

A theoretical study of the gas-phase pyrolysis of nitroethylene

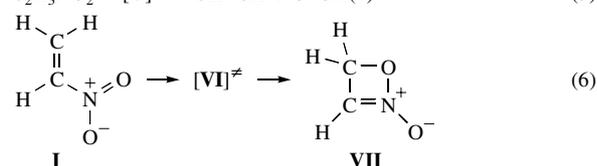
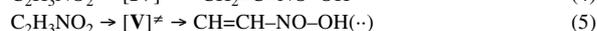
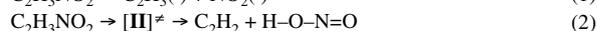
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The most probable mechanism involving a primary act with the formation of a cyclic intermediate and the subsequent degradation to experimentally detected products was proposed for the gas-phase decomposition of nitroethylene based on a quantum-chemical study.

The following two main mechanisms were experimentally found for the gas-phase decomposition of aliphatic nitro compounds: homolytic cleavage of the C–NO₂ bond with the formation of free radicals and elimination of HNO₂.^{1–4} Degradation of mono-nitroalkanes having a hydrogen atom in the α-position and for α-halogen nitro compounds RCH₂CHXNO₂ (X = Hal)^{2,3} via a molecular mechanism was observed at relatively low temperatures (up to 350 °C). It is believed^{2,3,5} that the gas-phase decomposition of nitroethylene and other α-nitroolefins occurs via a similar mechanism. For mononitroalkanes, the molecular mechanism of HNO₂ elimination was supported by the product composition at the initial steps of decomposition^{1,2} and by the results of quantum-chemical studies.^{6–8} In the case of nitroethylene, there is no data on the product composition at the initial steps, and this mechanism is hypothetical. The quantum-mechanical data^{9,10} on nitroethylene are insufficient to come to conclusions on the primary step of unimolecular gas-phase degradation or to reject the elimination of nitrous acid. The activation barrier of nitrous acid elimination [method B3LYP/6-31G(d)]^{11,12} is higher than the experimental activation energy of the gas-phase degradation. Here, we report on the results of a non-empirical study of various mechanisms of the unimolecular degradation of nitroethylene:



The calculations were performed by the B3LYP/6-31G(d) and B3LYP/6-311++G(df,p) methods,^{13,14} which gave minimum errors in the experimental and theoretical values of the heats of reactions and compounds that participate in unimolecular degradation of aliphatic nitro compounds.^{1,11,12} Biradicals were calculated by a published procedure,¹⁵ which provided a correct

asymptotic form of the electron density distribution on bond fission. Table 1 summarises the activation parameters calculated for nitroethylene and nitroethane in reactions (1)–(6).

According to calculated data, the reaction barrier for HNO₂ elimination from nitroethylene increases as compared with the corresponding reaction of nitroethane. Considerable differences in these values (up to 33–50 kJ mol⁻¹ in different bases) are higher than the possible error of estimation of the reaction barrier.

The results of calculations are inconsistent with the conclusion^{2,3,5} that the gas-phase degradation of nitroethylene occurs via the HNO₂ elimination mechanism.

Among the examined primary reactions of unimolecular decomposition of nitroethylene, reaction (6) associated with the formation of cyclic product VII is most favourable. The calculated barrier is close to the experimental energy of gas-phase nitroethylene degradation (192.05 kJ mol⁻¹).⁵ The difference is about 8.5 kJ mol⁻¹, which is within the limits of experimental error. On the other hand, an error of 8–13 kJ mol⁻¹ is also possible in the calculation of the activation energy.^{7,11,12} Thus, the calculated and experimental data should be considered consistent.

This mechanism was initially proposed for the high-temperature pyrolysis of β-nitrostyrenes.¹⁶ Benzophenone and acetonitrile were experimentally detected as the main degradation products. On this basis, the above mechanism was suggested. However, this mechanism was not substantiated¹⁶ in terms of kinetics and thermodynamics.

Although the occurrence of VII in the course of thermal degradation of nitroethylene was not detected experimentally, similar compounds were prepared by the cyclisation of substituted nitroethylenes.¹⁷

Reaction (6) is a rearrangement. Thus, secondary processes of the degradation of intermediate VII should be examined in order to demonstrate that it could really result in the end products of the thermal decomposition of nitroethylene with an activation energy no higher than that of reaction (6).^{11,12}

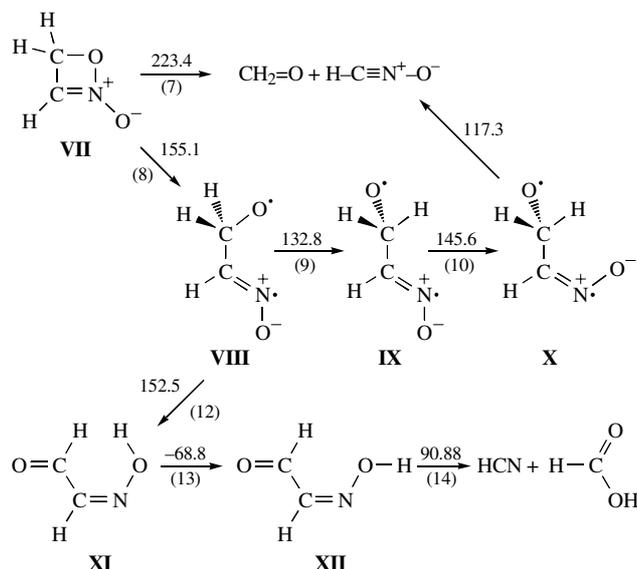
The results of a study of the secondary processes of degradation of VII are summarised in Scheme 1.

Simultaneous reaction (7), which results in the reaction products, formaldehyde and nitrile oxide, exhibits a barrier higher than the experimental activation energy of nitroethylene decomposition and the calculated enthalpy of activation of primary act

Table 1 Activation parameters for reactions (1)–(6)/kJ mol⁻¹.

No.	Process	Compound	Energy + ZPE ^a at 0 K		Enthalpy at 298.15 K	
			6-31G(d)	6-311++G(df,p)	6-31G(d)	6-311++G(df,p)
1	C–N bond fission	C ₂ H ₃ NO ₂	275.2	262.5	281.2	268.4
		C ₂ H ₅ NO ₂	229.5	219.4	235.9	225.6
2	HO–N=O elimination	C ₂ H ₃ NO ₂	242.5	223.1	243.4	223.9
		C ₂ H ₅ NO ₂	190.5	175.4	190.1	174.8
3	Nitro–nitrite rearrangement	C ₂ H ₃ NO ₂	241.3	237.3	241.5	237.4
		C ₂ H ₅ NO ₂	261.0	251.5	262.5	251.5
4	1,3-H shift to <i>aci</i> -form	C ₂ H ₃ NO ₂	257.2	248.9	257.6	249.2
		C ₂ H ₅ NO ₂	282.8	272.2	281.9	271.2
5	1,4-H shift	C ₂ H ₃ NO ₂	298.8	278.8	300.3	280.2
6	Cyclisation	C ₂ H ₃ NO ₂	202.9	205.6	201.3	202.9

^aZPE = zero-point energy.



Scheme 1 The figures over arrows indicate the relative enthalpies of formation (in kJ mol^{-1}) for the transition states corresponding to the given processes. The heat of formation of nitroethylene was taken as zero. The above values were calculated in the 6-311+G(df,p) basis for normal conditions.

(6). Consequently, it cannot be the main channel of pyrolysis. An alternative process occurs *via* singlet biradical intermediate **VIII** [reaction (8)], which decomposes to formaldehyde and nitrile oxide (11) after a number of conformational transitions (11), (12).

Intermediate **VIII** is generated in reaction (8) in the *cis* conformation of O–C–C–N. An analysis of charge distribution at the oxygen atom and the NO group in the structure of **VIII** demonstrates it is not a zwitterion (in particular, the charge at the oxygen atom decreases by 0.1 and that at the NO group increases by the same value as compared with **VII**). In contrast, spin density in **VIII** is strongly polarised (–0.83 and 1.0 at the oxygen atom and NO group, respectively).

Reaction (9) is the rotation about the C–C bond through 130° . The transition state corresponds to the rotation through 54° . The second transition state corresponds to the *trans* orientation of the O–C–C–N group (rotation through 180°). It separates one *gauche* conformation from another, equivalent, different only in the sign of rotation.

Reaction (10) is the pendulum movement of the N–O bond in the C–C–N–O plane. In the transition state, the arrangement of the atomic triad C–N–O is close to linear.

Another reaction path in the degradation of biradical **VIII** is its rearrangement (12) into aldoxime **XI**. This latter, after conformational transition (13), which is the rotation of the OH group about the N–O bond, undergoes decomposition (14) to hydrocyanic acid and formic acid.

These two channels are almost equivalent in terms of energy. As mentioned above, aldehydes and ketones were detected as the main products of pyrolysis of β -nitrostyrenes.¹⁶

Moreover, there are unexamined reaction paths, which, for example, result in cyclic peroxides. However, the main conclusion drawn in this work remains unchanged: the found secondary reactions of degradation of cyclic intermediate **VII** exhibit much lower enthalpies of activation than the experimental activation enthalpy of the primary act of the gas-phase decomposition of nitroethylene and result in the experimentally detected products of nitroolefin pyrolysis. Thus, we found that the formation of **VII** is the primary rate-limiting step in nitroethylene degradation. The barriers of all other alternative processes are higher, as it was also supported by independent non-empirical estimations.¹⁰

The only acceptable path of decomposition of intermediate **VII** in terms of energy is the formation of singlet biradical **VIII**. The great number of conformations of **VIII** is responsible for a variety of possible transformations.

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