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Thermal decomposition of aliphatic nitro-compounds

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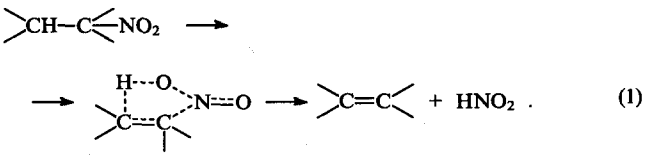
Abstract. Literature data on the thermal decomposition reactions of aliphatic nitro-compounds are surveyed and described systematically. Information concerning the influence of molecular structure on the rates and mechanisms of the gas-phase reactions is presented and the structures of the transition states in the C–N dissociation and HNO_2 elimination processes are examined. The characteristic features of the decomposition of nitro-compounds in the condensed phase are described. Data are presented on the C–N bond dissociation energy and the influence on the latter of electronic, steric, and conformational effects. The bibliography includes 86 references.

I. Introduction

The high rates of development of the chemistry of aliphatic nitro-compounds observed during recent decades were associated mainly with the search for new explosives and rocket fuel oxidants. The predominance of this aspect was responsible for the vigorous investigation of the thermal decomposition reactions of both the high-energy compounds themselves and of their numerous analogues and models. Thermal decomposition of virtually all the structural types of nitro-compounds has been studied: mononitroalkanes, *gem*-dinitroalkanes, 1,1,1-trinitroalkanes, pentane derivatives containing between 4 and 8 nitro-groups, unsaturated nitro-compounds, aliphatic-aromatic nitro-compounds, and α-halonitro-compounds, as well as numerous compounds with linked mixed functional groups in which the $C-NO_2$ fragments are the most reactive parts of the molecules. Whereas only 8 compounds were examined in the first (and hitherto the only) review on this topic published in 1968,[1] at the present time the number of systems investigated has exceeded 100 and in almost all cases the studies have reached the stage in which the decomposition mechanism has been established. This makes it possible to classify the available data not only in terms of the types of substances but also in terms of the reaction mechanisms. In the classification based on the mechanisms, large reaction series arise within the framework of which it is easy to trace the relation between structure and reactivity and to predict the stability of new compounds. It is also useful to consider separately the gas phase and the condensed state in which the decomposition reactions have a number of characteristic features.

On the basis of all the available data, one may conclude that the following principal decomposition mechanisms operate in the gas phase:

1. The molecular mechanism involving the elimination of HNO_2 *via a five-membered transition state:*



(1)

2. The radical mechanism, where the reaction proceeds via the dissociation of the C–N bond with formation of free radicals:

$$RNO_2 \longrightarrow \dot{R} + NO_2^{\cdot} . \qquad (2)$$

Mononitroalkanes having a hydrogen atom in the α-position, α-halonitro-compounds of the type RCH_2CHXNO_2 (X = halogen), and many α-nitroolefins decompose via the first mechanism at moderate temperatures (up to 300 °C). Owing to the reduced strength of the C–N bond, the decomposition of *gem*-dinitroalkanes, 1,1,1-trinitroalkanes, α,α-dihalo-derivatives RCX_2NO_2, and other compounds with a large number of nitro-groups proceeds via the second mechanism. At fairly high temperatures, reaction (2) becomes dominant in all cases because it has a higher pre-exponential factor in the expression for its rate constant than reaction (1).

II. Gas-phase decomposition via the molecular mechanism

1. Mononitroalkanes

The gas-phase decomposition of mononitroalkanes is complicated by a heterogeneous reaction on the surface.[2,3] The dependence of the rate of reaction on the ratio of the surface area to the volume of the vessel (S/V) is significant in the case of primary [2] nitroalkanes and is virtually absent for tertiary nitroalkanes.[3] Accordingly, an appreciable scatter of the literature data, due to failure to take into account heterogeneous reactions, is observed only in the case of primary nitroalkanes.[1] The 'elimination' of the heterogeneous reaction is achieved by calculating the dependence of the observed rate constants k_o on the parameter S/V.

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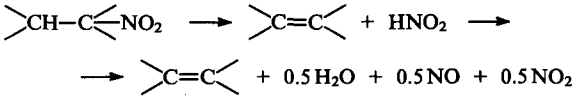
Table 1. Characteristics of the molecular decomposition of nitroalkanes.[4]

Compound	T/ °C	E/kJ mol^{-1}	lg(A/s^{-1})	ω_{rel} at 570 K	D(C–N)/kJ mol^{-1}	Q/kJ mol^{-1}	ε_0/kJ mol^{-1}
Nitroethane	320–380	188.5	12.24	1.00	237.1	70.3	118.2
1-Nitropropane	320–380	188.1	12.15	1.09	247.2	64.3	123.8
1-Nitrobutane	320–380	181.8	11.79	1.47	227.9	67.4	114.4
1-Nitropentane	320–380	181.8	11.82	1.66	–	–	–
1-Nitrohexane	320–380	181.4	11.81	1.79	–	–	–
2-Methyl-1-nitropropane	320–380	182.7	11.65	0.93	–	–	–
3-Methyl-1-nitrobutane	320–380	183.9	11.99	1.59	–	–	–
2-Nitropropane	280–340	182.3	12.72	11.7	246.4	81.5	100.8
2-Nitrobutane	280–340	181.4	12.70	13.5	251.8	–	–
2-Nitrohexane	280–340	183.1	12.93	15.7	–	–	–
3-Methyl-2-nitrobutane	280–320	179.3	12.68	–	–	–	–
3,3-Dimethyl-2-nitrobutane	280–320	177.2	12.74	36.2	–	–	–
2-Methyl-2-nitropropane	250–320	179.3	13.63	170.0	242.2	84.8	94.5
2-Methyl-2-nitrobutane	250–300	173.0	13.30	312.3	–	–	–
3-Methyl-2-nitropropane	250–280	170.5	13.33	363.0	–	–	–
2,3-Dimethyl-2-nitrobutane	230–280	170.5	13.43	721.0	–	–	–

Note. The thermochemical data for the calculation of D and Q were taken from Lebedev et al.[12]

The characteristics of the homogeneous gas-phase reactions are presented in Table 1.

The decomposition of nitroalkanes results in the formation of the corresponding olefins.[4–6] During the reaction, they are oxidised, but these processes do not proceed to an appreciable extent[3] and in all cases the final gas pressure is close to $2.5p_0$ (p_0 is the initial pressure), i.e. is the same as for the expected initial process.



In the decomposition of secondary and tertiary nitroalkanes, the yield of alk-1-enes and alk-2-enes is close to the statistical value and is almost independent of temperature (Table 2). Only in the case of 2,3-dimethyl-2-nitrobutane is steric hindrance to the formation of alk-2-ene observed.

a. The importance of the pre-exponential factor

The increase in rate on passing from primary to tertiary nitroalkanes is caused to a significant extent by the increase in the pre-exponential factor A. If account is taken of the change in the statistical reaction factor σ, which is equal to twice the number of hydrogen atoms in the β-positions, then, within the limits of the series of primary, secondary, and tertiary nitroalkanes, the values of lg(A/σ) are approximately constant and equal on average to 11.34, 11.80, and 12.35 respectively. These differences between the values can be explained by the stepwise increase in the barrier to the internal rotation V_{int} about the C–N bond on α-alkylation (from <4 kJ mol^{-1} for primary nitroalkanes to >40 kJ mol^{-1} for tertiary nitroalkanes). The increase in the barrier to the internal rotation about the C–C bond also exerts some influence on the change in A. The loss of this partly hindered rotation is responsible for the reduced value of A/σ in *tert*-nitroalkanes (compared with the 'normal' value $A = 10^{13.5}$ s^{-1}). The details of the calculation of A for reactions involving elimination from primary nitroalkanes have been published.[7]

Table 2. The relative yields (γ) of alk-1-enes on decomposition of nitrocompounds.[4]

Compound	T/ °C	γ(%)	
		experiment	calculation
2-Nitrobutane	250	55	60
	330	56	60
2-Nitrohexane	300	58	60
3-Methyl-2-nitrobutane	300	78	75
2-Methyl-2-nitrobutane	190	77	75
	250	77	75
3-Methyl-3-nitropentane	250	43	42.8
2,3-Dimethyl-2-nitrobutane	250	95	85.7

b. The polar nature of the HNO_2 elimination reaction

Reaction (1) is endothermic and its activation energy is

$$E = Q + \varepsilon_0,$$

where Q is the heat of reaction and ε_0 the activation energy for the reverse process involving the addition of HNO_2 to the olefin.

It is seen from Table 1 that under the influence of alkyl substituents Q and ε_0 change in opposite directions and the energy E therefore remains almost constant.

α-Methylation has comparatively little influence on the rate of reaction (1) (Table 3) and, in terms of this feature, the elimination of HNO_2 can be assigned (in Maccoll's terminology[9]) to weak quasi-heterolytic processes. However, in terms of another feature of these reactions, according to which the rate of elimination depends directly on the degree of charge separation in the transition state, reaction (1) can be assigned to highly polar reactions, since its rate exceeds those of any other reactions of this type. There is no doubt that the high electronegativity of the NO_2 group and the high dipole moment of the nitroalkane molecule (~3.5 D), which is almost twice as high as for haloalkanes (~2.0 D), facilitate the formation of a highly polar transition state. As a result of the low polarisability of the C–N bond and the simultaneously high electronegativity of the NO_2 group, the bond is polarised to the maximum extent already in nitroethane and, on further alteration of the structure of the alkyl residue, the state of this bond and the charge on the nitro-group hardly vary and hence the rate of the decomposition reaction varies only little. The extent of the change in the polarisation of the C–N bond on α-methylation may be estimated from the relative increase in the dipole moment $\Delta\mu$ on passing from CH_3X to *tert*-C_4H_9X. For example, $\Delta\mu$ is 20% for X = Cl and only 5% for X = NO_2. Similarly, $\Delta\mu$ is small in the series of alcohols, amines, esters, and isocyanates[8] and hence there is only a slight variation of the rate of α-methylation of these compounds.

Table 3. The influence of α-methylation on the relative rate of elimination of HX from the alkyl derivatives RX.[8]

X	R = *iso*-C_3H_7	R = *tert*-C_4H_9
Cl	223	41000
Br	280	78000
I	100	35000
CH_3COO	26	1600
HCOO	20	720
SCN	38	800
NO_2	12	172
$H_2C=CHO$	13	126
OH	10	38

Note. The relative rate is unity for R = C_2H_5.

In terms of the change in ε_0 ($\Delta\varepsilon_0$) for the reaction involving addition to olefins of different structure, HNO_2 does not differ from other acids HX (Table 4) and the above process is quantitatively consistent with the theoretical calculations for four-centre reactions based on the polar transition state model made up of two semi-ionic pairs in proximity.[10]

Using ε_0 for nitroethane, the $\Delta\varepsilon_0$ data for olefins,[11] and additive schemes for the calculation of the enthalpies of formation of nitro-compounds,[12] it is possible to estimate Q and E for the elimination reactions involving many nitroalkanes. Absence of a preferential elimination from *sec*-nitroalkanes has been explained by the mutual compensation of Q and ε_0 (Table 1).

2. α-Halonitroalkanes

The α-halogenation of nitroalkanes lowers the activation energy and increases the rate of reaction (Tables 1 and 5). However, this decrease is small (4–12 kJ mol^{-1}) and reaches 20 kJ mol^{-1} in only one case ($C_2H_5CHClNO_2$). However, on the whole the activation energy for the molecular decomposition of α-halonitroalkanes is in the range 166–184 kJ mol^{-1}, as for nitroalkanes.

In terms of their influence on the rate of the decomposition reaction, the halogens can be arranged in the sequence Cl > Br > F. This sequence in the influence of the halogens may be accounted for within the framework of the concept of the polar nature of the transition state. The inductive effect of the halogen atoms, which diminishes the electron density of the NO_2 group, should increase the rate of decomposition of halonitroalkanes in the sequence Br < Cl < F. On the other hand, the ability of the halogens to exhibit a positive mesomeric effect decreases the rate of decomposition in this series. The mesomeric effect may be expressed by the stabilisation of the transition state or by the supply of electrons to the NO_2 group in the ground state.

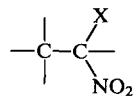


Table 5. Characteristics of the reactions involving the elimination of HNO_2 from halonitroalkanes.[13]

Compound	T/ °C	E/kJ mol^{-1}	lg(A/s^{-1})	ω_{rel} [a]
CH_3CHFNO_2	300–340	184.3	12.62	5.4
$C_2H_5CHClNO_2$	250–300	165.9	12.55	174.0
$C_2H_5CHBrNO_2$	280–320	173.9	12.48	31.6
$(CH_3)_2CClNO_2$	240–300	176.8	13.62	24.5
$(CH_3)(C_2H_5)CClNO_2$	250–280	171.8	13.37	36.3
$(CH_3)_2CBrNO_2$	250–290	176.8	13.40	14.8
$(CH_3)_2CHCCl(NO_2)CH_3$	230–270	167.6	13.20	40.0
$(CH_3)_2CHCBr(NO_2)CH_3$	230–270	165.9	13.19	40.0

[a] ω_{rel} is the ratio of the rate of decomposition of the halonitroalkane to the rate of decomposition of the analogous unsubstituted nitroalkane at the temperature corresponding to $k = 10^{-4}$ s^{-1} for the nitroalkane.

The sequence in the influence of the halogens is in fact a consequence of the superposition of these two effects. The same sequence has been observed in the decomposition of α-polyhaloalkanes.[8,9,14]

3. α-Nitroolefins

In terms of the rate and kinetic parameters of their decomposition reactions, α-nitroolefins are close to their saturated analogues (Table 6). β-Alkylation influences the rate and activation energy more than does α-alkylation. The quantity lg(A/σ) for the decomposition of nitroalkenes is actually equal to that for the decomposition of *sec*-nitroalkanes. In the case of nitroalkenes, the internal rotation about the C–N bond is lost on formation of a cyclic transition state, while in the case of nitroalkenes the internal rotation about the C–N and C–C bonds is lost. Consequently the potential barrier to the internal rotation of the nitro-group in nitroalkenes is higher than in *sec*-nitroalkanes.

The decomposition of unsaturated nitro-compounds can also proceed via other mechanisms, but these too are of the molecular type. It has been shown for 2-methyl-3-nitroprop-2-ene that,[15] when the NO_2 and CH_3 groups are forced to

Table 6. Characteristics of the molecular decomposition of nitroalkenes.[13]

Compound	T/ °C	E/kJ mol^{-1}	lg(A/s^{-1})	ω_1	ω_2
$CH_2=CHNO_2$	340–400	191.9	12.10	1.0	1.3
$CH_3CH=CHNO_2$	307–360	176.8	11.82	9.2	8.1
$C_2H_5CH=CHNO_2$	290–340	176.0	11.92	13.8	8.3
$C_6H_5CH=CHNO_2$	290–350	176.0	12.04	18.2	–
$C_2H_5C(NO_2)=CH_2$	323–380	187.3	12.16	2.6	0.25

Note. The following notation has been adopted: ω_2 is the relative rate at 350 °C and ω_2 is the ratio of the rates of decomposition of the nitroalkene and of its saturated analogue at the temperature corresponding to $k = 10^{-4}$ s^{-1} for the nitroalkene.

Table 4. The absolute change $\Delta\varepsilon_0$ (kJ mol^{-1}) in reactions involving the addition of HX to olefins.[8]

Olefin	Orientation[a]	Calculation	Experiment for HX					
			HCl	HBr	HI	H_2O	CH_3OH	HNO_2
C_2H_4	–	0	0	0	0	0	0	0
C_3H_6	M	−17.6	−23.1	−17.2	−19.7	−26.0	–	−17.6
	AM	+1.7	−3.3	−0.8	–	−0.8	–	+5.7
C_4H_8	M	−24.7	−35.2	−31.4	–	–	–	−23.9
	AM	−2.1	−3.3	−3.3	–	–	–	−3.7
iso-C_4H_8	M	−50.3	−62.0	−49.4	−42.7	−43.1	−44.0	−23.6

[a] The following notation has been adopted: M — addition in accordance with the Markovnikov rule, AM — addition contrary to the Markovnikov rule.

assume the *cis*-disposition, decomposition via isomerisation takes place readily.

$$(CH_3)_2C{=}CHNO_2 \longrightarrow H_2C{=}\underset{\displaystyle CH_3}{\overset{|}{C}}{-}CHNOOH \longrightarrow \text{products}$$

For this compound, we have

$$k = 10^{11.8} \exp\left(-\frac{151680}{RT}\right).$$

The composition of the products of the decomposition of $PhCH=C(CH_3)NO_2$ at 600 °C and a pressure of 10^{-3} torr has been determined.[16] Since the main products are PhCHO and CH_3CN, one may conclude that the reaction proceeds via an intramolecular oxidation mechanism.

$$PhCH{=}C(CH_3)NO_2 \longrightarrow Ph{-}\overset{H}{\underset{O\cdots N\rightarrow O}{C}}{=}\overset{CH_3}{C} \longrightarrow$$

$$\longrightarrow PhCHO + CH_3CN + O$$

However, in order to confirm this mechanism, it is essential to carry out further studies on this reaction and in the first place to determine its kinetic parameters, to elucidate the influence of p_0 on the composition of the products and on the rate, and to investigate nitrostyrene analogues.

It has been shown[17] that on hot (650 °C) iron and nickel surfaces nitroethylene loses an oxygen atom and is converted into nitrosoethylene. The reaction was carried out at low pressures with activation by collisions with the surface. Nitrosoethylene was in fact obtained for the first time by this method and its reactions on the surface were elucidated.

$$H_2C{=}CH{-}NO \longrightarrow CH_2{=}CH{-}N{:} \longrightarrow H_3CCN$$

III. Gas-phase decomposition via the radical mechanism

1. The chemical mechanism

The decomposition reactions the first stage of which is the dissociation of the C–N bond are complicated by chain processes only in the case of mononitro-compounds such as nitromethane[18–21] and chloropicrin.[22] For nitromethane, heterogeneous decomposition on the surface is also important.[18] The mechanism of the decomposition of nitromethane at all temperatures up to the inflammation temperature[23–25] includes at least 26 reactions. Some of the reactions presented in Scheme 1 are kinetically important and explain the formation of the principal intermediates (CH_2O, NO, NO_2) and final products (CH_4, CH_3OH, HCN, H_2O) at moderate temperatures.

Scheme 1

$$CH_3NO_2 \longrightarrow \dot{C}H_3 + NO_2$$

$$CH_3NO_2 + \dot{C}H_3 \longrightarrow CH_4 + \dot{C}H_2NO_2$$

$$\dot{C}H_3 + NO_2 \longrightarrow CH_3\dot{O} + NO$$

$$CH_3NO_2 + CH_3\dot{O} \longrightarrow CH_3OH + \dot{C}H_2NO_2$$

$$\dot{C}H_2NO_2 \longrightarrow CH_2O + NO$$

$$\dot{C}H_3 + NO \longrightarrow CH_3NO$$

$$CH_3NO \longrightarrow HCN + H_2O$$

Starting with *gem*-dinitroalkanes, the polynitro-compounds decompose unimolecularly. The surface, pressure, and impurities do not as a rule affect the rate. Nitrogen oxide and dioxide, formed in the decomposition, inhibit all the free-radical processes. Processes on the surface are characteristic only of substances of the type of di- and tri-nitromethane having a hydrogen atom in the α-position.[26] Typical decomposition reactions of polynitro-compounds are presented in Scheme 2. The scheme is based on the composition of the products of the decomposition of 1,1,1-trinitroethane (Table 7).[27] All the stages in this scheme, except the fourth, correspond to the generally accepted ideas concerning the reactions of free radicals in NO_2 and NO. The fourth reaction is new and is observed only for compounds having at least two nitro-groups at one carbon atom. The yield of nitriles increases following the addition of NO. RCN and ClCN are formed from $RCCl(NO_2)_2$.[14] When iodine is added to $C(NO_2)_4$ and $ClC(NO_2)_3$, ICN is formed in the first case, while in the second only ClCN is produced.[28]

Scheme 2

$$CH_3C(NO_2)_3 \longrightarrow CH_3\dot{C}(NO_2)_2 + NO_2$$

$$CH_3\dot{C}(NO_2)_2 \longrightarrow CH_3\dot{C}O + NO + NO_2$$

$$CH_3\dot{C}(NO_2)_2 + NO_2 \longrightarrow CH_3\dot{C}O + NO + 2\,NO_2$$

$$CH_3\dot{C}(NO_2)_2 + NO \longrightarrow CH_3C(NO)(NO_2)_2 \longrightarrow$$

$$\longrightarrow CH_3CN + NO_2 + NO_3$$

$$CH_3\dot{C}O \longrightarrow \dot{C}H_3 + CO$$

$$CH_3\dot{C}O + NO_2 \longrightarrow CH_3CO\dot{O} + NO$$

$$CH_3CO\dot{O} \longrightarrow \dot{C}H_3 + CO_2$$

$$CH_3CO\dot{O} + RH \longrightarrow CH_3COOH + \dot{R}$$

$$CH_3CO\dot{O} + \dot{C}H_3 \longrightarrow CH_3COOCH_3$$

$$\dot{C}H_3 + NO_2 \longrightarrow CH_3NO_2$$

$$\dot{C}H_3 + NO_2 \longrightarrow CH_3\dot{O} + NO$$

$$\dot{C}H_3 + NO \longrightarrow CH_3NO \longrightarrow HCN + H_2O$$

$$CH_3NO + 2\,NO \longrightarrow \dot{C}H_3 + N_2 + NO_3$$

$$CH_3NO + NO_2 \longrightarrow CH_3NO_2 + NO$$

$$\dot{C}H_3 + RH \longrightarrow CH_3OH + \dot{R}$$

$$CH_3\dot{O} + NO_2 \longrightarrow CH_3ONO_2$$

$$CH_3\dot{O} + NO_2 \longrightarrow CH_2O + HNO_2$$

$$CH_3\dot{O} + NO \longrightarrow CH_3ONO$$

$$CH_3\dot{O} + NO \longrightarrow CH_2O + HNO$$

$$2\,HNO \longrightarrow H_2O + N_2O$$

$$NO_2 + CH_2O \longrightarrow NO + CO_2 + H_2O$$

Table 7. Dependence of the yield of the products of the decomposition of 1,1,1-trinitroethane on the degree of reaction at 170 °C.[27]

Product	Degree of reaction (%)						
	2	10	20	37	48	86	100[a]
CH_3NO_2	0.09	0.10	0.13	0.15	0.09	0.16	0.11
CH_3CN	0.01	0.02	0.02	0.03	0.05	0.02	–
CH_3OH	0.02	0.04	0.02	0.05	0.04	0.04	0.01
CH_3ONO_2	0.34	0.24	0.22	0.13	0.12	0.12	0.47
CH_3COOCH_3	–	0.001	0.004	0.008	0.005	0.005	–
CH_3COOH	–	0.10	0.13	0.34	0.42	0.52	–
CH_3NO	0.20	0.04	0.02	–	–	–	–
CH_3ONO	–	traces	traces	–	–	–	0.01

[a] In an excess of NO_2.

The decomposition of compounds of the type of hexanitroethane with a vicinal disposition of the nitro-groups results in the formation of olefins. Thus it has been shown[29] that the vacuum pulse pyrolysis of hexanitroethane affords a high yield of tetranitroethylene. Since the kinetic parameters of the decomposition of this compound correspond to the abstraction of NO_2 and not the elimination of N_2O_4, it must be recognised that the olefin is formed as a result of a secondary reaction involving the ejection of NO_2 from the radical $(NO_2)_3CC(NO_2)_2$. The splitting off of two NO_2 molecules on decomposition of 1,2-difluorotetranitroethane in the gas phase at low pressures[30] and other instances of the decomposition of vicinal dinitroalkanes can be explained similarly.

The reactions of the 1-adamantyl radical, formed on radical decomposition of 1-nitroadamantane (600 °C), have been traced.[31]

2. Activation energies for the decomposition reactions and the strength of the C–N bonds in polynitro-compounds

Data on the radical decomposition of nitro-compounds are presented in Table 8. The activation energy for the decomposition reaction is determined by the strength of the C–N bond, $D(C-N) = E - RT_{av}$, and varies within wide limits. There is no doubt that D(C–N) is influenced by the inductive, steric, and resonance effects of the substituents. The resonance effect stabilises the transition state with a planar radical, remaining after the abstraction of the nitro-group. The mesomeric effect explains the sharp decrease in D(C–N) on passing from CH_3NO_2 to $PhCH_2NO_2$. It may be that the very strong influence of the sulfur atom in the α-position on D(C–N) (compounds **43–50**, Table 8) is associated with this effect. The steric effect of bulky α-substituents is reflected by the increase in the rate in the sequence H < Cl < Br < I for methane derivatives (compounds **6–10**, **14–16**, and **24–26**, Table 8 — see over).

The influence of all α-substituents on D(C–N) has been attributed[7] solely to the steric effect, which appears unlikely. The nitro-groups in polynitro-compounds are known to undergo mutual polarisation. Furthermore, the Cl, Br, and NO_2 substituents influence equally the strength of the C–H and C–F bonds, which are not subject to steric hindrance.[44] It has been shown[45] that the rate of reaction is influenced primarily by the electronic charges on the reaction centre. In a series of isotypical compounds without α-steric effects (compounds, **1**, **2**, **17**, and **27–32**, Table 8), the inductive effect is manifested in a pure form and is expressed by the relation

$$D(C-N) = 220 - 15.2\sigma^*. \quad (3)$$

The values of σ^* for substituents containing nitro-groups may be calculated from literature data.[46,47] Thus the constants σ^* are respectively 4.65, 4.54, and 2.93 for $C(NO_2)_3C(NO_2)_2$, $C(NO_2)_3$, and $CH_3C(NO_2)_2$.

We may also note that a method has been proposed[48] for the estimation of the activation energies for the radical decomposition of *C*-nitro-compounds based on the empirical correlation

$$E = 46.73 + 2.52(\Delta H_{CN} - 70) + 0.22(\Delta H_{CN} - 70)^2,$$

where ΔH_{CN} is a simplified energy characteristic of the C–N bond,[49] which is calculated by the MINDO/3 method and requires little computer time.

The study of the influence of molecular structure on D(C–N) has shown that there are two rules. The first is that a fluorine atom in the α-position acts on the bond not like an electronegative substituent but like a neutral hydrogen atom or alkyl group. Whereas D(C–N) decreases successively by 2–4 kJ mol^{-1} on replacement of the NO_2 group by Cl, Br, or I, its replacement by F increases D(C–N) by 20 kJ mol^{-1}. This increased stability of α-fluoronitro-compounds is associated with this fact. The unusual behaviour of fluorine as a α-substituent is characteristic not only of the C–N bond but also of the C–H and C–Hal bonds. The equivalence of hydrogen and fluorine as α-substituents was first noted by Vedeneev and Purmal'[50] and may be traced on the basis of data published in a handbook.[44]

The second rule concerns the manifestation of the field effect (the *F*-effect, anchimeric participation) in pentane derivatives with a large number of nitro-groups (compounds **33–36** and **38–42**, Table 8). In the main conformation of these compounds,[51] which is fixed under the influence of steric strain, one of the oxygen atoms of the γ-nitro-group approaches the terminal carbon atom to a distance corresponding to the van der Waals radius. This weakens the C–NO_2 bond as a result of the stabilisation of the radical, formed following the abstraction of NO_2, by the electron density on the oxygen of the γ-nitro-group. The effect intensifies with increase in the bulk of the second γ-substituents (H < F < Cl < Br).

The enthalpies of formation of the nitroalkyl free radicals (Table 9) and then D(C–H), D(C–C), or D(C–Hal) (Table 10) in nitro-compounds may be determined from the values of D(C–N) found by the kinetic method. The dissociation energies D calculated in this way differ somewhat from those found by a thermochemical method[12] from the variation of the enthalpies of formation of the compounds and supplement them. We may note that, with increase in the number of nitro-groups, D(C–H) also increases (owing to the polarisation of the C–H bond). Following a one-sided introduction of electronegative substituents, D(C–C) increases, whilst for a symmetrical disposition of the substituents it falls sharply.

Table 9. Enthalpies of formation of nitroalkyl radicals.

Radical R	D(R–NO_2)/ kJ mol^{-1}	$\Delta H_f^\circ(\dot{R})$/ kJ mol^{-1}	
		from D(C–N)	data of Lebedev et al.[12]
CH_2NO_2	230.5	103.5	132.4
$CH(NO_2)_2$	173.9	139.1	157.1
CH_3CHNO_2	193.6	62.0	76.3
$C_2H_5CHNO_2$	197.3	21.4	24.7
$(CH_3)_2CNO_2$	199.0	90.9	91.3
$CH_3C(NO_2)_2$	177.2	65.8	62.4
$C_2H_5C(NO_2)_2$	173.5	44.4	36.7
$(NO_2)_3CC(NO_2)_2$	147.1	276.5	271.1
$FC(NO_2)_2$	174.3	−42.7	–
F_2CNO_2	194.4	−243.0	–
$FC(NO_2)_2C(NO_2)_2$	150.0	30.2	–
$ClC(NO_2)_2$	153.3	160.0	–
$BrC(NO_2)_2$	148.3	120.7	–
$C(NO_2)_3$	140.7	10.9	–

Note. The values of ΔH_f° for the compounds RNO_2 necessary for the calculation of $\Delta H_f^\circ(\dot{R})$ were taken from Lebedev and coworkers and Carpenter et al.[12,52,53]

3. Characteristics of the variation of the pre-exponential factor

The pre-exponential factor in the expression for the rate constant for the dissociation of the R_3C-NO_2 bond reaches high values for several reasons.[54] The principal of these are as follows:

1. The decrease in the frequencies of the deformation vibrations associated with the C–N bond. Judging from the secondary kinetic deuterium isotope effect,[55] the frequency of the deformation vibration, which becomes the out-of-plane vibration of the R_3C radical, diminishes by a factor of 2. The frequencies of the two rocking vibrations of the R_3C group and of the analogous vibrations of the NO_2 group also decrease by this factor.

Table 8. Kinetic characteristics of the radical decomposition of aliphatic nitro-compounds.

No.	Compound	T/ °C	E/kJ mol^{-1}	lg[(A/σ)/s^{-1}]	$\Delta S^{\#}$/e.u.	Ref.
1	CH_3NO_2	360–390	227.5	14.34	4.2	18
		620–1200	245.1	16.21	12.72	21
2	$C_2H_5NO_2$	490–555	233.1	15.90	15.9	32
3	n-$C_3H_7NO_2$	600–900	245.1	15.36	8.8	33
4	iso-$C_3H_7NO_2$	600–900	226.3	15.38	8.9	33
5	$PhCH_2NO_2$	380–430	176.4	13.75	1.4	ü.[a]
6	Cl_3CNO_2	140–170	156.7	15.35	8.8	22
7	$Cl_2C(NO_2)_2$	110–150	143.7	14.96	7.0	34
8	$ClC(NO_2)_3$	120–165	152.5	15.27	8.4	34
9	$BrC(NO_2)_3$	110–160	151.7	15.58	10.0	34
10	$IC(NO_2)_3$	113–150	144.1	14.77	6.1	34
11	$FC(NO_2)_3$	178–236	175.6	14.92	6.8	35
		–	(178.0)	(15.20)	(8.8)	–
12	$HFC(NO_2)_2$	244–264	203.2	16.38	13.5	26
		–	(199.0)	(15.98)	(11.4)	–
13	$F_2C(NO_2)_2$	235–270	198.6	15.88	9.8	35
14	$FClC(NO_2)_2$	170–214	173.9	15.44	9.0	36
15	$FBrC(NO_2)_2$	170–210	165.5	15.00	7.2	36
16	$FIC(NO_2)_2$	160–197	166.3	15.40	9.0	36
17	$HC(NO_2)_3$	180–200	177.6	15.46	9.3	26
18	$C(NO_2)_4$	86–177	160.1	15.70	10.4	37
19	$CH_3CH(NO_2)_2$	197–260	197.4	16.44	13.8	38
20	$C_2H_5CH(NO_2)_2$	215–265	201.1	16.60	14.5	38
21	$C_3H_7CH(NO_2)_2$	220–265	201.7	16.70	15.0	38
22	$CH_3C(NO_2)_2CH_3$	175–210	211.6	18.20	21.8	39
		–	(199.0)	(16.81)	(15.5)	–
23	$CH_3CF(NO_2)_2$	214–262	199.9	16.70	15.0	35
24	$CH_3CBr(NO_2)_2$	160–190	169.9	15.84	11.0	14
25	$CH_3CCl_2NO_2$	190–235	178.5	15.22	8.2	14
26	$C_2H_5CCl_2NO_2$	200–258	178.9	15.15	7.9	14
27	$CH_3C(NO_2)_3$	160–210	181.0	16.70	15.0	40
28	$C_2H_5C(NO_2)_3$	160–200	177.2	16.32	13.5	40
29	$C_3H_7C(NO_2)_3$	160–200	182.7	17.22	17.3	40
		–	(178.1)	(16.72)	(15.00)	–
30	$FC(NO_2)_2C(NO_2)_2F$	107–180	176.8	17.4	18.2	35
31	$FC(NO_2)_2C(NO_2)_3$	88–140	152.9	16.60	14.5	35
32	$(NO_2)_3CC(NO_2)_3$	90–135	150.0	16.52	14.1	37
33	$[(NO_2)_3CCH_2]_2CHNO_2$	120–140	148.5	15.08	7.5	41
34	$[(NO_2)_3CCH_2]_2CFNO_2$	120–140	147.2	15.42	9.1	41
35	$[(NO_2)_3CCH_2]_2CClNO_2$	120–140	146.2	15.43	9.1	41
36	$[(NO_2)_3CCH_2]_2CBrNO_2$	120–140	143.3	15.15	7.7	41
37	$[F(NO_2)_2CCH_2]_2$	150–200	192.7	15.84	11.0	41
38	$[F(NO_2)_2CCH_2]_2CHNO_2$	180–220	172.6	15.00	7.1	41
39	$[F(NO_2)_2CCH_2]_2CFNO_2$	160–200	165.5	14.77	6.1	41
40	$[F(NO_2)_2CCH_2]_2CClNO_2$	160–200	165.5	15.48	9.4	41
41	$[F(NO_2)_2CCH_2]_2CBrNO_2$	160–200	162.1	15.12	7.7	41
42	$[F(NO_2)_2CCH_2]_2C(NO_2)_2$	130–160	152.1	15.22	8.2	41
43	$CH_3SC(NO_2)_3$	50–80	129.0	15.72	10.5	42
44	$PhSC(NO_2)_3$	80–100	194.0	15.52	9.6	42
45	2,4-$(NO_2)_2C_6H_3SC(NO_2)_3$	75–90	133.2	15.72	10.5	42
46	$CH_3SC(NO_2)_2CH_3$	120–150	161.3	17.45	18.4	42
47	$PhSC(NO_2)_2CH_3$	120–150	160.0	17.70	19.5	42
48	2,4-$(NO_2)_2C_6H_3SC(NO_2)_2CH_3$	120–135	157.1	17.25	18.2	42
49	$CH_3SO_2C(NO_2)_2CH_3$	160–190	164.7	14.85	6.5	42
50	$PhSO_2C(NO_2)_2CH_3$	170–195	163.0	14.70	5.8	42
51	$ClCH_2OCH_2C(NO_2)_2F$	210–256	196.3	16.50	14.0	43
52	$O_2NCH_2CH_2C(NO_2)_2F$	200–235	194.0	16.55	14.3	43

Note. σ is the statistical factor for the reaction equal to the number of equivalent nitro-groups. The entropies $\Delta S^{\#}$ were calculated for 200 °C from the relation $A = \sigma(ekT/h)\exp(\Delta S^{\#}/R)$. Data corrected by means of Eqn. (3) are indicated in brackets.

[a] The authors' unpublished data.

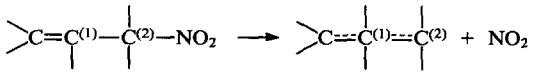
Table 10. Bond dissociation energies in nitro-compounds (kJ mol^{-1}).

Bond	From data in Table 8	From data of Lebedev et al.[12]
$H-CH_2NO_2$	375.8	–
$H-CH(NO_2)CH_3$	380.4	395.1
$H-CH(NO_2)C_2H_5$	394.7	397.6
$H-CH(NO_2)C_3H_7$	383.4	387.2
$H-C(NO_2)(CH_3)_2$	393.4	396.4
$H-CH(NO_2)_2$	416.9	434.9
$H-C(NO_2)_2CH_3$	410.2	411.9
$H-C(NO_2)_2C_2H_5$	393.9	400.6
$H-C(NO_2)_2C_3H_7$	405.2	398.0
$H-C(NO_2)_3$	419.4	427.4
$F-C(NO_2)_3$	426.1	–
$F-C(NO_2)_2F$	474.7	–
$F-C(NO_2)_2CH_3$	442.4	–
$F-C(NO_2)_2C(NO_2)_3$	486.9	–
$F-C(NO_2)FC(NO_2)_2F$	495.2	–
$F-C(NO_2)_2C(NO_2)F$	447.5	–
$Cl-C(NO_2)_3$	306.3	–
$Br-C(NO_2)_3$	221.2	–
$I-C(NO_2)_3$	145.0	–
$H_3C-CH_2NO_2$	348.2	371.2
$C_2H_5-CH_2NO_2$	333.5	362.4
$C_3H_7-CH_2NO_2$	323.0	352.0
$CH_3-CH(NO_2)CH_3$	344.4	354.5
$C_2H_5-CH(NO_2)CH_3$	329.7	357.4
$CH_3-CH(NO_2)C_2H_5$	357.0	355.3
$CH_3-C(NO_2)(CH_3)_2$	356.1	357.4
$CH_3-CH(NO_2)_2$	384.2	397.6
$C_2H_5-CH(NO_2)_2$	356.1	381.3
$C_3H_7-CH(NO_2)_2$	357.4	375.4
$C_4H_9-CH(NO_2)_2$	348.6	365.5
$CH_3-C(NO_2)_2CH_3$	363.3	359.5
$CH_3-C(NO_2)_3$	395.9	399.7
$C_2H_5-C(NO_2)_3$	382.1	390.5
$C_4H_9-C(NO_2)_3$	372.5	380.5
$O_2NCH_2-CH_2NO_2$	302.9	360.8
$(CH_3)_2(NO_2)C-C(NO_2)(CH_3)_2$	294.1	306.3
$CH_3(NO_2)_2C-C(NO_2)_2CH_3$	266.5	267.3
$CH_3(NO_2)_2C-C(NO_2)_3$	257.7	266.0
$(NO_2)_3C(NO_2)_2C-CH_3$	385.1	375.4
$(NO_2)_3C-C(NO_2)_3$	246.8	262.7
$F(NO_2)_2C-C(NO_2)_2F$	267.3	–
$F(NO_2)_2C-C(NO_2)_3$	244.3	–

2. The liberation of the internal rotation about the C–N bond. The maximum contribution by this factor to the activation entropy $\Delta S^{\#}$ is 3 e. u. (0.6 lg A).

3. The decrease in the frequencies of the torsional vibrations (up to free rotation) of the groups R adjoining the reaction centre. In the case of nitro-compounds, R may be alkyl groups and NO_2. The effect of the neighbouring groups can be very large but it was never observed previously.

4. In unsaturated and aliphatic-aromatic compounds, there is a possibility of a negative effect of the neighbouring groups owing to the conjugation of the double bond with a free valence on the reaction centre. Thus the order of the $C^{(1)}-C^{(2)}$ bond in the transition state of the reaction



is 1.5, as a result of which the torsional vibration frequency increases and $\Delta S^{\#}$ diminishes.

In the case of nitromethane, for which the barrier to the internal rotation V_{int} is low,[56] the factors 2–4 do not play any role and the slight increase in $\Delta S^{\#}$ compared with the normal value $\Delta S^{\#} = 0$ is due solely to the first cause. The decrease in the frequencies of the one asymmetric deformation vibration (1482 cm^{-1}) and the four rocking vibrations (1087, 1100, 605, and 477 cm^{-1})[57] by a factor of 2–2.5 increases $\Delta S^{\#}$ by 6 e. u., which is consistent with the experimental value.[18]

A detailed calculation of the pre-exponential factors for the decomposition reactions of $CH_3(NO_2)$, $HC(NO_2)_3$, $F_2C(NO_2)_2$, $HFC(NO_2)_2$, and $CH_3CF(NO_2)_2$ has been carried out by the MINDO/3 quantum-chemical method on the basis of the Rice–Ramsperger–Kassel–Marcus theory.[58] The best agreement with experiment was achieved within the framework of the semirigid activated complex model with a critical C–N bond length of 2.45 Å. The introduction of halogen atoms or of the NO_2 group into the nitromethane molecule leads to an increase in V_{int} and of $\Delta S^{\#}$ by a further 2 e. u.

The positive effect of the neighbouring groups is manifested only slightly for the NO_2 group (compounds **11–13**, **17**, and **18**, Table 8) and very markedly for alkyl substituents (compounds **19–23** and **27–29**, Table 8). NMR data indicate a marked hindrance of the rotation about the C–C bond in 1,1,1-trinitroethane.[59] A β-deuterium isotope effect is observed on decomposition of this compound,[55] which indicates a change in the vibration frequencies of the CH_3 group in the transition state.

There is no positive effect of the neighbouring NO_2 and alkyl groups in compounds having the large chlorine, bromine, and iodine atoms in the α-position (compounds **24–26**, Table 8), which hinder the rotation of the groups not only in the initial tetrahedral form but also in the planar form of the R_3C group. As already mentioned, steric factors influence also D(C–N) in these compounds.

$\Delta S^{\#}$ is smaller for $PhCH_2NO_2$ than for CH_3NO_2 owing to the negative effect of the Ph group.

4. Competition between the radical and molecular mechanisms

The quantitative characteristics described above make it possible to predict the characteristics of different decomposition pathways and to find the temperature T_{eq} at which the rates of elimination of HNO_2 and of the dissociation of the C–N bond are equal. The radical decomposition predominates above this temperature. The data for typical compounds are presented in Table 11. Approximate estimates of T_{eq} for certain mono- and di-nitro-compounds have also been carried out by Shaw.[60]

5. The nitro-nitrite rearrangement

Apart from the processes described above, which occur in the gas-phase reactions of nitroalkanes[15,16] the possibility of the nitro–nitrite rearrangement (NNR) as an alternative to the radical decomposition has been considered for several years. Thus the formation of CH_2O, which might have been a product of the NNR, has been observed in a study[61] of the decomposition of nitromethane in a molecular beam during laser heating (1078 cm^{-1}). The rate of rearrangement was 60% of the rate of dissociation of the C–N bond and its activation energy (233 kJ mol^{-1}) proved to be close to the C–N bond dissociation energy. The first theoretical calculation by the MINDO/3 method[62] yielded an activation energy of 188 kJ mol^{-1} for the NNR. However, later and more rigorous calculations[63] failed to confirm this result and indicate that the activation energy for the NNR is higher by 40 kJ mol^{-1} than the C–N bond dissociation energy.

In principle, the NNR can actually occur as a reaction accompanying the dissociation of the C–N bond and not as a kinetically independent process. This is possible when the decomposition proceeds via a loose transition state[64] in which there is a considerable distance between the fragments R and NO_2 being separated and when they execute three-dimensional rotation. The recombination of R with NO_2 can also occur in this state through an oxygen atom with the simultaneous elimination of NO. The loose transition state arising under these conditions is similar to that formed on decomposition of nitrobenzene and its

Table 11. Competition between the radical and molecular mechanisms of the decomposition reaction.

Compound	Radical decomposition				Molecular decomposition				T_{eq}/ °C
	I	II	III	IV	I	II	III	IV	
$CH_3CH_2NO_2$	–	–	233	15.9	–	–	189	12.2	340
$(CH_3)_2CHNO_2$	238	15.0	–	–	–	–	182	12.7	1000
$(CH_3)_3CNO_2$	234	15.2	–	–	–	–	179	13.6	1500
$CH_3CH(NO_2)_2$	–	–	197	16.7	176	13.0	–	–	80
$C_2H_5CH(NO_2)_2$	–	–	201	16.9	176	12.8	–	–	50
$C_2H_5CHClNO_2$	200	15.0	–	–	–	–	165	12.5	550
CH_3CHFNO_2	239	14.8	–	–	–	–	184	12.6	960
$CH_3CF(NO_2)_2$	–	–	200	17.0	172	13.0	–	–	100
$C_2H_5C(NO_2)_3$	–	–	177	16.8	168	13.5	–	–	−130
$CH_3CCl_2NO_2$	–	–	179	15.1	163	13.2	–	–	160
$CH_3CBr_2NO_2$	178	15.2	–	–	167	13.2	–	–	10
$CH_3CF_2NO_2$	239	14.8	–	–	176	12.2	–	–	1000
$CH_2{=}CHNO_2$	272	14.5	–	–	–	–	191	12.1	1600

Note. The following notation has been adopted: I, III — E/kJ mol^{-1}; II, IV — lg(A/s^{-1}); I, II — calculated values; III, IV — experimental values.

derivatives [D(C–N) > 288 kJ mol^{-1}], for which the NNR is, incidentally, observed.[65] The decomposition of aliphatic nitro-compounds always proceeds via a semirigid transition state (this is indicated by the constants for the recombination of alkyl radicals with NO_2)[66] and the rearrangement of such compounds is unlikely to be a secondary process accompanying the dissociation of the C–N bond. An experimental solution of the problem of the occurrence of the NNR can be achieved by studying the decomposition of CH_3NO_2 in the presence of $N^{18}O_2$ (in a medium comprising RH hydrogen donors) from the dependence of the ratio $CH_3OH/CH_3{}^{18}OH$ on the $N^{18}O_2$ concentration.

IV. Reactions in the condensed state

Mononitro- and halonitro-alkanes having a hydrogen atom in the α-position, dinitro-compounds with terminal $CH(NO_2)_2$ groups, and nitroform decompose in the liquid state much faster than in the vapour phase apparently as a result of isomerisation to nitronic acids or ionisation and autoprotolysis. For example, liquid nitroform decomposes at an appreciable rate at 80 °C whereas in the vapour phase the reaction does not begin until 180 °C. The liquid-phase reactions are subjected to fairly pronounced autocatalysis with the aid of NO and NO_2. They may be stabilised on acidification, which prevents the formation of the aci-form and ionisation.

The influence of the aci-form on the decomposition of liquid nitro-compounds and their capacity for detonation has been demonstrated convincingly in relation to nitromethane and nitroethane.[67] A characteristic feature of these compounds is the decrease in the critical detonation diameter under the influence of small amounts of added bases (dimethylenetriamine, pyridine), high pressure, which shifts the equilibrium towards the formation of the aci-form (the molar volume of which is smaller by 15% than that of the keto-form), and UV irradiation, under the influence of which isomerisation also occurs. A marked isotope effect in the decomposition of CD_3NO_2 is observed at a pressure of 10 kbar.[68]

The formal kinetic characteristics have been determined for liquid nitromethane and an expression has been obtained for its rate of decomposition with the maximum filling of the vessel by the test substance:

$$\frac{d\eta}{dt} = 10^{12.42}\exp\left(-\frac{173900}{RT}\right)(1-\eta) + 10^{3.64}\exp\left(-\frac{62850}{RT}\right)(1-\eta)\eta^2.$$

An even lower activation energy (136 kJ mol^{-1}) has been observed for the first-order decomposition reaction of nitromethane in the liquid phase at pressures of 40–50 kbar and temperatures of the order of 140 °C.[70] It was noted in the above study that the decomposition of nitromethane obeys a second-order equation at low pressures and temperatures below 120 °C.

In order to explain the decrease in the activation energy for the decomposition of nitromethane in the liquid state compared with the gas phase, a bimolecular decomposition mechanism, justified by quantum-chemical calculations, has been proposed.[69,70]

$$2\,CH_3NO_2 \longrightarrow (CH_3NO_2)_2 \longrightarrow TS \longrightarrow CH_3NO + HOCH_2NO_2$$

The enthalpies of formation of the dimer and the transition state (TS) proved to be −88.4 and 89.7 kJ mol^{-1} respectively.[69] Thus the calculated activation energy (178 kJ mol^{-1}) agreed with the experimental value. However, it is possible that this is merely fortuitous. The decrease in the activation energy in the liquid phase can be explained also by the decomposition of nitromethane via the aci-form and autoprotolysis and not via the transfer of oxygen. We may note that the calculation carried out by Khrapkovskii et al.[69] refers to free molecules and in no way takes into account the specific features of the condensed state. On the other hand, in the gas phase there is no bimolecular interaction. The question of the mechanism of the decomposition of nitromethane can apparently be elucidated, as pointed out by Khrapkovskii et al.,[69] by a detailed study of the kinetics of the decomposition of nitromethane in solutions. In order to identify the reactions involving the isomerisation of nitroalkanes, it is desirable to have information about the reactions of nitronic acids. Unfortunately, the kinetics and mechanisms of these reactions have not so far been investigated. These substances are known to be unstable.[71,72] On the basis of quantum-chemical estimates, the elimination of water has been suggested[7] for nitroalkanes having two hydrogen atoms in the α-position.

$$H_2C(NO_2)_2 \longrightarrow H(NO_2)C{=}NOOH \longrightarrow H_2O + O_2NC{\equiv}N^+{\rightarrow}O^-$$

$$CH_3NO_2 \longrightarrow H_2C{=}NOOH \longrightarrow H_2O + HC{\equiv}N^+{\rightarrow}O^-$$

The conversion of nitronic acids of the type ArCH = NOOH into ArCHO and ArCH = NOH has been postulated.[73]

The decomposition of nitromethane in the gas phase at high pressures and temperatures in the range 400–860 °C,[74] i.e. under supercritical conditions, apparently proceeds via the aci-form. For a vapour density of 0.6 g cm^{-3}, the activation volume is between −25 and −15 cm^3 mol^{-3}, i.e. has the same value as for the isomerisation reaction.

An ionic decomposition mechanism has been observed[75,76] for compounds containing the trinitromethyl group in structures of the type $ROCH_2C(NO_2)_3$. Analysis of the volumes of the evolved gas (cm^3 g^{-1}) over a period of 48 h at 100 °C, carried out by Khrapkovskii et al.,[7] showed that the stability of such compounds differs markedly from that of their $RCH_2C(NO_2)_3$ analogues.

$(NO_2)_3CCH_2CH_3$	0.5
$(NO_2)_3CCH_2OCH_2CH_3$	>25
$(CN)(NO_2)_2CCH_2OCH_3$	≫ 25
$(CN)(NO_2)_2CCH_2CH_2OAc$	>25
$(CN)(NO_2)_2CCH_2CH(OAc)_2$	≫ 25
$[(NO_2)_3CCH_2NH]_2C=O$	0.8
$[(NO_2)_3CCH(CH_3)NH]_2C=O$	>25 (5 h, 90 °C)
$(NO_2)_3CCH(OAc)CH_3$	19 (20 min, 100 °C)

The following reaction has been proposed for them:

$$(NO_2)_3CCH_2OCH_2CH_3 \longrightarrow (NO_2)_3C^- + {}^+CH_2OCH_2CH_3.$$

Branching at the β-carbon atom also stabilises the positive charge and promotes the heterolytic cleavage of the C–C bond.

It may be expected that the decomposition of polynitro-compounds having substituents separated by a large distance and not containing a α-hydrogen atom proceeds at the same rates in the liquid phase as in the vapour. Direct measurements have been made for $C(NO_2)_4$, $IC(NO_2)_3$, and $MeC(NO_2)_3$.[77] The activation energies for the decomposition reactions and their rates in the liquid and gas phases are virtually identical with the gas-phase parameters. Table 12 presents data on the decomposition of certain nitro-compounds in solutions.[78,79] The decomposition of all the compounds listed in the table with the exception of hexanitroethane hardly differs from their decomposition in the gas phase and is independent of the nature of the solvent. In the case of hexanitroethane, such a dependence is manifested. Presumably, being a strong acceptor, hexanitroethane is capable of being influenced by even weak donors owing to the formation of charge-transfer complexes.

An attempt has been made[80,81] at a direct determination by IR spectroscopy of the influence of solvation and other intermolecular interactions on the activation energies for unimolecular bond dissociation reactions. The method is based on the use of the relation

$$E = \frac{c\hbar\omega_0^2}{4(\chi_{11})},$$

where ω_0 is the bond vibration frequency and χ_{11} is the anharmonicity of the vibration in which the involvement of the bond is fairly considerable (the C–N bond stretching vibration with ω_0 = 920 cm^{-1} in nitromethane). An experiment with nitromethane yielded the following values of E: 211 kJ mol^{-1} for the liquid state, 193 kJ mol^{-1} for a solution in CCl_4, and 377 kJ mol^{-1} for the solid phase (experiments at −173 °C). This apparently requires a more rigorous justification and tests.

The influence of complex formation, the mechanism of the decomposition of nitronic acids, and kinetic study of the proposed heterolytic reactions are apparently not the only problems which must be investigated in order to understand the essential features of the liquid-phase decomposition of nitrocompounds. New aspects may appear in the study of compounds with mixed functional groups in which the di- and trinitromethyl groups are the most reactive components of the molecules. Such studies are already being carried out.[82–85] Thus processes involving the evolution of gaseous products on rapid (up to 200 K s^{-1}) heating of the compounds $(NO_2)_3CCH_2N(NO_2)CH_2C(NO_2)_3$, $[(NO_2)_3CCH_2N(NO_2)CH_2]_2$, and $Cl(NO_2)_2CCH_2N(NO_2)CH_2C(NO_2)_2Cl$ have been described.[82] There is no doubt that the decomposition of the trinitromethyl group is the primary process for the first two substances.

The introduction of nitroamino-, azide, or nitrate groups into nitroalkane molecules increases the melting points and intensifies the explosive properties of the compounds. Comparison of the kinetic characteristics of the decomposition of monofunctional compounds permits the conclusion that, in the absence of mutual influence, the trinitromethyl group always decomposes at a higher rate than reactive groups such as $-CH_2N(NO_2)CH_2-$, $-CH_2ONO_2$ and $-CH_2N_3$. On the other hand, the fluorodinitromethyl group is more stable than the above fragments. Intramolecular interactions and the solid phase may introduce significant corrections to the above prediction. In the series of nitroalkanes, the decomposition in the solid state has been investigated for only one compound — hexanitroethane,[79] which has a melting point of 135 °C and the rates of its decomposition in the solid state can be easily measured. Crystals of this substance exist in a plastic state and the crystal lattice inhibits the decomposition only slightly: the rate in the solid state is lower by a factor of 5–7 than in the vapour phase.[79] In compounds with high melting points and strong intermolecular interactions, the effect of the solid phase may be much greater[86] and the crystal lattice may exert different influences on the decomposition of different groups. In this case, polynitro-compounds of the mixed type can serve as convenient models for experimental studies.

Table 12. Characteristics of the decomposition reactions of polynitro-compounds in solutions.[78,79]

Compound	Solvent	T/ °C	E/kJ mol^{-1}	$\lg(A/s^{-1})$	ω_{rel} at 85 °C
$C(NO_2)_4$	Carbon tetrachloride	85–150	166.3	16.7	1
	Freon-114B	120–135	173.0	17.7	–
	Freon-113	100–135	166.7	16.8	–
$ClC(NO_2)_3$	Carbon tetrachloride	85–146	159.9	16.5	8.5
$BrC(NO_2)_3$	"	85–131	155.9	16.6	17
$ClC(NO_2)_2C(NO_2)_2Cl$	Freon-113	45–85	129.9	16.6	1.8×10^6
$C(NO_2)_3C(NO_2)_3$	Carbon tetrachloride	70–120	158.3	18.6	860
	Heptane	70–120	119.3	13.0	3296
	Cyclohexane	70–120	88.0	9.1	6593

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