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Thermal Decomposition of Aliphatic Nitro-compounds

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Two mechanisms of decomposition of nitro-compounds are discussed: molecular, when a molecule of HNO_2 is detached and the corresponding alkene is formed, and free-radical, in which the reaction starts with the breaking of the C–N bond. Study of the reactions of the first type is of considerable interest in the light of the general theory of elimination reactions in the gas phase. The radical decomposition of nitroalkanes is characterised by high values of the pre-exponential factors. The activation energy in this instance equals the energy for breaking the bond. Secondary reactions have little influence on the rate of radical decomposition of *gem*-polynitroalkanes, therefore the study of the kinetics of the decomposition can be an effective method of determining the energy for the breaking of the C–N bond in these compounds. Bibliography of 48 references.

CONTENTS

I. Introduction 603
II. Decomposition of mononitro-compounds 604
1. Nitromethane 604
2. Nitroethane, 1-nitropropane, and 2-nitropropane 607
3. Chloropicrin 609
III. Polynitro-compounds 610
1. 2,2-Dinitropropane 610
2. Hexanitroethane 611

I. INTRODUCTION

The investigation of the kinetics of the reactions of thermal decomposition of aliphatic nitro-compounds began in the middle of the 1930s, when the first paper on the decomposition of nitromethane appeared[1], and several papers were published[2,3] which dealt with the thermal decomposition of chloropicrin. The mononitroalkanes nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane were the chief subjects of further investigations; these account for about three-quarters of all the work completed up till now. These four compounds were thoroughly studied by various authors in the period from 1950 to 1959, and the main features of their decomposition mechanisms were found. Considerably less attention has been paid to the polynitro-compounds. A quantitative study of the reactions during the decomposition of substances in this class was begun in 1962 and completed for only two compounds: 2,2-dinitropropane[4] and hexanitroethane[5]. Despite the comparatively small number of substances studied and the incompleteness of some of the studies, the results obtained are of considerable interest for the solution of a series of scientific and technical problems and merit careful examination.

The explanation of the mechanism of decomposition of nitro-compounds is inseparably connected with such problems as the determination of the energy of breaking of the C–N bond (and also bonds of another type) in substances of various structures, of finding the heats of formation of nitroalkyl free radicals, the conversion of free radicals in systems containing NO and NO_2, the influence of the state of aggregation and of the solvent on the radical reactions, topochemical processes in molecular crystals, and various other problems where the decomposition of nitro-compounds can serve as a model. A series of peculiarities of the reactions in the decomposition of nitro-compounds, for example, the possibility of decomposition by two competing mechanisms—radical and molecular—the dependence of these mechanisms on the structure of the molecule and the experimental conditions, and the existence of high pre-exponential factors in the radical decomposition are of undoubted interest to the theory of unimolecular reactions.

Among the technical problems which were responsible for the practical value of a study of the decomposition of nitro-compounds and to a certain extent stimulated these studies there is above all the industrial synthesis of mononitroalkanes by the vapour-phase nitration of hydrocarbons with nitrogen dioxide or nitric acid[6,7] and also the possibility of using certain nitroalkanes as additives to fuels for air-breathing and rocket engines[8].

The establishment of the detailed mechanism of the decomposition of any nitro-compound and the determination of the rate constants of the separate stages would have definite value in considering problems in the theory of combustion of liquid monopropellents.

A general introduction to the conditions and results of the studies of the reactions in the decomposition of nitro-compounds is given in Table 1.

In addition to Table 1, we note that the decomposition of all the substances except hexanitroethane was studied in the gas phase and in every instance the reaction obeyed a first-order law. Despite the simplicity of the formal kinetic laws there are often serious discrepancies between the results of different authors in determining the rate constants and for the choice of reliable quantities it is necessary to compare all the data. This is even more true of the treatment of the decomposition mechanism. A consideration of the accumulated material shows certain general features, inherent in the decomposition reactions of nitro-compounds, which in turn promote a better understanding of the mechanism of decomposition of other substances.

In connection with what has been stated above, in this review all the experimental data will be briefly examined, the mechanisms for the decomposition of nitro-compounds will be judged from various viewpoints, and the problems which we consider to be of greatest interest for further investigations will be emphasised.

Table 1. Some information about the reactions in the decomposition of the nitro-compounds.

Compound	Temp. range, °C	Decomposition conditions	E_{act}, kcal mole^{-1}	lg$A$ (A in s^{-1})	Hypothetical mechanism	Refs
1	2	3	4	5	6	7
Nitromethane	380–420	in a static system	61.0	–	CH_3–$NO_2 \rightarrow CH_3NO + O$	1
	310–440	ditto, P_0 = 4–40 mmHg	42.8	11.4	breaking of the C–N bond	9
	380–430	ditto, P_0 = 40–400 mmHg	53.6	14.6	ditto	10, 11
	420–480	in a flow system*, 6–18 mole % in N_2	50.0	13.4	$CH_3NO_2 \rightarrow CH_2O + HNO$	12, 13
	447	ditto, 0.04 mole % in He	–	–	breaking of the C–N bond	14
	355	in a static system, P_0 = 12.2–20 atm	–	–	$CH_3NO_2 \rightarrow CH_3NO + O$	15
	312–340	ditto, P_0 = 40 atm	49.2	13.73	breaking of a C–N bond	16
	430	in a flow system, in the presence of NO_2 and HNO_3	–	–	ditto	17
	872–1187	in a shock tube	13 ± 7	–	participation of excited states	18
	220–245	in a static system, P_0 = 36 atm over Cr_2O_3	36.0	11.0	breaking of a C–N bond or the formation of *aci*-forms	22
Nitroethane	310–440	ditto, 4–40 mmHg	41.5	11.53	breaking of C–N bond	9
	355–405	ditto, 50–405 mmHg	47.0	13.0	$C_2H_5NO_2 \rightarrow C_2H_4 + HNO_2$	19
	430–485	in a flow system, 0.04–0.5 mole % in He	39.0	11.0	breaking of C–N bond	14
	414–442	ditto, 10% in N_2	41.4	11.35	$C_2H_5NO_2 \rightarrow C_2H_4 + HNO_2$	20
	320–360	in a static system	39.7	10.83	ditto	21
	490–535	in a flow system, 10% in N_2	60.6	17.56	breaking of the C–N bond	21
	380–470	ditto, 10% in N_2	40.2	11.41	–	7
1-Nitropropane	210–440	in a static system, P_0 = 4–40 mmHg	41.5	11.73	breaking of C–N bond	9
	350–440	ditto	49.6	–	elimination of HNO_2	19
	430–477	in a flow system	48.5	13.30	breaking of C–N bond	14
	414–442	ditto	47.7	13.40	rearrangement $C_3H_7NO_2 \rightarrow C_2H_5CH{=}NOOH$	20
2-Nitropropane	310–440	in a static system, P_0 = 4–40 mmHg	39.0	11.34	breaking of C–N bond	9
	366–393	in a flow, 10% in N_2	39.0	11.00	elimination of HNO_2	20
	250–337	in a static system	39.3	11.05	ditto	23
Chloropicrin	138–170	ditto, 60–200 mmHg	37.67	15.69	rearrangement $CCl_3NO_2 \rightarrow Cl_2CO + ClNO$	2
	–	–	–	–	$CCl_3NO_2 \rightarrow CCl_2O + NO + Cl$	24
	–	–	–	–	breaking of C–N bond	25
2,2-Dinitropropane	175–210	ditto	50.5	18.5	breaking of C–N bond and chain process	4
Hexanitroethane	60–100	decomposition in the solid state	38.9	18.6	loss of two nitro-groups from one or two carbon atoms	5
	–	ditto**	39.0	17.4		
	60–100	solution in CCl_4	37.8	18.5		
	85–100	solution in n-heptane	28.0	13.0	formation of complexes with	
	85–100	solution in cyclohexane	21.0	9.1	solvent with transfer of charges	

* In all the experiments carried out by the flow method the total pressure was 1 atm.

** Personal communication of Rosen, cited in Ref.5.

II. DECOMPOSITION OF MONONITRO-COMPOUNDS

1. Nitromethane

Taylor and Vesselovsky, who first investigated the kinetics of thermal decomposition of nitromethane[1], found that under static conditions at initial vapour pressures of P_0 = 27–198 mmHg the reaction obeys a first-order equation and is homogeneous (the increase in the ratio of the surface to the volume of the reaction vessel by a factor of 6.3 has no influence on the initial rate of reaction). By distillation of the reaction products a small fraction with b.p. 84°C was isolated; this b.p. corresponds with that of formaldehyde oxime, an isomer of nitrosomethane. From this it was supposed that the first stage of the decomposition of nitromethane is the loss of oxygen from the nitro-group:

$$CH_3NO_2 \rightarrow CH_3NO + O\,. \qquad (1)$$

However, in an analysis of Taylor and Vesselovsky's experimental results Cottrell and coworkers noted[11] that the rate constant for the decomposition of nitromethane depends on the pressure, decreasing systematically with decrease in P_0. A more careful study of the decomposition of nitromethane, made by Cottrell and coworkers[10,11] by a manometric method, showed that the reaction is indeed homogeneous but the rate constant ceases to depend on the pressure only at an initial pressure $P_0 > 200$ mmHg.

In this connection criticism must be directed at both Taylor and Vesselovsky's results and those of Frejacquens[9], who determined the activation energy for the decomposition of nitromethane and the influence of other gases on the rate of this reaction at $P_0 = 4-40$ mmHg.

The activation energy found by Cottrell, 53.6 kcal mole^{-1}, was considerably less than that of Taylor (61 kcal mole^{-1}) and is in good agreement with the thermochemically determined energy for the dissociation of the C–N bond in CH_3NO_2†. This was an important point in support of a mechanism with primary breaking of the C–N bond. Cottrell's approximate thermochemical calculation[11] showed that $D(CH_3NO-O) \geqslant 73$ kcal mole^{-1}—that is, approximately the same value as D(NO–O)—and hence reaction (1) seems improbable.

A semiquantitative analysis of the decomposition products was made with the aid of various methods (infrared and mass spectroscopy, gas analysis). The main products were H_2O, CO, and CH_4 (Table 2). In addition small amounts of CO_2, N_2O, C_2H_4, and C_2H_6 were detected.

From these results, Cottrell proposed the following scheme for the decomposition of nitromethane[11]:

$$CH_3NO_2 \rightarrow CH_3 + NO_2 , \quad (2)$$

$$CH_3 + CH_3NO_2 \rightarrow CH_4 + CH_2NO_2 , \quad (3)$$

$$CH_2NO_2 + NO_2 \rightarrow CH_2O + NO + NO_2 , \quad (4)$$

$$CH_2O + NO_2 \rightarrow CO + NO + H_2O , \quad (5)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 . \quad (6)$$

Table 2. Composition of the products (in mole fractions) in the initial stages of the decomposition of nitromethane at various pressures.

Product	200–400 mmHg (Ref.11) (420°C)	153 mmHg (Ref.15) (418°C)	12.2 atm (Ref.15) (355°C)	16.8 atm (Ref.15) (355°C)
CO_2	0.04	0.07	0.08	0.20
CO	0.31	0.51	0.17	0.21
CH_4	0.32	0.27	0.19	0.10
HCN	—	0.15	0.35	0.40
CH_3CN	—	traces	0.05	0.01
C_2H_5CN	—	—	0.04	0.01
CH_2O	—	—	0.06	0.04
NO	1.00	0.56	0.42	0.54
N_2O	0.03	0.02	0.02	0.04
N_2	—	0.10	0.04	0.01
H_2O	0.61	0.78	1.01	0.94
C_2H_6	0.01—0.02	0.02	—	—
C_2H_4	0.01	—	—	—

The possibility of the following reactions was also noted:

$$CH_2NO_2 \rightarrow CH_2O + NO , \quad (7)$$

$$CH_3 + NO \rightarrow CH_3NO \rightarrow HCN + H_2O . \quad (8)$$

After Cottrell's work, Hillenbrandt and Kilpatrik[12] studied the decomposition of nitromethane in a flow system.

Nitrogen saturated with water vapour was used as the carrier gas, and reproducible results were obtained by this procedure. The nitromethane was analysed polarographically. Formaldehyde (hydroxylamine method), methane, carbon monoxide, and nitrogen monoxide (adsorption gas analysis) were determined in the products. The rate of decomposition in the stream is independent of the changes in the nitromethane concentration for mole fractions between 0.06 and 0.18. The parameters of the Arrhenius equation are close to those obtained by Cottrell (Table 1). However, unlike Cottrell's results, a large proportion of formaldehyde was found in the decomposition products. The yield of formaldehyde per mole nitromethane was 0.5 mole in the initial stages at 420°C and reached 0.9 mole at 473°C. With increase in the extent of the conversion the yield of formaldehyde decreases, reaching a constant value of 0.4 mole at 473°C and 0.2 mole at 420°C. According to Cottrell's scheme, even allowing for reaction (7) the yield of formaldehyde cannot be $> 50\%$. Hillenbrandt and Kilpatrik suggested that the reaction proceeds at least partly by an intramolecular rearrangement:

$$CH_3NO_2 \rightarrow CH_2O + HNO . \quad (9)$$

The low concentration of formaldehyde in Cottrell's static experiments was explained by reaction (5), which proceeds very slowly at temperatures > 200°C.[29]

Hillenbrandt and Kilpatrik's conclusions were criticised by Gray and coworkers[14]. These authors investigated the kinetics of the decomposition of nitromethane, also under flow conditions (but at a lower concentration of nitromethane in the mixture), and determined the formaldehyde by reaction with dimedon; they found that the yield of formaldehyde is considerably less than had been claimed[12]. For example, at 447°C and a contact time of 1.1 s (extent of conversion 13%) the yield of formaldehyde was 16%. Gray considers that in the earlier work[12] there were two sources of error in determining the yield of formaldehyde: (1) the accuracy in calculating the $[CH_2O]/[CH_3NO_2]$ ratio decreases with decrease in the extent of decomposition; (2) it is possible that in the analysis the sum of the formaldehyde and formaldehyde oxime (obtained by isomerisation of nitrosomethane) was determined.

By use of metallic mirrors, Gray established that active free radicals are formed in the decomposition of nitromethane. He therefore supports Cottrell's viewpoint concerning the radical nature of the decomposition of nitromethane.

The formation of nitrosomethane (which under static conditions is converted into hydrogen cyanide and water) during the decomposition of nitromethane was proved convincingly by Müller, who studied the decomposition at 355°C in the range of pressures 12.2–20 atm. The reaction was studied by an ampoule method with mass spectrometric analysis of the nitromethane and the decomposition products. It was found that, in addition to nitric oxide and water, hydrogen cyanide is formed, its yield increasing with the pressure (Table 2). For comparison with Cottrell's results an experiment was run at 418°C and $P_0 = 158$ mmHg. Table 2, which gives these results, shows clearly that in addition to the products noted by Cottrell (CH_4, CO, NO, CO_2, H_2O) hydrogen cyanide and nitrogen are formed in comparatively large quantities.

To explain the large yield of hydrogen cyanide Müller suggested that the decomposition of nitromethane proceeds not solely by the Cottrell mechanism but partly by reaction (1) proposed by Taylor; the part played by this reaction increases with the pressure.

However, this conclusion was not convincing and has been criticised by Makovky and Gruenwald[16]. By using

† Three values for the heat of formation of nitromethane in the gas phase have been published: 17.8,[26] 12.35,[27] and 13.1[28] kcal mole^{-1}. The use of the last two values, obtained subsequently and evidently more accurate, gives for D(C–N) the values 52.0 and 52.7 kcal mole^{-1} respectively.

mass spectrometric analysis these authors found that the rate of decomposition of nitromethane at $P_0 > 1$ atm depends weakly on pressure, but the value of the activation energy determined at a pressure of 40 atm agrees well with Cottrell and Hillenbrandt's results (Table 1). The dependence on pressure of the hydrogen cyanide yield was confirmed and, furthermore, it was shown that its formation is facilitated by addition of nitric oxide to the nitromethane.

Makovky and Gruenwald consider that all these results are explained by Cottrell's scheme and the formation of hydrogen cyanide follows from reaction (8). The primary stage of this reaction—the formation of nitrosomethane—is termolecular and its rate depends more strongly on pressure than the rates of competing processes (3) and (10)‡:

$$CH_3 + NO_2 \rightarrow CH_3O + NO\ , \qquad (10)$$

which also explains the increase in the yield of hydrogen cyanide with increase in pressure.

From the material considered clearly Cottrell's scheme gives a satisfactory explanation for both the observed activation energy and the composition of the decomposition products. Therefore it can be considered correct in both features.

Additional information about secondary processes which take place during the decomposition of nitromethane can be obtained on considering the effect on the rate of this reaction of adding certain gases.

It was found[15,16] that the addition of NO_2 greatly retards the decomposition of nitromethane. Makovky explains this fact by the reversibility of reaction (2). As has been shown[30,31] in studies of the reactions of the methyl radical with nitrogen dioxide, this interaction takes place in two ways. The first leads to recombination:

$$CH_3 + NO_2 \rightarrow CH_3NO_2 \qquad (11)$$

and the second, to oxidation by Eqn. (10). Here $k_{10} \simeq 2k_{11}$.[30,32] In the decomposition of nitromethane the methyl radical not only reacts with nitrogen dioxide but also undergoes conversion by reaction (8) and possibly (3). A considerable yield of methane, especially at low pressures and in the initial stages, does not allow this reaction to be ruled out although with considerable concentrations of nitrogen dioxide and monoxide its role will be small. If it is assumed that the methyl radical is consumed only in reactions (3), (6), (10), and (11), then for the rate of decomposition of nitromethane under conditions when the concentration of methyl radical is stationary we obtain the expression§

$$-\frac{d[CH_3NO_2]}{dt} = k_3[CH_3NO_2]\left\{1 - \frac{k_{11}[NO_2] - k_3[CH_3NO_2]}{(k_{10}+k_{11})[NO_2] + k_7[NO] + k_3[CH_3NO_2]}\right\}. \qquad (12)$$

With a large excess of nitrogen dioxide the rate constant is $k_2[1 - k_{11}/(k_{10} + k_{11})]$ and if it is assumed that $k_{10} = 2k_{11}$ the rate can be expected to be ~ 30% less. As a matter of fact, the addition of 36–37% nitrogen dioxide reduces the rate of decomposition by approximately half[16]. This fact shows the presence of some other reactions of radicals with the nitromethane which are inhibited by additions of nitrogen dioxide. It should be noted that in studies of the decomposition of nitromethane the possibility of reaction (10) and the fate of the methoxy-radical have not been considered at all. This radical is undoubtedly formed in the decomposition of nitromethane and its recombination with nitrogen monoxide and dioxide hardly occurs at the temperatures of the experiments. Possibly the methoxy-radical is destroyed by the reactions:

$$CH_3O + NO \rightarrow CH_2O + HNO\ , \qquad (13)$$

$$CH_3O + NO_2 \rightarrow CH_2O + HNO_2\ , \qquad (14)$$

which also explains the absence of methanol in the decomposition products. Observations concerning the retarding action of nitrogen dioxide were made at temperatures not above 355°C, when it does not react directly with nitromethane. At higher temperatures the accelerating influence of nitrogen dioxide is observed. Thus Schay and coworkers[17] found, in studying the influence of nitrogen dioxide and nitric acid on the decomposition of nitromethane at 430°C with a contact time of 1–2 s, that both substances increase the rate of decomposition and at a concentration ratio of $NO_2 : CH_3NO_2 = 17 : 1$ the formation of polynitro-compounds is observed. These facts are explained by the reactions:

$$NO_2 + CH_3NO_2 \rightarrow HNO_2 + CH_2NO_2\ ,$$

$$NO_2 + CH_2NO_2 \rightarrow CH_2(NO_2)_2\ .$$

According to Eqn. (12) the addition of nitric oxide to nitromethane should accelerate the decomposition at $k_{11}[NO_2] > k_3[CH_3NO_2]$ and decrease the rate under the opposite conditions. Some observations[11,15,16] show that the addition of nitric oxide in amounts up to 10% to nitromethane does not alter the rate but at higher concentrations nitric oxide retards the decomposition. This fact can be taken as confirmation of the correctness of Cottrell's conclusion concerning reaction (3) in the scheme of decomposition of nitromethane.

Investigations by several authors[14–16] showed that the addition of oxygen accelerates the decomposition of nitromethane. For example, at 330°C and $P_0 = 40$ atm the addition of 8–35% oxygen increases the rate of decomposition by 20–25%.[15] The forward reaction of oxygen with nitromethane under these conditions is improbable, since oxygen is less active in reactions at the C–H bond than is nitrogen dioxide, for which the reaction with nitromethane is not observed. Possibly the oxygen affects the decomposition through the $CH_3OO^{\cdot}$ radical, which is formed in the reaction of oxygen with the methyl radical. The reaction of this radical with nitrogen monoxide and dioxide requires an activation energy. It is therefore comparatively long-lived and can react with nitromethane:

$$CH_3O\dot{O} + CH_3NO_2 \rightarrow CH_3OOH + CH_2NO_2\ . \qquad (15)$$

The decrease in the yield of hydrogen cyanide observed on adding oxygen[15] is indirect proof of the reaction of oxygen with methyl radicals.

The decomposition of nitromethane at high temperatures (872–1157°C) was studied by Bradley[18] with the aid of the shock tube method. The reaction was carried out in a mixture with argon (1 : 9) at pressures of 6–10 mmHg with analysis of the products every 50–100 μs on a time-of-flight mass spectrometer. The stoichiometry of the reaction corresponds to the equation:

$$2CH_3NO_2 \rightarrow CH_4 + CO + H_2O + 2NO\ .$$

The yields of methanol and formaldehyde are very small. The decrease in nitromethane equals the rate of formation of the products. Throughout the whole temperature range of the reaction the first-order equation is obeyed but the activation energy decreases as the temperature is raised, the mean value being 13 ± 7 kcal mole^{-1}.

‡Reaction (10) is not taken into account in Cottrell's scheme.

§ For k_7 read k_8 in Eqn. 12 (Ed. of Translation).

To explain these factors a mechanism was proposed which includes two successive excitations of the nitromethane molecules. However, before a definite conclusion can be drawn about the decomposition paths for nitromethane which are new in principle it is necessary to be convinced that the experiments were made in the range where the rate constants of the unimolecular reaction are independent of pressure.

The catalytic decomposition of nitromethane into various oxides was described by Makovky[32,33], who found that the decomposition is catalysed only by oxides which are basic. Evidently, the formation of *aci*-forms of nitromethane in layers adsorbed on oxides plays a part. The compounds can be arranged in the following order of catalytic activity:

$$Cr_2O_3>ThO_2>ZnO>MnO_2>CaO>Co_2O_3>TiO_2>PbO>MgO>$$
$$>CdO>HgO>Fe_2O_3>Al_2O_3>CuO>CeO_2>SbO_2>$$
$$V_2O_5, WO_3, CrO_3, MoO_3, SiO_2, P_2O_5$$

(the last does not act below 350°C). The decomposition of nitromethane over chromium oxide has been studied in most detail[22]. This catalyst has a very great effect on both the rate of decomposition (see Table 1) and the composition of the decomposition products, among which large proportions of ammonium hydrogen carbonate have been observed.

2. Nitroethane, 1-Nitropropane, and 2-Nitropropane

In distinction from nitromethane, the decomposition of which starts with rupture of the C–N bond, the decomposition of remaining mononitroalkanes that have been studied takes place (at least, at temperatures up to 450°C) by a unimolecular mechanism with elimination of nitric acid and formation of the corresponding alkene:

$$-\overset{H}{\underset{}{C}}-\overset{NO_2}{\underset{}{C}}- \rightarrow >C=C< + HNO_2. \qquad (16)$$

This mechanism was first proposed by Cottrell[19] in studying the decomposition of nitroethane and 1-nitropropane under static conditions. On using a manometric method, Cottrell found that the decomposition of nitroethane proceeds according to a first-order equation and is independent of the pressure at $P_0 > 30$ mmHg. The activation energy (~ 47 kcal mole^{-1}) was considerably below the dissociation energy of the C–N bond in this compound (56 kcal mole^{-1}) which can be evaluated from thermochemical data[26,28]. Infrared spectroscopy showed the presence in the products of CO_2 (~ 18%), NO (~ 45%), and C_2H_4 (~ 36%).

On the basis of these results Cottrell also proposed reaction (16), that is, a mechanism analogous to the molecular decomposition of alkyl halides[34]. This mechanism was disputed by Gray and coworkers[14]. The contradiction was resolved in the detailed studies by Wilde[20,21].

Gray investigated the kinetics of decomposition of nitroethane in flow at temperatures higher than in Cottrell's experiments. The mole fraction of nitroethane in helium was 4×10^{-4}–5×10^{-3}. Polarographic determination of the nitroethane was used to observe the reactions. CH_2O (by dimedon), NO_2 (Griess reaction), CO_2, NO, C_2H_4, C_2H_6 (adsorption analysis) were determined in the decomposition products. CO, CH_4, and N_2 were determined by the mass spectrometric method. The results of the analyses gave the following overall equation for the decomposition of nitromethane at 477°C:

$$C_2H_5NO_2 = 0.4\,C_2H_4 + 0.03\,C_2H_6 + 0.367\,CH_4 + 0.22\,CH_2O + 0.483\,CO + 0.07\,CO_2 + 0.657\,H_2O + 0.29\,N_2 + 0.08\,NO_2 + 0.34\,NO.$$

Gray found the activation energy to be 39 kcal mole^{-1}, even lower (and, as further investigation showed, more correct) than that of Cottrell. By the metallic mirror method Gray found that the decomposition of nitroethane at temperatures above 500°C is accompanied by the formation of free radicals. At the same time the artificial introduction of methyl radical (formed in the decomposition of di-t-butyl peroxide) depresses the decomposition temperature of nitroethane by a hundred degrees. One of the main products in this is formaldehyde. On the basis of these facts Gray proposed the following scheme for the decomposition of nitroethane:

$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2, \qquad (17)$$
$$C_2H_5 + NO_2 \rightarrow C_2H_5NO_2, \qquad (18)$$
$$C_2H_5 + NO_2 \rightarrow C_2H_5O + NO, \qquad (19)$$
$$C_2H_5O \rightarrow CH_2O + CH_3, \qquad (20)$$
$$C_2H_5O \rightarrow CH_3CHO + H, \qquad (21)$$
$$CH_3CHO \rightarrow CH_4 + CO, \qquad (22)$$
$$CH_3 + RH \rightarrow CH_4 + R, \qquad (23)$$
$$CH_3 + NO \rightarrow CH_3NOH \rightarrow HCN + H_2O. \qquad (8)$$

The formation of ethylene is explained by the reaction

$$C_2H_5 \rightarrow C_2H_4 + H \qquad (24)$$

and partly by the occurrence of process (16). Furthermore, Gray assumes reaction of methyl radicals with nitroethane, which he thinks leads to the low value of the activation energy.

Wilde[20,21] carried out a detailed investigation of the decomposition of nitroethane in flow and under static conditions. In the first instance the method used was analogous to that employed by Hillenbrandt for nitromethane[12]. At a total pressure of 750 mmHg the rate of decomposition is independent of the composition of the $C_2H_5NO_2$–N_2 mixture. Nitroethane, acetaldehyde, and formaldehyde were determined polarographically, ethylene and nitrogen monoxide by chemical methods. It was shown that the main products (in the temperature range 414–442°C) are ethylene and nitric oxide. Hydrogen cyanide, water, and a little nitrogen dioxide were also observed, and at 442°C, methane and carbon monoxide. The discrepancy with Cottrell's results is explained by the fact that hydrogen cyanide, formaldehyde, and acetaldehyde are decomposed and oxidised under static conditions, giving, in particular, carbon dioxide. The activation energy determined for 412–442°C was 41.4 ± 1.1 kcal mole^{-1}. The inclusion of a point at 453°C gave the value 46.8 ± 3 kcal mole^{-1}, with much greater error.

Wilde also studied the decomposition of nitroethane under static conditions at lower temperatures (see Table 1), with analysis of the nitroethane by infrared spectroscopy. The temperature dependence of the rate constants obtained both under static and flow conditions (up to 442°C) are well described by a single Arrhenius' equation $k = 10^{10.83} \exp(-39\,700/RT)$ s^{-1}, with an activation energy almost equal to that determined by Gray. The same activation energy was found by Geiseler and Reinhardt[7] under flow conditions at 380–470°C.

Wilde considers that the high yield of ethylene combined with the low activation energy can be explained only within the framework of the Cottrell molecular mechanism, which (at least, up to 450°C) is the predominant path for the decomposition of nitroethane. Actually not one of the schemes including the primary decomposition of nitroethane at the C–N bond with subsequent formation of ethylene by the reaction:

$$C_2H_5 + NO_2 \rightarrow C_2H_4 + HNO_2 , \quad (25)$$

or

$$C_2H_5NO_2 \rightarrow C_2H_4NO_2 + HNO_2 , \quad (26)$$

$$C_2H_4NO_2 \rightarrow C_2H_4 + NO_2 , \quad (27)$$

can explain the low activation energy.

The low value of the pre-exponential factor ($\sim 10^{11}$ s^{-1}) also agrees well with this mechanism, as the most frequent reason for a low pre-exponential factors is[35,36] the formation of a cyclic transition state in which one or more internal rotational degrees of freedom are inhibited.

The existence of free radicals, observed by Gray at temperatures above 500°C and the formation of such products as CH_2O, CH_3CHO, HCN, CH_4, CO, and CO_2 cannot be explained without reference to free-radical processes. Wilde therefore suggests that part of the nitroethane decomposes by a radical mechanism (Gray's scheme), the fraction of which rises with the temperature. From Wilde's results, the decomposition at the C–N bond begins to affect significantly the total reaction rate for the decomposition at ~ 450°C. Consequently, at temperatures above 450°C a change in the mechanism of decomposition of nitroethane should occur.

To check this conclusion, Wilde investigated the decomposition of nitroethane at 400–525°C under flow conditions at contact times of 0.1–1 s.[21] Despite the high accuracy of the experiments it was found that the reaction obeys the first-order equation and the activation energy is 60.6 ± 5 kcal, that is, close to the energy of dissociation of the C–N bond in nitroethane. The same products were found qualitatively as were observed at low temperatures: ethylene, nitrogen monoxide, and formaldehyde.

Wilde considers that the high activation energy can be explained either within the framework of a non-chain radical decomposition:

$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2 , \quad (17)$$

$$C_2H_5 + NO_2 \rightarrow C_2H_5O + NO. \quad (19)$$

$$C_2H_5O \rightarrow CH_3 + CH_2O , \quad (20)$$

$$CH_3 + NO \rightarrow HCN + H_2O , \quad (8)$$

$$C_2H_5 + NO_2 \rightarrow C_2H_4 + HNO_2 , \quad (25)$$

$$2HNO_2 \rightarrow H_2O + NO + NO_2 , \quad (28)$$

or by a chain process:

$$C_2H_5NO_2 \rightarrow C_2H_5 + NO_2 , \quad (17)$$

$$C_2H_5NO_2 + NO_2 \rightarrow C_2H_4NO_2 + HNO_2 , \quad (26)$$

$$C_2H_4NO_2 \rightarrow C_2H_4 + NO_2 , \quad (27)$$

for binary chain breaking (bimolecular decomposition of nitrogen dioxide or reaction of nitrogen dioxide with ethylene) should have an activation energy of ~ 50–55 kcal $mole^{-1}$.

A high value of the pre-exponential factor A found by experiment ($10^{17\pm1}$ s^{-1}) agrees best with a non-chain mechanism. Change of the molecular path of the decomposition to a radical one leading to a higher activation energy unavoidably suggests the existence of high values of A for stage (17). This conclusion can be easily correlated with theory[35–37] if it is assumed that in nitroethane rotation around the C–N bond is hindered. Many examples have shown that high pre-exponential factors in unimolecular reactions are observed when the initial state of the molecule has restricted internal rotational motion, which is freed in the formation of the transition complex. When a calculation was made (decomposition of C_2H_6 and N_2O_4) it was shown that replacement of the torsional vibrations by free internal rotation alone cannot give the experimentally observable increase in activation entropy and it is necessary to assume that a significant part is played by other types of motion (pronounced weakening of the deformation vibrations or even free three-dimensional rotation of the radicals in the activated molecule). Nitroethane is evidently not excluded from the general rule and the presence of a high pre-exponential factor in its decomposition is completely natural.

Similarly increased values of A can be expected for reactions of radical decomposition of any nitro-compounds having restricted rotation around the C–N bond.

The possible difference of 5–6 orders of magnitude between the pre-exponential factors of molecular and radical decompositions ensures successful competition for the latter at 400–450°C, even when the activation energy is 15–20 kcal $mole^{-1}$ greater than in molecular cleavage. In this connection a more careful study of the decomposition of nitroethane and other mononitro-compounds at high temperatures which would ensure the predominance of a radical mechanism, merits attention.

The decomposition of 1- and 2-nitropropanes at temperatures below 450°C proceeds as for nitroethane, according to a molecular mechanism[20]. The chief products are propene and nitrogen monoxide. The activation energy for the decomposition of 2-nitropropane is 39 kcal, and the pre-exponential factor has the diminished value of 10^{11} s^{-1}. 1-Nitropropane is characterised by a higher activation energy (Table 1) and the normal value of the pre-exponential factor. The last fact led Wilde to reject the mechanism of simple molecular elimination. Instead of it he advanced the hypothesis of the primary rearrangement of nitropropane with the formation of the *aci*-form:

$$CH_3CH_2CH_2NO_2 \rightarrow CH_3CH_2CH{=}NOOH ,$$

which is also the active species in the decomposition. Such explanation, in turn, seems improbable and hence the problem of the difference in the pre-exponential factor of 1-nitropropane from the corresponding values for the nitroethane and 2-nitropropane remains unsolved.

2-Nitropropane was studied in greater detail than 1-nitropropane. The rate of decomposition of this substance was determined by three methods—under static conditions using the yield of propene[23] and the change in total pressure[9], and also in flow from the decomposition of 2-nitropropane itself[20]. All three methods gave the same result (Table 1). Complete analysis of the decomposition products, carried out by Smith and Calvert[23] with the aid of mass spectrometry and gas chromatography, showed the considerable part played by side-processes in this reaction. At degrees of decomposition from 4 to 55% it was found that propene, nitric oxide, and water are formed in approximately equivalent amounts and constitute 65–75% of the total quantity of products. Acetone, acetonitrile, and formaldehyde amounted to 25–15% and various nitroalkane hydrocarbons, carbon monoxide and dioxide, to ~ 10%. The addition of propene did not affect and the addition of nitric oxide increases the rate of decomposition and alters the composition of the products (the

yield of nitroalkanes and acetonitrile is increased). The addition of nitrogen dioxide at 250°C did not affect the decomposition rate. Increasing the S/V ratio 100 times (by packing the vessel with glass wool) leads to a considerable increase in the rate and a rise in the yields of acetone, acetonitrile, and water. The ratio C_3H_6/NO is almost independent of the experimental conditions. The yield of propene does not alter on adding nitric oxide or propene itself nor on altering S/V. These facts show the formation of propene by the reaction:

$$(CH_3)_2CHNO_2 \rightarrow CH_3CH=CH_2 + HNO_2 .$$

As regards other carbonaceous products their production is explained by the occurrence of side-reactions, which occur because of the presence of the hydroxyl radical:

$$HNO_2 \rightarrow OH + NO \quad (29)$$

$$OH + CH_3CHNO_2CH_3 \begin{cases} \rightarrow H_2O + CH_3\dot{C}NO_2CH_3 & (30) \\ \rightarrow H_2O + CH_3CHNO_2\dot{C}H_2 & (31) \end{cases}$$

$$CH_3\dot{C}NO_2CH_3 \rightarrow CH_3COCH_3 + NO \quad (32)$$

$$CH_3CHNO_2\dot{C}H_2 \rightarrow CH_3CHNO + CH_2O \quad (33)$$

$$CH_3CHNO_2\dot{C}H_2 \rightarrow CH_3CH{=}CH_2 + NO_2 \quad (34)$$

$$CH_3CHNO \rightarrow CH_3CNOH \quad (35)$$

$$CH_3CNOH + NO \rightarrow CH_3CN + HNO_2 . \quad (36)$$

The ratio CH_3CN/CH_3COCH_3 increases with the temperature, as reaction (31) has a higher activation energy than (30).

The weak link in the above scheme is reaction (29). The decomposition of nitric acid according to Eqn. (29) requires an activation energy of 48 kcal mole^{-1} and evidently cannot compete with reaction (28). Moreover, the assumption that the decomposition of nitrous acid initiates side-processes in the molecular decomposition of nitroalkanes cannot explain two features—the influence of the surface on the rate and the comparatively high yield of the products of radical origin at low temperatures—which distinguish 2-nitropropane from nitroethane and 1-nitropropane.

It is possible that in the decomposition of 2-nitropropane, because of its considerable acidity, a significant part is played by processes (decomposition of ionised form and reaction with nitric oxide) taking place in layers adsorbed on the surface.

In connection with the molecular mechanism of decomposition of mononitroalkanes a consideration of these reactions from the standpoint of the general theoretical concepts of gas phase eliminations merits attention. The most significant achievement in this region is the introduction of the concept of quasiheterolytic reactions in the gas phase[34,38]. It was shown[34] that in a series of gas-phase reactions just the same effect of substituents on the rate is observed as in ionic reactions of elimination or substitution, taking place in polar solvents. Hence the conclusion was drawn that the transition state of such gas-phase reactions has a polar nature and the internal supply of electrons is the main factor which determines the decomposition rate. In quantity and direction of the action of the substituents two types of quasiheterolytic reactions are distinguished. Reactions of the first type, which include the elimination of hydrogen halides from alkyl halides, are similar to S_N1 and $E1$ liquid-phase reactions; the reactions of the second type, represented by the elimination of alkenes from esters and alkyl vinyl ethers, are analogous to $E2$ reactions. Judging by the relative rates (Table 3) the decomposition of mononitroalkanes, at least in the quantitative respect, differs strongly from other eliminations in the gas phase. Nevertheless, from the standpoint of the polar nature of these reactions the nature of the change in activation energy in the series $C_2H_5NO_2$, n-$C_3H_7NO_2$, iso-$C_3H_7NO_2$ (39.7, 47.7, and 39.0 kcal mole^{-1} respectively) can be explained qualitatively. The value of the potential barrier for the detachment of HNO_2 from nitroalkanes $\epsilon_0 = E - Q$ (E is the activation energy, Q the heat of the process) varies symbathically with such properties as acidity or chemical shift of α-protons in the NMR spectra (Table 4), that is, it reflects the real change in the distribution of electron density in the molecule¶.

Table 3. Relative rates of reaction eliminations in the gas phase[34].

R	RCl	RBr	RNO_2^*	ROAc	HCO_2R	$ROCH{=}CH_2$
C_2H_5	1	1	1	1	1	1
n-C_3H_7	3.9	3.3	0.5	—	—	—
iso-C_3H_7	223	280	2.8	26	20	17

* The rates for the nitroalkanes were calculated from Wilde's results[20]. The temperatures of comparison were selected as for the alkyl halides[34].

Table 4. Correlation of the values of E and ϵ_0 with change in acidity and the chemical shift on the α-hydrogen atom.

Formula	E, kcal mole^{-1} (Ref.20)	Q^*, kcal mole^{-1}	ϵ_0, kcal mole^{-1}	pK	Chemical shift of α-H (in τ units) (Ref.42)
$C_2H_5NO_2$	41.4	16.1	25.3	8.49[39]	5.62
n-$C_3H_7NO_2$	47.7	14.6	33.1	8.98[40]	5.70
iso-$C_3H_7NO_2$	39.0	18.8	20.2	7.675[39]	5.42

* Data for the calculation taken from Refs.26 and 28.

The limited information does not allow more definite conclusions to be drawn about the nature of the molecular decomposition of mononitroalkanes, but undoubtedly these substances, being comparatively convenient for experimental investigation and exhibiting a great variety of structures, will merit attention as model compounds for studying gas-phase eliminations.

3. Chloropicrin

The first qualitative observation of the decomposition of chloropicrin CCl_3NO_2 was made in 1919 by Gardner and Fox[43]; on boiling (112°C), chloropicrin slowly decomposes into carbonyl chloride and nitrosyl chloride. In 1935 Rădulescu and Zamfirescu[3], using the method of titration of chloropicrin with permanganate, established the first order of the reaction for the decomposition and determined the rate constants at 130–160°C. Later[23] these results were used to estimate the activation energy, 40 kcal mole^{-1}.

¶ The reaction of nitrogen dioxide with an alkyl residue is evidently not limited solely to an induction mechanism. This is shown, for example, by the fine effects in the change in acidity of mono- and di-nitroalkanes[39-41]. It is easy to see that in the RX series, where X = Cl or Br (and the interaction of X with R is purely inductive), a linear relation is observed between ϵ_0 and Taft's induction constant σ^* of the group R.

In their detailed investigation of the decomposition of chloropicrin[23] Steacie and Smith found, with the aid of a manometric method, that the reaction proceeds homogeneously and is independent of P_0 in the range 60–200 mmHg. The decomposition products are carbonyl chloride, nitrosyl chloride, chlorine, and nitric oxide, the relative proportions of the last three compounds being close to equilibrium. Starting from these results a mechanism was proposed for the decomposition which included intramolecular rearrangement.

$$CCl_3NO_2 \rightarrow Cl_2CO + NOCl\,, \quad (37)$$

$$NOCl \rightleftarrows NO + {}^1/_2 Cl_2\,. \quad (38)$$

As, however, equilibrium (38) is established slowly (in the decomposition of chloropicrin to the extent of 50% there is 1% decomposition of the nitrosyl chloride at 160°C), to explain the observed composition of the products it was suggested that in stage (37) the activated molecule (NOCl*) is formed; this is rapidly decomposed into NO and Cl.

An analogous mechanism with primary decomposition of chloropicrin into carbonyl chloride, chlorine, and nitric oxide was proposed by Ashmore and Norrish[24].

In 1955, Gray[25] expressed the opinion that the decomposition of chloropicrin proceeds by a free radical mechanism and the first stage is the breaking of the C–N bond.

Gray's scheme:

$$CCl_3NO_2 \rightarrow CCl_3 + NO_2\,, \quad (39)$$

$$CCl_3 + NO_2 \rightarrow [CCl_3ONO] \rightarrow CCl_3O + NO\,, \quad (40)$$

$$CCl_3O \rightarrow Cl_2CO + Cl\,, \quad (41)$$

$$Cl + NO \rightleftarrows NOCl\,, \quad (42)$$

$$2Cl + M \rightarrow Cl_2 + M\,, \quad (43)$$

agree with all the experimental facts. The low value of the dissociation energy of the C–N bond, the value of which, according to the scheme, equals the activation energy of the decomposition can be attributed to the influence of three chlorine atoms[25]. In methane derivatives the introduction of electronegative substituents usually decreases the strength of the bonds[44]. This conclusion is indirectly confirmed by the force constant and frequency of the vibrations of the C–N bond in chloropicrin as compared with nitromethane (842 and 917 cm^{-1} respectively[45]).

The most convincing proof of the radical mechanism of the decomposition of chloropicrin gives an anomalously high value of its pre-exponential factor (Table 1). Only within the framework of the radical decomposition does this fact find a natural explanation (see p. 608). In rearrangements which include a cyclic transition state the pre-exponential factor can have only a normal or a low value.

Hence the replacement of hydrogen atoms in nitromethane by chlorine leads to a singificant decrease in the strength of the C–N bond and correspondingly to a very pronounced increase in the rate of decomposition. The mechanism of the first stage here remains unchanged but the secondary reactions in the case of chloropicrin are appreciably simpler and do not affect the initial state.

III. POLYNITRO-COMPOUNDS

Two of the polynitro-compounds (PNC) studied—2,2-dinitropropane (DNP)[4] and hexanitroethane (HNE)[5]—differ considerably in structure, decomposition rates, and the conditions under which their decomposition rates were studied. For these substances completely different mechanisms were proposed: breaking of the C–N bond and a chain process for DNP, and the formation of biradicals for HNE. Here, however, a situation analogous to that with chloropicrin is repeated. On closer examination it becomes almost certain that both substances have the same mechanism and decompose by a non-chain radical path with primary breaking of the C–N bond. Here the activation energy equals D(C–N).

1. 2,2-Dinitropropane

Fluornoy[4] studied the decomposition of DNP at 175–210°C by the ampoule method with mass spectroscopic analysis of the decomposition products. There are three initial products: acetone, nitric oxide, and nitrogen dioxide, which are formed in equivalent proportions. On increasing the extent of the decomposition the nitrogen dioxide concentration decreases rapidly (which is explained by its reaction with acetone) and carbon monoxide and dioxide and water appear. The rapid oxidation of acetone directly by nitrogen dioxide at temperatures above 100°C was shown in special experiments. At 2.3% decomposition the yield of nitrogen dioxide amounted to 75 mole % from the DNP and at 7.6% decomposition almost all the nitrogen of the products was found as nitric oxide. The decomposition of DNP proceeds homogeneously and the nature of the surface does not affect the reaction. The first-order rate constant is $3.2 \times 10^{18} \exp(-50\,500/RT)\ s^{-1}$.

Fluornoy considers that the decomposition of DNP starts with the breaking of the C–N bond, the strength of which should be less than in mononitro-compounds. The 2-nitropropyl radical formed in the first stage is converted into acetone, either on reaction with NO_2 with the intermediate formation of a nitro-nitrite:

$$(CH_3)_2\dot{C}NO_2 + NO_2 \rightarrow \left[\begin{array}{c} CH_3 \\ | \\ O_2N{-}C{-}ONO \\ | \\ CH_3 \end{array}\right] \rightarrow NO_2 + (CH_3)_2 + CO + NO \quad (44)$$

or intramolecularly according to (32), as Smith and Calvert assume (see p. 609). The direct unimolecular rearrangement of DNP into the nitro-nitrite is thought by Flournoy to be impossible owing to steric hindrance.

To explain the high pre-exponential factor, Flournoy suggested that in parallel with Eqn. (44) there is a reaction of the 2-nitropropyl radical directly with DNP:

$$(CH_3)_2\dot{C}NO_2 + (CH_3)_2C(NO_2)_2 \rightarrow (CH_3)_2C(NO_2)(ONO) + (CH_3)_2\dot{C}NO_2 \quad (45)$$

and hence the chain decomposition of the latter is effected. However, in the light of contemporary theory which allows the high value of A to be explained within the framework of a mechanism with breaking of a single bond (as occurs for nitromethane and chloropicrin) the hypothesis about chains is superfluous. Reaction (45) is evidently thermoneutral [$D(C{-}NO_2) \simeq D(C{-}ONO)$ [25]] and its activation energy should be not less than 10 kcal $mole^{-1}$. It is not known whether the 2-nitropropyl radical is removed by reaction with nitric oxide, but in the initial stages when there is a considerable concentration of nitrogen dioxide, reaction (45) cannot compete with (44) and the occurrence of the chain process is impossible.

We note that a high yield of acetone allows a molecular path for the decomposition of DNP to be excluded. Hence the change from mono- to *gem*-di-nitro-radicals is accompanied by a change in mechanism. The endothermicity of the reaction for loss of nitrous acid on going from 2-nitropropane to DNP can only decrease and even if it is assumed that the activation energy of the molecular decomposition is 15 kcal $mole^{-1}$ less than the strength of the

C–N bond (and the radical mechanism is affected only because of the high activation entropy), then $E \geqslant 35$ kcal mole^{-1} and the value of ϵ_0 (see p. 609) will be greater or equal to ϵ_0 for 2-nitropropane. The weakening of the C–N bond and the greater mobility of the β-hydrogen atom in *gem*-dinitro-compounds[46] should facilitate an increase in ϵ_0. As this does not take place, it can be assumed that the drop in electron density at the nitro-groups exerts an opposite effect and compensates the first two effects. A study of the decomposition of nitroalkanes of the type $RCH_2CH(NO_2)_2$ and $RCH_2C(NO_2)_3$ offers a further possibility of solving the problem of the competition of molecular and radical mechanisms.

2. Hexanitroethane

HNE is a strong oxidant and reacts with organic compounds of almost all classes[47]. Exceptions are hydrocarbons with branched chains and substances with a high concentration of halogens. A quantitative study of the decomposition was undertaken[5] for solid HNE and for dilute solutions (2×10^{-2}–4×10^{-2} M) in carbon tetrachloride, chloroform, perfluorokerosene, n-heptane, and cyclohexane. The reactions were observed by three methods: from the change in intensity of the absorption bands in the infrared spectra at 6.10 and 6.17 μm, from the yield of nitric oxide and dioxide, determined titrometrically, and manometrically from the increase in pressure of the decomposition products. All three methods give the same results. Tables 1 and 5 give the results on decomposition rates.

The agreement of the rates for decomposition in carbon tetrachloride, chloroform, and perfluorokerosene show the inertness of these solvents in relation to HNE. Hence the activation parameters found in carbon tetrachloride characterise the unimolecular decomposition of HNE. The decomposition in n-heptane and cyclohexane is considerably faster (and with a lower activation energy) than in inert solvents. This result is explained by the formation between HNE and the solvent of unstable molecular compounds of the charge-transfer complex type. Undoubtedly the aliphatic HNC exhibit electron acceptor properties, the strength of which increases with saturation of the molecule with nitro-groups. The idea of complex formation as a first stage in the interaction with different donors can play an important part in the study of the compatibility of PNC with other substances.

The decomposition of the HNE in the solid state proceeds more slowly than in inert solvents. The ratio of the constants k_{diss}/k_{solid} at 85°C is, according to Marshall and coworkers[5], 3.5; according to other results it is significantly greater, 56 (see Table 5). It should be noted that the accuracy of the determination of k_{solid} in this study[5] is somewhat doubtful. Thus the authors of this work write that the solid-state decomposition of HNE obeys a first-order equation. However, it is known that topochemical reactions never obey a first-order law and the reaction has to be accompanied by acceleration[48]. In this study[5] no information is given about the kinetics of the initial stage of the decomposition of HNE. Possibly acceleration of the reaction takes place in this stage and the value of k_{solid} corresponding to the initial rates will be less than that calculated[5]. Another reason for the differences in the available data can be the difference in the physical state and purity of the HNE specimens. The agreement of the activation energy in the decomposition of HNE in inert solvents and in the solid state suggests (by analogy with other instances[48] of the decomposition of solid organic substances) that the decomposition of HNE proceeds at places where there is pronounced strain in the ideal crystal lattice (surface micro-blocks, dissimilar type of defects) and the rate of reaction depends on the fraction of the molecules found at these points.

As noted by Marshall and coworkers[5], HNE itself is a fine model for investigating the regularity of the reactions of thermal decomposition of molecular crystals. The decomposition of HNE proceeds with an appreciable rate in the range of temperatures far from the melting point and is not accompanied by the formation of a liquid phase and condensed products, which could affect the reaction, by dissolving HNE or forming a new crystalline phase.

Table 5. Comparison of the rate constants (s^{-1}) for the decomposition of hexanitroethane in the solid state and in solutions.

t, °C	Solvent						
	without solvent	without solvent*	CCl_4	$CHCl_3$	perfluoro-kerosene	n-heptane	cyclo-hexane
85	$6.41 \cdot 10^{-6}$	$4 \cdot 10^{-7}$	$2.24 \cdot 10^{-5}$	$2.43 \cdot 10^{-5}$	—	$7.35 \cdot 10^{-5}$	$1.53 \cdot 10^{-4}$
100	$6.79 \cdot 10^{-5}$	$3.55 \cdot 10^{-6}$	$2.22 \cdot 10^{-4}$	—	$2.03 \cdot 10^{-4}$	$3.46 \cdot 10^{-4}$	$5.68 \cdot 10^{-4}$

* Private communication of Rosen cited in Ref. 5.

The final products of the decomposition of HNE are nitrogen oxides and carbon oxides. Their composition corresponds approximately to the equation:

$$HNE \rightarrow 3NO_2 + NO + N_2O + 2CO_2,$$

and the rate of formation equals the rate of decomposition of HNE. The absence of information on the structure of the intermediate products does not permit any judgement about the secondary reactions, as a result of which the HNE molecule is destroyed. As possible primary stages of the decomposition two processes were proposed, including the simultaneous breaking of two nitro-groups

$$HNE \rightarrow (O_2N)_2\dot{C}-\dot{C}(NO_2)_2 + 2NO_2 \quad (46)$$

$$HNE \rightarrow (O_2N)_3C-\dot{C}(NO_2) + 2NO_2, \quad (47)$$

since the decomposition of the molecule into three species could explain the high values of the activation entropy. However, reactions (46) and (47) are no less than 10 kcal mole^{-1} more endothermic than the simple breaking of a single bond

$$HNE \rightarrow (O_2N)_3C\dot{C}(NO_2)_2 + NO_2 \quad (48)$$

and their occurrence is possible only for a considerably greater (by at least four orders of magnitude) pre-exponential factor. All this suggests that reaction (48) is the most probable primary act of decomposition of HNE. A conclusive solution of the problem is possible only on studying and comparing the decomposition of other PNC and determining the energy of the C–N bond in polynitro-derivatives of methane and ethane.

The problem of finding the energies of breaking of C–N bonds in aliphatic PNC has real prospects of solution in the study of thermal decompositions and makes it desirable to carry out further work to explain the mechanism of the decomposition of typical representatives of PNC of various structures. In experimental respects a study of these reactions should evidently not present great difficulty, since it can be expected that characteristic signs of the decomposition processes are general for DNP and HNE: the

combination of comparatively low activation energies with high pre-exponential factors, and in consequence the moderate decomposition temperatures at which nitrogen monoxide and dioxide found in the reaction products do not react with the initial components, do not inhibit chain processes, ensuring the unimolecularity of the process even under static conditions, the speed of the secondary reactions and the possibility of using a manometric method, is retained also for other nitro-compounds with a geminal distribution of the nitro-groups.

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