Kinetic study by manometric, gravimetric, and calorimetric methods with small quantities in the reaction vessel (in the manometric experiments $m/V = 10^{-4}$ g cm^{-3}) at 150 to 170 °C showed[61] a first-order reaction with $E_a = 45.0$ kcal $mole^{-1}$ and $A = (3.8–4.8) \times 10^{18}$ s^{-1} (depending on the mode of measurement). These kinetic parameters were used[62] to calculate those of thermal explosion. Good agreement was found between calculation and experiment.

However, later research showed[63] that the decomposition of dina has more complicated kinetics: with sufficiently high m/V ratios at sufficiently low temperatures the reaction is autocatalytic, the more strongly so the higher the ratio and the lower the temperature. With decrease in the ratio and rise in temperature, however, autocatalysis becomes increasingly weaker, and finally disappears altogether. Thus with $m/V = (5–10) \times 10^{-4}$ g cm^{-3} at 160 °C the rate of decomposition falls monotonically during the reaction, but more slowly and not in conformity with a first-order law: in other words, if the process is described formally by a first-order equation, the observed rate constant increases during the reaction. The first order reported in Ref.61 was apparently due precisely to the use of low m/V ratios (10^{-4} g cm^{-3}) at high temperatures (150–170 °C).

The dependence of the rate of decomposition of dina on the m/V ratio indicates the participation of a gaseous product in the rate-determining stage. This is most probably nitrogen dioxide, which, as we have noted, tends to oxidise the nitramino-group. Indeed, with increase in the ratio and fall in temperature (i.e. on passing to conditions of appreciable autocatalysis) the content of this gas among the reaction products diminishes[63], which can be attributed to an increasing role of redox processes involving it under conditions ensuring autocatalysis.

Detailed experiments with additions of water revealed[63] that the autocatalysis is probably largely due to acid hydrolysis of dina, which becomes more intense with accumulation of water, nitrogen dioxide, and nitric acid. In this respect dina resembles many other nitric esters, in particular nitroglycerin. However, there is no complete analogy with the latter, since the above redox processes play an important part in the decomposition of dina, which also contains a nitramino-group readily oxidised by nitrogen dioxide and perhaps nitric acid.

The complicated character of the thermal decomposition of dina probably prevents determination of the kinetic parameters of the first step even from the initial rates; the rate constants of the initial stage of decomposition themselves are obviously effective values, and depend on the experimental conditions. It is therefore not surprising that the activation parameters obtained[63] (on the assumption of a first-order equation) differed somewhat from those in Ref.61: with $m/V = (5–20) \times 10^{-4}$ g cm^{-3} at 100–170 °C, the activation energy and the pre-exponential factor were respectively 42.0 kcal $mole^{-1}$ and 10^{17} s^{-1}; with $m/V = (6–12) \times 10^{-2}$ g cm^{-3} at 70–90 °C the corresponding values were 41.5 and 10^{16}.

Subsequent research has confirmed and developed the earlier results[61,63]. The kinetics of the decomposition of dina has been studied[64] calorimetrically with very high m/V ratios (with the reaction vessel almost completely filled): the reaction velocity exceeds some hundredfold the value when $m/V = 10^{-4}$ g cm^{-3}, which is fully consistent with the accelerating role of gaseous reaction products. Kinetic curves for the evolution of heat under isothermal conditions between 103 and 111 °C are complicated with two maxima, which indicates the occurrence of two processes separated in time and responsible for the acceleration of decomposition; they have activation energies of 34 and 32 kcal $mole^{-1}$. The observed activation energy diminishes non-uniformly with the degree of decomposition over the range $\eta = 0.1–0.45$, after which it remains unchanged at 32 kcal $mole^{-1}$. The conclusion[64] that two processes accelerate the thermal decomposition of dina is consistent with a contribution[63] by acid hydrolysis and redox stages to this reaction.

The kinetics of decomposition has also been investigated[65] calorimetrically over the pressure range 0.05–5 atm. A rise in pressure favours dissolution of gaseous products in liquid dina, and according to the above discussion should accelerate the reaction. This is indeed observed, with the activation energy and pre-exponential factor (45.0 kcal $mole^{-1}$ and 3×10^{18} s^{-1}), obtained at 0.05 atm on the assumption of a first-order reaction, showing good agreement with the above values[61]. Rise in pressure to 1 atm is accompanied by

gradual increase in the contribution by gaseous products to the overall reaction, with a consequent fall in the activation energy to 35 kcal mole^{-1} and in the pre-exponential factor to 2.5×10^{13} s^{-1}. Further rise in pressure to 5 atm does not affect the activation energy, but the rate constant continues to increase somewhat (owing to the pre-exponential factor). The kinetic parameters for 1 atm were used[65] to calculate parameters of thermal explosion in good agreement with experimental values.

Thermographic investigation of the decomposition of dina gave heating curves[66] with two exothermic peaks, indicating as before[64] two time-separated reactions accelerating the decomposition. A computer simulation was based on the simplified formal scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad (1)$$

$$A + B \xrightarrow{k_3} 2B + C \quad (2)$$

Stage (1) represents a series of consecutive reactions (perhaps $B = NO_2$) and stage (2) an autocatalytic process (perhaps acid hydrolysis). Activation energies E_1–E_3 corresponding to the rate constants k_1–k_3 were obtained of 43.8, 28.6, and 28.7 kcal mole^{-1}, with corresponding pre-exponential factors A_1–A_3 of 1.1×10^{18}, 4.3×10^9, and 4.3×10^{11} s^{-1}. The kinetic parameters corresponding to the stage A → B are closely similar to values observed previously[61,63], and those corresponding to the other two stages to values observed at high m/V ratios[64] and under high pressures[65].

The macrokinetic characteristics of the thermal decomposition of dina have been studied[67] also by impulse calorimetry.

It was suggested[63] that the primary stage in the thermal decomposition of dina, as of other nitric esters, involves rupture of the O–NO_2 bond. However, it must be recalled that in the gas phase simple nitric esters and nitramines have closely similar activation parameters: i.e. nitrato- and nitramino-groups are similar in reactivity. Furthermore, the above activation parameters for dina[61,63], though not fully representing the primary step, are nevertheless closely similar to corresponding values for other nitramines. Thus the nature of the first stage in the thermal decomposition of dina remains an open question.

7. Nitramides and *N*-Nitrocarbamates

In 1955 White showed[68] that heating *N*-n-butyl-*N*-nitroacetamide in tetrachloromethane solution at 77 °C for 15 h gives n-butyl acetate (in 75% yield) with acetic acid and but-1-ene (each in 23% yield) as well as nitrous oxide. This reaction was subsequently[69,70] extended to a wide range of nitramides $R^1N(NO_2)CO.R^2$ and *N*-nitrocarbamates $R^1N(NO_2)COOR^2$ (where R^1 = Alk and R^2 = Alk, Ar). By analogy with nitrosamides, which by that time had been studied in detail (for reference see Refs.68–70), a reaction mechanism with intermediate formation of a diazoxy-ester was suggested:

$$R^1N(NO_2)C(O)R^2 \rightarrow [R^1N{=}N^+(O^-)OCR^2] \cdot$$

This intermediate is unstable, and can decompose in two ways:

$$[R^1N{=}N^+(O^-)OCR^2] \rightarrow R^1OC(O)R^2 + N_2O$$

$$[R^1N{=}N^+(O^-)OCR^2] \rightarrow R^2COOH + N_2O + \text{Alkene},$$

where the alkene corresponds to detachment of a hydrogen atom from R^1. Thermal decomposition is accompanied by isomerisation. For example[70] *N*-isobutyl-3,5-dinitrobenzonitramide in tetrachloromethane solution at 76 °C gives not only isobutyl 3,5-dinitrobenzoate but also the corresponding s-butyl and t-butyl esters in respective yields of 16% and 1–3% relative to the isobutyl compound. A weighty argument in support of the suggested mechanism was that the diazoxy-ester was obtained *in situ* by an independent method, and on decomposition gave the same products as did the corresponding nitramide.

Table 12. Rate constants for the thermal decomposition of nitramides, nitrosamides, and nitrocarbamates[71].

N-Nitro-compound	Solvent	Temp., °C	k, s^{-1}
n-$C_4H_9N(NO)COCH_3$	xylene	90	$7.59 \cdot 10^{-3}$
$C_2H_5N(NO_2)COC_2H_5$	decane	90	$2.70 \cdot 10^{-4}$
n-$C_4H_9N(NO)COOCH_3$	dodecane	90	$4 \cdot 10^{-6}$
n-$C_4H_9N(NO_2)COOCH_3$	decane	90	$7.4 \cdot 10^{-8}$
iso-$C_3H_7N(NO)COCH_3$	xylene	60	$4.2 \cdot 10^{-3}$
s-$C_4H_9N(NO)COOCH_3$	dodecane	90	$2 \cdot 10^{-4}$
s-$C_4H_9N(NO_2)COOCH_3$	decane	90	$1.86 \cdot 10^{-6}$
t-$C_4H_9N(NO)COOCH_3$	CH_2Cl_2	0	10^{-2}
t-$C_4H_9N(NO_2)COOCH_3$	decane	0	$4.4 \cdot 10^{-10}$
t-$C_4H_9N(NO_2)COOCH_3$	decane	90	$7.52 \cdot 10^{-5}$
$(C_2H_5)CN(NO_2)COOCH_3$	heptane	90	$1.65 \cdot 10^{-3}$

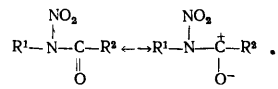
Table 13. Activation parameters for the thermal decomposition of nitrocarbamates, nitramides, and nitrosamides[71].

N-Nitro-compound	Solvent	E_a, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.
n-$C_4H_9N(NO_2)COOCH_3$	decane	34.3±0.5	−2.4
s-$C_4H_9N(NO_2)COOCH_3$	decane	30.8±0.2	−4.6
t-$C_4H_{19}N(NO_2)COOCH_3$	decane	28.8±1.2	−2.2
t-$C_4H_9N(NO_2)COOCH_3$	acetonitrile	26.2±0.2	−3.7
$(C_2H_5)_3CN(NO_2)COOCH_3$	heptane	25.9	−2
$C_2H_5N(NO_2)COC_2H_5$	heptane	27.8±1.5	−2.5
n-$C_4H_{19}N(NO)COCH_3$	xylene	29.0	—
$C_6H_5CH_2N(NO)COCH_3$	pseudocumene	28.2	—
$C_6H_5CH_2N(NO)COC(CH_3)_3$	pseudocumene	21.4	—
cyclo-$C_6H_{11}N(NO)COCH_3$	pseudocumene	23.3	—

A detailed kinetic investigation[71] of the thermal decomposition of several nitramides and nitrocarbamates was directed mainly at the influence of structure on reactivity. Decomposition followed a first-order equation, the rate presumably[71] determined by the first stage, i.e. formation of the diazoxy-ester. Tables 12 and 13 include for comparison data on related *N*-nitro-compounds. It is evident that reactivity is indeed very strongly dependent on structure. Qualitative explanations were based[71] on the view that the greater thermal stability of nitrocarbamates than of nitramides[70] was due to enhancement of the resonance stabilisation of the former by the alkoxy-group:

$$R^1{-}N(NO_2){-}C(O){-}O{-}R^2 \longleftrightarrow R^1{-}N(NO_2){-}C^+(O^-){-}O{-}R^2 \longleftrightarrow R^1{-}N(NO_2){-}C(=O^+){-}O^-{-}R^2 \cdot$$

The resonance form indicated on the extreme right is absent from nitramides:



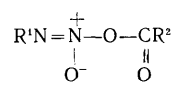
Since the transition state involves little or no resonance interaction of the alkoxy-group, the lower energy of the ground state of nitrocarbamates than of nitramides leads to a lower activation energy of decomposition of the latter.

Thermal decomposition of nitrocarbamates becomes significantly more rapid with increase in size of the substituent R^1, which may be due to non-bonding interactions of R^1 with nitro and alkoxycarbonyl groups. To a first approximation the energy of the transition state is independent of the size of R^1 (owing in particular to the near perpendicularity of the alkoxycarbonyl group to the plane of the molecule); yet as a consequence of the above non-bonding interactions the energy of the ground state is proportional to the size of R^1. As a result, increase in size lowers the activation energy of the reaction and causes "steric acceleration".

Nitramides and *N*-nitrocarbamates are thermally more stable than the corresponding *N*-nitroso-compounds. This may be partly due to greater nucleophilicity of the nitroso- than of a nitro-oxygen atom. Another explanation may be the possibility of non-bonding interaction between R^1 and a nitro-oxygen atom in the transition state. All the above factors are energetic in character, and do not affect the entropy of activation.

The above results show that nitramides and *N*-nitrocarbamates differ significantly in thermal stability, mechanism of decomposition, and dependence of reactivity on structure from the nitramines discussed previously. Since the first step in breakdown of the first two groups—formation of a diazoxy-ester—involves rupture of an NO_2.N–CO bond, it must be supposed that this bond has been weakened by the carbonyl or carboxyl group. Similar weakening is absent from nitramines, so that they decompose by a different mechanism, although it must be borne in mind that Robertson's mechanism[14,26] for the decomposition of hexogen with cleavage of the ring (subsection 1) resembles the mechanism of the decomposition of nitramides and nitrocarbamates.

The mechanism of decomposition of the diazoxy-ester



is unknown. It may consist in elimination of nitrous oxide with formation of R^1 and R^2COO radicals, which then interact in the solvent cage.

8. *N*-Fluoronitramines

Graff **et** al.[72–74] made a series of kinetic investigations on the thermal decomposition of the isomeric *N*-fluorobutylnitramines. The first study already showed[72] that *N*-fluoro-n- and -s-butylnitramines have about the same reactivity, whereas the t-butyl compound decomposes more rapidly by a factor of 20.

A detailed kinetic investigation[73] indicated a first-order equation with parameters listed in Table 14. The course of decomposition is appreciably influenced by the nature of the solvent. Thus in ethylcyclohexane, tetrachloromethane, and a mixture of the latter with ethanol (2.5 : 1) the rate constants at 61.7 °C are (in 10^{-4} s^{-1}) respectively 14.62, 8.41, and 5.64. Table 14 shows that the activation parameters are still more strongly influenced by the nature of the solvent.

Table 14. Kinetics of the thermal decomposition of $RN(NO_2)F$ in solution[73].

T, °C	10^4k, s^{-1}	*T*, °C	10^4k, s^{-1}
R = n-C_4H_9* ($\Delta H^{\neq}$ = 26.3±0.6 kcal mole^{-1}; $\Delta S^{\neq}$ = 0.9 e.u.)		R=R = t-C_4H_9* ($\Delta H^{\neq}$ = 31.6±1.5 kcal mole^{-1}; $\Delta S^{\neq}$ = +22,7 e.u.)	
70.1	2.13±0.10	56.2	6.53±0.20
77.2	4.37±0.26	58.6	9.72±0.97
80.8	6.15±0.20	61.3	13.63±6.60
83.3	8.53±0.40	66.1	20.00±0.28
86.4	12.08±0.42	77.3	63.33±3.3
R = s-C_4H_9* ($\Delta H^{\neq}$ = 29.7±1,0 kcal mole^{-1}; $\Delta S^{\neq}$ = +10,9 e.u.)		R R = t-C_4H_9** ($\Delta H^{\neq}$ = 22,9±0,4 kcal mole^{-1}; $\Delta S^{\neq}$ = 4,6 e.u.)	
71.4	1.99±0.10	55.6	4.26±0.18
72.3	3.21±0.38	60.0	7.54±0.18
75.5	3.87±0.21	63.1	9.71±0.38
81.4	7.55±0.20	66.4	13.39±0.77
84.9	12.22±0.83		

*Dissolved in ethylcyclohexane.
**Dissolved in tetrachloromethane.

Table 15. Products of the thermal decomposition of *N*-fluoro-t-butylnitramine in tetrachloromethane solution[73].

Compound	*s*, %*
Nitrous oxide	5.5
Methylpropene	1.6
Acetone	5.7
2-Methyl-2-nitropropane	17.5
2-Fluoro-2-methyl-1-nitropropane	19.5
2-Methyl-1-nitropropene	5.6
2-Methyl-1-nitropropan-2-ol	24.2

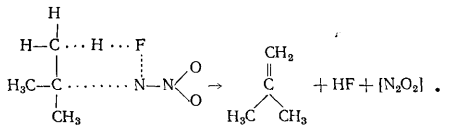
*s = relative area of chromatographic peak.

Table 15 gives the composition of the thermal decomposition products of *N*-fluoro-t-butylnitramine found chromatographically. The relative area of a chromatographic peak can be regarded to a first approximation as the proportion of the given product in the mixture. Besides the compounds listed in Table 15 hydrogen fluoride, and α-substituted isobutyraldehyde, and ammonium hexafluorosilicate were detected among the decomposition products. Nitrogen is not formed in the reaction. In special experiments on the decomposition of this nitramine labelled with nitrogen-15 in the nitro-group (5.64%) the isotope was detected in nitrous oxide (3.2%), ammonium hexafluorosilicate (4.02%), 2-fluoro-2-methyl-1-nitropropane (4.07%), and 2-methyl-1-nitropropan-2-ol (4.01%).

The complicated composition of the decomposition products led to the suggestion[73] that two mechanisms—molecular, involving a five-membered activated complex, and radical—might operate simultaneously. On the reasonable assumption that the former mechanism is characterised by a negative and

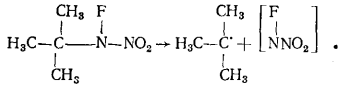
the latter by a positive entropy of activation, it may be concluded that the contributions by these mechanisms to the overall process should depend on the nature of the solvent. According to the results in Table 14 a radical mechanism predominates in ethylcyclohexane, and a molecular mechanism in tetrachloromethane.

The molecular mechanism can be represented by the scheme



It readily explains the formation of methylpropene and hydrogen fluoride, but encounters several objections. Firstly, little methylpropene is formed (Table 15), although a molecular mechanism can be expected to predominate particularly in tetrachloromethane solution. Secondly, this mechanism does not explain the formation of other decomposition products, in particular 2-methyl-2-nitropropane. Thirdly and finally, formation of nitric oxide—not nitrous oxide—must be expected from the above scheme.

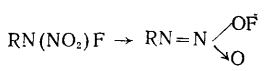
The radical mechanism was written[73]



Several special experiments were undertaken[73] to substantiate a radical mechanism. It was shown in particular that acrylonitrile readily polymerises in the presence of the isomeric *N*-fluorobutylnitramines. However, formation of the t-butyl radical could not be proved: it was not captured by the stable galvinoxyl radical; and 2,2,3,3-tetramethylbutane, which usually appears in the presence of t-butyl radicals, was not detected among the decomposition products. Finally, decomposition of the isomeric *N*-fluorobutylnitramines in toluene solution is not accompanied by formation of bibenzyl.

In the Reviewers' opinion the chief objection to a radical mechanism of decomposition lies in the low activation energies (Table 14), which do not correspond to the bond strengths in *N*-fluoronitramines: in fact the energy of dissociation of the N–F bond is close to 70 kcal mole^{-1},[72] the stability of the N–NO_2 bond has been much discussed in the preceding sections, and the C–N bond is in any case stronger than the N–N bond.

Thus the mechanism of the thermal decomposition of *N*-fluoronitramines remains in considerable measure obscure. As working hypothesis for future research it may be supposed that the mechanism is identical with that discussed in the preceding subsection for the decomposition of nitramides and nitrocarbamates. Furthermore, it would have been interesting to examine the possibility of a mechanism involving a rearrangement analogous to formation of the *aci*-form of nitro-compounds:



followed by elimination of nitrous oxide.

Analysis of the products of the thermal decomposition of *N*-fluoro-t-butylnitramine was extended to the n- and s-butyl derivatives (Tables 16 and 17).[74] Several unidentified compounds are also found in all three cases. Comparison of Tables 15–17 indicates that the n-butyl isomer on decomposition gives only n-butyl derivatives, whereas the s- and t-butyl isomers give both mono- and di-substituted butane derivatives. From this it was concluded[74] that the decomposition of the s- and t-butyl isomers, but not that of the n-butyl compound, may involve the above molecular mechanism.

Table 16. Products of the thermal decomposition of *N*-fluoro-n-butylnitramine[74].

Compound	s, %
Nitrous oxide	0.5
n-Butyl nitrate	10.3
1-Nitrobutane	16.5
n-Butyl butyrate	50.0
Butyric acid	5.9
1,1-Dinitrobutane	3.0

Table 17. Products of the thermal decomposition of *N*-fluoro-s-butylnitramine[74].

Compound	s, %
Nitrous oxide	2.3
But-1-ene	1.3
Butan-2-one	2.3
s-Butyl nitrate	2.0
2-Nitrobutane	37.0
1-Nitrobut-1-ene	9.8
2,2-Dinitrobutane	28.5

9. Primary Nitramines

Primary nitramines differ from secondary nitramines in the presence of a hydrogen atom attached to the amino-nitrogen atom: i.e. they have the general formula $RNHNO_2$. They are less thermostable than the secondary compounds, as is evident in the activation parameters of their decomposition.

The thermolysis of methylenedinitramine (medina) over the range 110–130 °C follows a first-order equation with activation energy 35.4 kcal mole^{-1} and pre-exponential factor $10^{15.6}$ s^{-1}.[75] Ethylenedinitramine (edna) also decomposes according to a first-order law, with corresponding parameters 30.5 kcal mole^{-1} and $10^{12.8}$ s^{-1} at 184–254 °C.[48]

The lower thermal stability of primary than of secondary nitramines suggests a difference in the mechanism of decomposition, most probably due to the mobile hydrogen atom of the primary nitramino-group.

Products of the thermal decomposition of medina and edna are similar in composition, consisting mainly of nitrous oxide and the corresponding aldehyde, respectively formaldehyde and acetaldehyde. Thus the thermal decomposition of edna follows essentially the stoichiometric equation[48]

$$C_2H_8N_4O_4 \rightarrow 2N_2O + CH_3CHO + H_2O.$$

It is interesting that the decomposition of primary nitramines in aqueous solution follows the same stoichiometric equation: for medina[76]

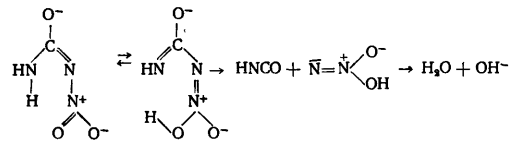
$$CH_2(NHNO_2)_2 \rightarrow 2N_2O + CH_2O + H_2O,$$

and for *N*-nitrourea[77]

$$H_2NCONHNO_2 \rightarrow HNCO + N_2O + H_2O.$$

However, ethylene glycol has also been detected[78] in the decomposition of edna in aqueous solution and in the solid phase (this paper[78] mentions that it was first detected in decomposition in aqueous solution by Franchimont and Klobbie as early as 1887).

Primary nitramines are weak acids[79], and the reactive form undergoing decomposition may correspond to the anion RN^-NO_2. Thus for nitrourea the thermolysis mechanism

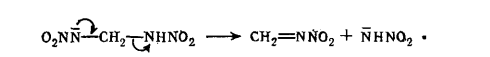


was suggested[77], with an activation energy of 27.5 kcal mole^{-1} and an activation entropy of 7.7 e.u. (pH 10). Since this compound is a nitramide, the typical mechanism (subsection 7)

$$H_2NC(O)NHNO_2 \rightarrow H_2NC(O)ON(\rightarrow O)=NH \rightarrow N_2O + H_2NCOOH \rightarrow HNCO + H_2O$$

is also possible. However, it is not altogether consistent with the kinetic results: Table 13 shows that the thermal decomposition of nitramides has negative activation entropies. Nevertheless, this mechanism cannot finally be rejected.

For the decomposition of medina in aqueous solution a mechanism has been suggested[76] analogous to the first of the above mechanisms for urea:



Subsequent processes may yield the final products:

$$CH_2=NNO_2 \rightarrow CH_2O + N_2O;\ \bar{N}HNO_2 \rightarrow N_2O + OH^-.$$

A similar scheme is in principle possible for edna:

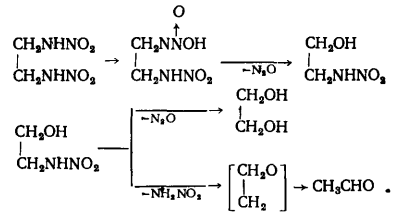
$$O_2N\bar{N}CH_2CH_2NHNO_2 \rightarrow \bar{N}HNO_2 + CH_2=CHNHNO_2;$$
$$CH_2=CHNHNO_2 \rightarrow N_2O + CH_2=CHOH;\ CH_2=CHOH \rightarrow CH_3CHO\ .$$

As primary nitramines give the same products of decomposition in the melt and in solution, identical mechanisms can be assumed. In the melt, however, the degree of ionisation is smaller and the concentration of the anionic form lower, which should tend to slow down decomposition. Primary nitramines do in fact decompose in the melt with measurable velocities at significantly higher temperatures than in aqueous solution.

In a medium of low polarity ionisation is almost completely suppressed, and a different mechanism of decomposition should operate. This apparently occurs when ring-substituted *N*-nitroanilines decompose in octan-2-ol solution[80]. Reaction takes place at a very high temperature (120 °C), nitrous oxide is not formed, and the products are nitrogen, water, the corresponding aromatic hydrocarbon, and octan-2-one. A mechanism involving intermediate formation of the *aci*-form of the nitramine and aryl radicals was suggested (RH = solvent, nitramine, or product molecule):

$$ArNHNO_2 \rightleftarrows ArN=N(\rightarrow O)OH\ ,$$
$$ArN=N(\rightarrow O)OH \rightarrow \dot{O}H + Ar\dot{N}=\bar{N}O \longleftrightarrow ArN=N\dot{O}\ ,$$
$$ArN=N\dot{O} + RH \rightarrow ArN=NOH + \dot{R}\ ,$$
$$ArN=NOH \rightarrow \text{Products of ionic cleavage}\ ,$$
$$2ArN=NOH \rightarrow ArN=NON=NAr + H_2O\ ,$$
$$ArN=NON=NAr \rightarrow \dot{A}r + N_2 + ArN=N\dot{O}\ .$$

A similar mechanism, also involving formation of the *aci*-form, was suggested[78] for the thermal decomposition of edna, in order to explain the formation of both acetaldehyde and ethylene glycol:



In neutral aqueous solution edna decomposes according to a first-order equation with activation energy 32.5 kcal mole^{-1} and pre-exponential factor 10^{13} s^{-1}; increasing the acidity of the medium accelerates the reaction[76].

Kinetic study[60] of the thermal decomposition of ferrocenylmethylnitramine $FcCH_2NHNO_2$ in 2% solution at 110–130 °C shows a first-order reaction with activation energy 33.2 kcal mole^{-1} and pre-exponential factor $10^{14.98}$ s^{-1}. Decomposition of this compound thus has the same activation parameters as that of other primary nitramines, and apparently the same mechanism.

IV. DECOMPOSITION BELOW THE MELTING POINT

An important feature of the decomposition of organic explosives and in particular of nitramines at temperatures below the melting point is the formation during the reaction either of liquid products in which the initial substance dissolves or of a eutectic mixture of this compound with the products. As a consequence the process has already acquired a two-phase character soon after the start: reaction takes place in both solid and liquid phases. The quantity of liquid products increases during decomposition, and with a consequent gradual increase in the role of the liquid-phase process and decrease in that of the solid-phase process. On the other hand, the great practical experience that has now accumulated indicates that a given compound decomposes considerably more rapidly in the liquid than in the solid phase (see below). Therefore the increasing role of the liquid-phase process during decomposition should inevitably lead to autocatalysis. And indeed the autocatalytic character of decomposition below the melting point is a general feature of organic explosives, including nitramines. A formal kinetic description has been given[81,82] for such processes.

1. Tetryl

Historically tetryl was the first nitramine whose decomposition below the melting point was investigated in detail. The fact that the solid decomposes considerably more slowly than the liquid was noted as early as the 1920s.[1,2] On the basis of Lewis's ideas Hinshelwood suggested that the difference in behaviour was due merely to a difference in activation energy, in turn equal to the latent heat of fusion[2]. Simple calculation then indicates that liquid tetryl should decompose more rapidly than the solid by a factor of at least 1300, but in fact the ratio of the reaction velocities is considerably smaller at 50–100. From this Hinshelwood made the important deduction that the initial solid tetryl contained impurities (and possibly catalysts) already causing partial

occurrence of the liquid-phase reaction in the very first stages of decomposition.

Hinshelwood's calculation was based on assumptions, of course, that nowadays might be regarded as oversimplified (if only because the topochemical character of solid-phase decomposition was completely ignored). Nevertheless, his main conclusion concerning the possible role of impurities in inducing liquid-phase decomposition below the melting point seems valid. Moreover, this conclusion applies not only to tetryl but also to other solid organic compounds. Therefore the possibility of partial occurrence of the reaction in the liquid phase must always be taken into account in the investigation of decomposition below the melting point. Such possibility creates considerable difficulties in research on the decomposition of solids, for methods of monitoring small quantities of impurities and removing them from solid organic compounds have been inadequately developed.

In the above work[2] the decomposition of tetryl was studied at low degrees of conversion (when the contribution of autocatalysis by picric acid was small), in conformity with Farmer's view[1] that autocatalysis in decomposition below the melting point may be due to appearance of a eutectic mixture of tetryl with its decomposition products. Experimental results showed good agreement with calculation, despite an error in the latter[2] that has since been corrected[82].

Table 18. Activation parameters for the thermal decomposition of tetryl below the melting point.

E_a, kcal mole^{-1}	A, s^{-1}	Ref.
52.0	$10^{22.5}$	[3.53]*
36.6	$10^{12.7}$	[81]**
54.9	—	[31]

*Calculated from experimental results in Ref.1.

**In Ref.81 unpublished results are quoted that had been calculated by Wiseman from experimental data in Ref.1.

On the assumption of first order in the initial stage several calculations were made, from the initial segments of the kinetic curves, of the activation parameters of the thermal decomposition of tetryl. Table 18 shows marked discrepancies between results obtained by different authors, which may have several explanations. One lies in the above possibility of an indefinite contribution by liquid-phase decomposition to the overall process. Furthermore, as is evident from the footnotes to Table 18, in several cases the estimates were based on the few results obtained by Farmer[1], moreover within a narrow temperature range. It must also be borne in mind that the measured kinetic parameters may be influenced by the experimental conditions, in particular the extent to which the reaction vessel is filled[83,84]. As a last reason, perhaps the most important, Hall[33] found, on processing experimental results obtained by various workers on thermal decomposition both above and below the melting point, that the Arrhenius law breaks down near this temperature (more precisely for a few degrees below it): whereas at temperatures substantially below the melting point the slope of the Arrhenius relation does not greatly differ from the slope for decomposition above the melting point, so that differences in rates above and below this point are determined mainly by the pre-exponential factor, the slope increases abruptly in the immediate vicinity of the melting point, and hence the observed activation energy and pre-exponential factor increase markedly. Thus the observed activation parameters for the thermal decomposition of tetryl depend on the temperatures (relative to the melting point) at which the measurements were made. In fact breakdown of the Arrhenius law in the vicinity of the melting point is evident not only with tetryl: it is very general in character, and has been observed in the decomposition of several solids[85]. This interesting phenomenon has not yet found a rigorous explanation.

It follows from the above discussion that kinetic results for the thermal decomposition of tetryl below the melting point do not admit of a simple physical interpretation. The main details of the mechanism of the solid-phase decomposition of tetryl also remain obscure.

2. Hexogen

Decomposition at temperatures below the melting point (and also above this temperature) has been studied in greater detail for hexogen than for other nitramines. The early work on the decomposition of solid hexogen[81,35,36] already established that the kinetics follows the sigmoid law characteristic of solid-phase processes. The results that have now accumulated show that the decomposition of hexogen is extremely complicated, being subject to the influence of various factors, which of course makes interpretation of the kinetic results difficult.

The influence on decomposition of the geometry of the specimen, more precisely of the accessibility of its surface to the surrounding atmosphere, has been studied[86] in experiments with hexogen either scattered on the surface of the reaction vessel or placed in special tubes whose number was varied from one experiment to another, although the total quantity of hexogen was the same in every experiment. The construction of the tubes was modified in certain experiments, by making the outlet smaller or dividing the tube into two connecting chambers, containing the compound in its usual compact state and in an almost disperse state respectively. Change in the geometry of the specimen was found to have different effects on individual stages of the process. In any case, enhancing the accessibility of the specimen surface to the surrounding atmosphere shortens appreciably the induction period and accelerates decomposition.

It can thus be regarded as reliably established that gaseous reaction products influence the kinetics of the decomposition of hexogen. Detailed analysis of this effect led to the conclusion[86] that the gas phase contains substances that both catalyse and retard decomposition. Such compounds have been listed[35]: nitrogen dioxide in small quantities shortens the induction period, but in large quantities increases the initial rate of decomposition; nitric oxide in small quantities shortens the induction period but in large quantities lowers the initial rate; and oxygen appreciably lengthens the induction period.

Results were also obtained[35] indicating the role of reactions involving gaseous products: the process became slower as the reaction vessel was filled. The explanation was that reaction in the condensed phase was accompanied by gas-phase decomposition of partly vaporised hexogen, the role of the latter process being smaller the greater the m/V ratio. Estimates showed that, in order to explain the results, it was necessary to suppose that hexogen breaks down in the gas phase more rapidly than in the liquid by a factor of 100. This value agrees quite well with results[21] showing that the

decomposition of hexogen in the gas phase inhibited by nitric oxide takes place 10 times as rapidly as in solution; the uninhibited gas-phase reaction occurs more rapidly than in solution by factors of 30–40.

However, the arguments in Ref.35 encountered the objection[86] that with large portions of hexogen giving high m/V ratios it takes a long time to heat up the reaction vessel, and an appreciable proportion of the reaction takes place under non-isothermal conditions, which casts doubt on the correctness of the kinetic results. Thus the nature of the influence of the m/V ratio on the kinetics of the decomposition of hexogen cannot be regarded as finally elucidated. Incidentally, the above difference between rates of decomposition of hexogen in gas and liquid phases may be due to a cage effect.

Other work on the influence of gases and in particular gaseous decomposition products on the kinetics of the decomposition of hexogen[87] showed that nitrogen, carbon monoxide and dioxide, and nitrous oxide have some retarding effect; water slows down the reaction more strongly; nitric oxide, formaldehyde, and methanol accelerate the reaction; oxygen and nitrogen dioxide are inhibitors; and propene and toluene have no appreciable influence on the kinetics. A detailed study has been made of the accelerating effect of formaldehyde[88]. Yet other workers have obtained similar results[17]: nitrogen, carbon monoxide and dioxide, nitrous oxide, and water retard the reaction; nitric oxide also diminishes the rate of decomposition, but to a less extent, and formaldehyde accelerate the process.

The explanation given for the influence of nitrogen, carbon monoxide and dioxide, and nitrous oxide was that these gases prevented the vaporisation of hexogen and diminished the contribution by its gas-phase decomposition. However, when decomposition occurs in a vacuum[86], a part of the hexogen evaporates and settles on the walls of the reaction vessel: i.e. what was termed[86] a change in specimen geometry takes place. The role of this geometry was interpreted[86] as facilitation of the removal of reactive gaseous products from the surface of the specimen with increase in contact between the latter and the surrounding medium. Without objecting to this concept, we note nevertheless that a possible alternative explanation is that the role of heterogeneous reactions of gaseous products with the hexogen surface becomes greater (not smaller) with increase in such contact. It should be noted that with restricted contact between specimen and surrounding atmosphere (e.g. when the hexogen is enclosed in a narrow tube) a gaseous product formed within the specimen must first pass through it, before escaping into the atmosphere. However, the time required for such escape is brief, in any case considerably shorter than the characteristic time of the overall process of thermal decomposition.

The discrepancy in the results for the influence of nitrogen dioxide on the kinetics of the decomposition of hexogen can apparently be attributed to measurement of respectively the quantity of gas evolved[35] and the degree of conversion[87]. Since the quantity of gas evolved on the decomposition of hexogen increases in the presence of nitrogen dioxide[87], a greater quantity of gas evolved may correspond to a lower degree of conversion. Thus nitrogen dioxide apparently inhibits the decomposition of hexogen. The reasons for this phenomenon are not very clear. A possible cause is that nitrogen dioxide may be involved in two opposite processes—oxidation of the initial compound (accelerating effect) and recombination with amino-radicals arising in the primary step (inhibition)—as already discussed in connection with the gas-phase pyrolysis of nitramines[9]. The role of the latter effect on decomposition in a condensed phase may be enhanced by the cage effect. Another explanation of the inhibiting action of nitrogen dioxide is that condensed decomposition products accelerate the reaction[87], not only physically (by liquefaction) but also chemically. It is possible that nitrogen dioxide may react with the above condensed products and lower their catalytic activity. This deduction might in principle be tested by studying the influence on the thermal decomposition of hexogen exerted by condensed decomposition products previously treated with nitrogen dioxide, but such experiments have not been undertaken as far as the Reviewers are aware.

The accelerating influence of formaldehyde[86–88] may be at least partly due to its ready reduction of nitrogen dioxide to nitric oxide[89]. It is also possible that formaldehyde is able to react with hexogen itself, attacking it at a nitro-group[87].

The acceleration of the decomposition of hexogen under the influence of methanol may be closely connected with the above reactions. Methanol is able to reduce nitrogen dioxide, being oxidised to formaldehyde; furthermore, methanol may inhibit the oxidation of formaldehyde by nitrogen dioxide[87].

Nitric oxide like other gases somewhat retards decomposition by impeding evaporation[17], but it also has a chemical effect, being involved in secondary reactions and accelerating decomposition. The nature of these reactions is unknown. The view was expressed[35] that nitric oxide may yield the nitroso-analogue of hexogen, but in the absence of additional experiments this suggestion may be regarded as purely hypothetical.

An objection has appeared[86] to the above view[13–17] that hexogen undergoes slight vaporisation below the melting point with partial decomposition in the gas phase, the contribution of which to the overall process may be very considerable. All the observations could be explained[86] by the above influence (both accelerating and retarding) of gaseous decomposition products of hexogen on the kinetics of its decomposition. It was also concluded[86] that liquefaction during decomposition of solid hexogen also is unconnected with a purely gas-phase process.

Without going into the essence of the controversy, we note that there appears to be no direct disproof of either view. Moreover, we feel that these concepts are not mutually contradictory, and both gas-phase decomposition of vaporised hexogen and the influence of active gaseous products on decomposition of the solid must be accepted as possible. Greater clarity can be introduced into this question only by detailed kinetic investigation of the decomposition of hexogen solely in the gas phase and solely in the solid phase.

Several studies have been made on the important kinetic influence of crystal size on the solid-phase decomposition of hexogen. Grinding crystals of size 1–2 mm to 0.1 mm had no kinetic effect[35], and another worker[90] also found no kinetic effect of crystal size. Working with finer crystals[21] showed that at 170 °C the ground hexogen had grown to 0.003–0.01 mm after 10–20 min. Nevertheless, the ground material decomposed considerably more rapidly than a specimen with larger crystals. This can be explained both by enhanced reactivity of surface molecules of the crystal and by the above[86] influence of specimen geometry on decomposition kinetics. Thus the influence of crystal size on the kinetics of the decomposition of hexogen remains in considerable measure obscure: further research is required to clear up this problem.

Occluded solvents and gases are evolved before decomposition of hexogen begins, and therefore do not influence its course[90]. Preparation of the crystals in different ways, and also terminating the reaction by cooling the system, likewise

have no effect on the kinetics. Somewhat different results have shown[21] that acetone (the solvent from which hexogen had been recrystallised) could not be removed by drying, and its escape from the crystals during decomposition increased the observed rate of gas evolution. However, purification by sublimation combined with preliminary degasification enabled the effect of impurities of the kinetics to be eliminated. The difference between these sets of results[21,90] may be due to the different conditions—temperature, sample size, volume of reaction vessel—under which the kinetic measurements were made. The decomposition of hexogen is influenced[90] by solid additives (copper sulphate, carbazole) and also by ultraviolet irradiation.

Table 19. Activation parameters for the thermal decomposition of hexogen below the melting point.

Method	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Manometric	177—200	45.5±2.0	$10^{17.7\pm0.7}$	[81]*
Manometric	150—197	52.0	$10^{19.1}$	[35]
Manometric	170—198	43—63**	—	[91]
Manometric	170—197	44***	—	[88]
Ignition	—	52.4	—	[92]
—	—	41.5	$10^{14.5}$	[19]
Manometric	130—180	59.5	$10^{11.7}$	[20]
Manometric	140—190	40±1	—	[21]
Vibrational	22—85	(43.4—46.5)****	($10^{25.8}$—$10^{27.2}$) ****	[93]

*Unpublished results of Adams quoted in Ref.81.

**Depending on the geometry of the specimen and the segment of the kinetic curve.

***In the presence of formaldehyde.

****Depending on the experimental conditions.

Because of the complicated character of the thermal decomposition of hexogen the activation parameters (Table 19) have been calculated from the initial portions of the kinetic curves on the assumption that at low degrees of conversion reaction occurs mainly in the solid phase and is described by a first-order equation. Calorimetric data have also been published[94], but without kinetic parameters. The complexity of the process and the influence of numerous factors are especially evident in the results from Refs.88 and 91 (Table 19), according to which the activation parameters are strongly influenced by gaseous decomposition products. There is therefore every reason to suppose that the majority of the activation parameters in Table 19 are effective values characterising not a single but a whole set of reactions. The contribution by each reaction to the observed rate constant depends in general on the experimental conditions, so that the considerable scatter between the results obtained by different workers is not surprising.

Especially noteworthy are results[20,21] showing a departure from the Arrhenius law in the vicinity of the melting point, as has already been discussed in connection with tetryl. Breakdown of this law may be one reason for the high activation parameters in Table 19. Those from Refs.19—21 had been obtained over a temperature range within which the Arrhenius law applies, and if they in particular are assumed to represent the solid-phase process, it is at once evident how close are the activation energies of reactions in gas phase, solution, and solid state. This naturally suggests a common reaction mechanism, in particular that the rate-determining step in the solid phase is rupture of an $N-NO_2$ bond. The diminished pre-exponential factor from Ref.20 may be due to a cage effect or to the topochemistry of the reaction, in particular its localisation at non-equilibrium lattice defects.

Nevertheless, kinetic data alone are insufficient to prove a common mechanism of decomposition under different phase conditions, so that the alternative view of different mechanisms in gas and condensed phases[17,18] cannot be regarded as incorrect. In this connection especial attention should be paid to the concept of a definite mutual orientation of hexogen molecules in the crystal lattice, making possible bimolecular interaction between two hexogen molecules in the first stage of decomposition[37,87].

Physical aspects—the influence of crystal structure on molecular reactivity—are no less important than the above chemical aspects. As little work has been done on this problem applied to the decomposition of molecular crystals, we can welcome the use of X-ray diffraction and electron microscopy[20,95] to study physical phenomena (plastic deformation, elastic stresses) in the thermal decomposition of hexogen.

In concluding this subsection we note that research on decomposition under the influence of various physical factors—impact[96,97], electric field[98,99], vibration[100,93]—may assist understanding of the solid-phase process. Thus an electron spin resonance signal arises when hexogen is subjected to impact, which indicates the formation of free radicals during decomposition, although their nature was not revealed[96]. It was also concluded[96] that rupture of an $N-NO_2$ bond occurs in the rate-determining step. This was confirmed by later results[97], though they were based on the doubtful assumption that in hexogen a nitrogen–nitrogen bond is more stable than a carbon–nitrogen bond. The model adopted in this work[97] assumes the transfer of lattice phonons to vibrational degrees of freedom of the hexogen molecule during impact compression. Such a model provides an explanation for several observed features, in particular the slowing down of the thermal decomposition of hexogen with increase in hydrostatic pressure. It would have been interesting to develop this model to apply to the purely thermal (not impact) decomposition of nitramines.

3. Octogen

As octogen is an analogue of hexogen, its thermal decomposition exhibits similar features. This compound can exist in various polymorphic modifications[101], each with its own thermal stability, as will be shown below.

Like other solid explosives octogen decomposes autocatalytically[35,36]. The initial rate diminishes with increase in the m/V ratio[35]. As with hexogen, this effect can be attributed either to the involvement of active gaseous decomposition products or to a contribution by gas-phase pyrolysis of partly vaporised octogen to the overall reaction. The latter explanation is less probable in the case of octogen (at least in the absence of additional experiments), since it is less volatile than hexogen.

The gaseous decomposition products—nitrogen and oxides of nitrogen and carbon (Table 20)—have the usual composition for nitramines. The temperature dependence of the composition apparently indicates that these products are formed by secondary reactions. Each product is characterised by its own activation parameters, and its contribution to the overall rate depends on the temperature. Data on the isotopic composition of the decomposition products were given

in a paper[39] already mentioned in connection with liquid-phase decomposition.

Several studies have been made on the kinetic influence of crystal size. According to Maksimov[35] grinding crystals of size 1–2 mm down to 0.1 mm does not affect the initial rate of decomposition, but at the later stage of acceleration the fine crystals decompose more slowly. Visual observation showed that large crystals had retained their shape and transparency of being heated at 176 °C for 2–3 h: they began to become cloudy after 20–30 h, after the evolution of 0.5–1% of gases; but cracking began after 100–200 h (5% of gases).

Table 20. Composition of gaseous products of thermal decomposition of the β-modification of octogen (moles mole^{-1} octogen).[101]

Temp., °C	N_2O	N_2	NO	CO	CO_2	HCN	CH_2O
230	2.52	0.42	0.31	0.42	0.50	0.02	0.89
254	2.49	0.47	0.53	0.47	0.53	0.06	0.56

Table 21. Activation parameters for the thermal decomposition of octogen below the melting point.

Method (cryst. modification)	ΔT, °C	E_a, kcal mole^{-1}	A, s^{-1}	Ref.
Manometric	176–230	37.9	$10^{11.2}$	[35]
Thermal analysis (δ)	245–280	59–65*	—	[103]
DSC (α)	—	210	—	[33]
DSC (β)	—	180±15		[33]
Manometric (β)	150–170	36.0	$10^{10.8}$	[19]
		67.0	10^{25}	[20]
Manometric (α)	180–210	41.0	$10^{12.6}$	[20]
Derivatographic**	185–280	41.2	$2.2\cdot10^{14}$	[102]
Derivatographic***	160–250	27.0	$1.1\cdot10^{9}$	[102]
DSC	251–263	42±2	—	[34]
DTA	220–241	44.2–63.2 ****	—	[104]

*Depending on method of measurement.
**Crystal size 160–315 μm.
***Crystal size <50 μm.
****Depending on the temperature.

Different results have been obtained[102] by workers using finer crystal. Derivatographic investigation showed that octogen of mean crystal size 160–315 μm under non-isothermal conditions at 185–280 °C decomposes in a single stage. If, however, the octogen is ground to below 50 μm, the reaction occurs in two stages, the first of which has already begun at 160 °C. This was explained[102] in topochemical terms, by the effect of grinding in producing surface defects and dislocations possessing excess energy and hence enhanced reactivity. However, an alternative explanation is the involvement of active gaseous products, i.e. what has been termed the specimen geometry effect (subsection 2).

Table 21 shows a considerable scatter among the kinetic data obtained by different workers for the decomposition of octogen. The above complicating factors—role of gaseous decomposition products, appearance of a liquid phase during decomposition, breakdown of the Arrhenius law in the vicinity of the melting point—are partly responsible. Yet the aggregate of results reliably indicates the kinetic influence of the crystalline modification. This is supported also by the dependence of the thermal stability of octogen on its mode of recrystallisation[105] (though in this case the possible role of occluded solvent is not clear) and by vigorous decomposition of the δ-modification of octogen even at 150 °C.[106]

Despite the considerable scatter the results of several studies[19,20,34,35,102,104] show quite good mutual agreement, with activation energy ~40 kcal mole^{-1} and pre-exponential factor 10^{13} s^{-1}, values characteristic of the pyrolysis of nitramines in gas and liquid phases, which involves rupture of an N–NO_2 bond in the rate-determining stage. However, this hypothesis cannot be accepted as strictly based, and the possibility of a different mechanism for solid-phase decomposition is not excluded. In particular, the rate-determining stage in the solid-phase decomposition of octogen may be electron transfer in the crystal lattice[103,107].

The enhanced thermal stability of solid octogen in comparison with hexogen[19,20] has been explained by the greater energy of interaction between its molecules in the crystal.

In conclusion we may mention another study[94] of the thermal decomposition of octogen, but without determination of the kinetic parameters.

4. Primary Nitramines

Study of the thermal decomposition of methylenedinitramine (medina) at 70–100 °C reveals[75] a more complicated course than the sigmoid law followed by the preceding nitramines: the kinetic curve has two points of inflexion. Initially the rate of decomposition diminishes with time, after which a period of autocatalysis ensues, which is followed by fresh retardation of the reaction. At 80 °C the rate is described by the equation (t = time)

$$w = 5.5(1-e^{-0.16t}) + 0.00192t^{1.76}.$$

The results were interpreted in terms of a topochemical model[75], according to which the reaction develops on surface nuclei, whose number remains unchanged. At each centre the compound decomposes according to a first-order law until a definite quantity has changed, after which decomposition follows a power law (e.g. a second-order equation) with a significantly smaller rate constant than for the preceding first-order reaction. Analysis of this model yields an equation identical with that given above. Moreover, the model indicates that the duration of the induction period (from the start of reaction to the first point of inflexion on the kinetic curve) should depend on temperature according to the Arrhenius law, as is observed in fact with an activation energy of 27.8 kcal mole^{-1}. It was shown also that picric acid coating the crystal surface inhibits reaction, diminishing the degree of conversion during the induction period.

The chemical mechanism of the solid-phase decomposition of medina was not discussed[75], and available data are insufficient for definite conclusions to be drawn.

An undoubted merit of this work[75] is its development of a topochemical model with a complete description of the kinetic curve, which has not been done for other nitramines. However, it must be borne in mind that agreement between calculated and experimental values is not sufficient proof of the correctness of the model, since an alternative model might also agree with available experimental results. Furthermore, we do not know how far the induction period is due to impurity processes, which are extremely widespread in solid-phase decomposition.

Data on the solid-phase decomposition of ethylenedinitramine (edna) are also very sparse. As would be expected, reaction in the solid is considerably slower than in the liquid phase[48,78]. The kinetic curve resembles that for medina, with two points of inflexion; impurities and gaseous decomposition products accelerate the reaction[78]. The activation energy and the pre-exponential factor determined at 100–120 °C are respectively 36 kcal mole^{-1} and $10^{12.5}$–10^{13} s^{-1}.[78] However, this paper[78] gives results of unpublished work, according to which the activation energy depends on the temperature range, its value in a vacuum being respectively 37.0, 41.5, and 51.5 kcal mole^{-1} at 100–120, 120–135, and 135–145 °C; for atmospheric pressure the values at 120–135 and 135–145 °C were 43.5 and 59.5 kcal mole^{-1}. The pre-exponential factor remained almost unchanged over these temperature ranges at 10^{12}–10^{13} s^{-1}.

Without any grounds it is stated[78] that the decomposition of edna in a vacuum has a chain mechanism in its initial stages (2–3% conversion).

Kinetic data on the thermal decomposition of edna agree well with a first-order equation[49,30] in the initial stage (5% conversion). Between 5% and 10% a period of "autostabilisation" ensues: i.e. the observed first-order rate constant diminishes. After 10% conversion the reaction again accelerates, the rate constant increases, and a first-order equation is satisfied. The activation energy and the pre-exponential factor for the initial stage are 30.8 ± 2.0 kcal mole^{-1} and $10^{11.1 \pm 1.0}$ s^{-1}, the corresponding values in the region of "autostabilisation" being 71.7 ± 1.6 and $10^{31.6 \pm 0.8}$.[49] In view of the experimental error the values in Refs.78 and 49 show quite good agreement, and are close to those given above for the liquid-phase decomposition of primary nitramines. As in preceding cases this suggests identical reaction mechanisms in liquid and solid phases, although direct evidence for such a hypothesis is lacking.

5. Other Nitramines

Information has been published on the thermal decomposition of several other nitramines, for which kinetic parameters have not been determined. Differential thermal analysis was used to study the decomposition of nitroguanidine[28,108] and of nitramino-carboxylic acids and their salts[59]. Those of the latter that decompose below the melting point possess greater thermal stability than compounds that decompose in the liquid state. The thermal decomposition of 1,5-*endo*-methylene-3,7-dinitro-1,3,5,7-tetra-azacyclo-octane has been examined[33] by differential scanning calorimetry, and the activation energy roughly estimated as 100–300 kcal mole^{-1}.

V. CONCLUSION

It can be concluded from the above survey that considerable progress has now been made in understanding the main features of the thermal decomposition of *N*-nitro-compounds. Nevertheless, it is worth considering the unsolved problems and indicating possible routes to their solution.

In the kinetics of the gas-phase decomposition of *N*-nitro-compounds the most detailed attention has been paid to the nature of the first, rate-determining stage, although even here complete unanimity is absent, as discussed above in connection with hexogen and octogen. For the hypothesis of a radical mechanism of breakdown to be confirmed or refuted systematic investigations of the dissociation energies of bonds are necessary; these can be achieved by spectroscopic methods, thermodynamic estimates of the enthalpies of formation of nitro-compounds and free radicals, and quantum-mechanical calculations. At the same time estimation of pre-exponential factors with the help of the modern theory of unimolecular reactions will be extremely useful.

The time has arrived to pass from the first stage to a detailed analysis of the complete mechanism of the decomposition of *N*-nitro-compounds. Strange as it may seem, not even a first step has been taken in this direction: no complete quantitative analysis of the products at different stages of decomposition has been made, although standard methods of mass spectrometry and chromatography can be used for this purpose. In order to elucidate the mechanism of these reactions it is extremely important to make a kinetic study of the reactions of oxides of nitrogen, primarily of nitrogen dioxide, both with the nitramines themselves and with their decomposition products. Further, considerable interest attaches to the interaction of nitrogen dioxide with amino-radicals, mainly because this is the reverse reaction to the presumed first stage of decomposition of nitramines—rupture of an N–NO_2 bond—and its examination might reveal to what extent this first stage is reversible. Useful information on the mechanism of the thermal decomposition of *N*-nitro-compounds might be obtained from experiments on non-thermal decomposition, e.g. flash photolysis.

At the outset of research on the thermal decomposition of nitro-compounds Roginskii and Semenov put forward the hypothesis of a chain mechanism[6], but this idea was not developed. It is now considered that the decomposition is not a chain reaction, since oxides of nitrogen are formed, and these are effective inhibitors of chain processes. Clearly, however, this is not a decisive argument, and the involvement of a chain mechanism in the decomposition of nitro-compounds, including nitramines, remains an open question. Correlation analysis, enabling quantitative relations to be established between structure and reactivity, is at present widely used in organic chemistry. Unfortunately, this approach has not yet been duly applied to the pyrolysis of nitro-compounds, despite its obvious relevance. This gap must undoubtedly be bridged, for which purpose it is extremely desirable that the measurement of true rate constants of primary steps should be started and a larger number of compounds investigated to ensure statistical reliability of the results.

The problems formulated above for gas-phase pyrolysis are in urgent need of solution also for processes in the liquid phase, where moreover the use of powerful physico-chemical methods (electron spin resonance, chemical polarisation of nuclei, spin traps), permitting the study of reactive intermediates, becomes especially effective. Unfortunately, such methods, which have proved their value in the most diverse fields of chemistry, have not yet been applied to the decomposition of nitro-compounds. Incidentally, chemical polarisation of nuclei may perhaps help to reveal and study the cage effect, which has not yet been detected in the decomposition of nitro-compounds although widespread in radical liquid-phase reactions. Further investigation of the nature of catalysis and autocatalysis in the breakdown of nitro-compounds is of great practical interest, since solution of this problem is closely connected with the stabilisation of explosives. An example is tetryl, for which autocatalysis by picric acid has been reliably established, but the nature of the catalytic action is unknown.

The most urgent aspect of the solid-phase decomposition of *N*-nitro-compounds is to ascertain its topochemistry, which involves a wide range of unsolved problems: there is no proper topochemical model of the reaction (as stated above, such a model has been suggested only for medina, and then

its adequacy has not been rigorously proved); the kinetic influence of crystal size and polymorphic modification has not been ascertained; and only the first steps have been taken in studying the physical processes occurring in the crystals during decomposition (the above work by Klimenko et al.). An interesting problem in the kinetics of solid-phase decomposition is to establish the nature of the breakdown in the Arrhenius law near the melting point. The nature of the reaction centres involved in the thermal decomposition of *N*-nitro-compounds still remains unknown.

Future progress in research on the kinetics and the mechanism of the thermal decomposition of *N*-nitro-compounds will probably depend in considerable measure on the application of modern methods of investigation—field-ionisation mass spectrometry, optical spectroscopy, electron microscopy, X-ray diffraction, nuclear magnetic resonance, chemiluminescence, etc.—besides those mentioned above. The use of quantum-chemical calculations to analyse the reactivity of *N*-nitro-compounds is also promising.

It may be hoped that solution of the above problems will assist further development of the chemistry of *N*-nitro-compounds, extension of the possibilities for their practical application, and penetration of methods of chemical kinetics into the physics of combustion and explosion.

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