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A theoretical study of the mechanism of the gas-phase unimolecular decomposition of *N*-methylnitramine

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The principal reactions of the primary event of *N*-methylnitramine unimolecular decomposition have been investigated, and the results allowed us to propose a new reaction mechanism.

The spontaneous decomposition of nitro compounds at relatively low temperatures makes them useful model substances for studying thermodestruction reactions.[1,2] Arrhenius's parameters of the primary event of the reaction have been correctly determined for C-, N-, and O-nitro compounds in different aggregative states.[3] However, in a number of cases, it is difficult to find out a correlation between experimental data and a reaction mechanism.[2,3] For a long time, only two principle mechanisms of nitro compound thermal decomposition were considered, *viz.*, a homolytical cleavage of the least stable bond in the molecule (C–N, N–N and O–N for C-, N- and O-nitro compounds, respectively) and the elimination of HNO_2.[4] Some of the proposed mechanisms were suggested on the basis of quantum-chemical studies.[5,6] Nevertheless, for thermal decomposition only a few convincing mechanisms, which were proved by means of either theoretical assumptions or experimental assays, were proposed. Therefore, new data might extend our knowledge of general regularities determining the reactivity of nitro compounds and their unimolecular reactions.

Aliphatic *N*-nitramines are the most interesting and useful nitro compounds,[3,7,8] the kinetics of their thermodestruction is of considerable interest. However, the majority of experimental data were obtained for secondary *N*-nitramines, whose decomposition is assumed to involve a homolytical cleavage of the N–NO_2 bond.[3] This mechanism is also assumed[9] for the gas-phase decomposition of primary nitramines; however, this assumption is open to doubt due to the absence of reliable energy barrier evaluations for alternative mechanisms of the primary event of unimolecular decomposition of the above compounds. At the same time, the unimolecular decomposition of *N*-nitramines was investigated using quantum-chemical semi-empirical and non-empirical methods.[10–13]

Taking *N*-methylnitramine as a model substance, we studied the principal elementary steps involved in the primary event of *N*-methylnitramine gas-phase unimolecular decomposition [equations (1)–(4)].

$$MeNHNO_2 \rightarrow MeNH\cdot + \cdot NO_2 \quad (1)$$

$$MeNHNO_2 \rightarrow CH_2{=}NH + HNO_2 \quad (2)$$

$$MeNHNO_2 \rightarrow MeNHONO \quad (3)$$

$$MeNHNO_2 \rightarrow MeN{=}N(OH)O \quad (4)$$

Calculations were performed using the Gaussian 2003 software,[14] hybrid DFT method B3LYP, and 6-31G(d) and 6-311++G(df,p) bases that produce values, which allowed us to obtain the closest approximations to experimental data obtained for gas-phase unimolecular decompositions of various nitro compounds,[6] as well as by the non-empirical MP2 method using the above bases. In all cases, the transition state (TS) was proved by the occurrence of a single negative value in a Hessian matrix, while its correlation with the investigated process was proved by descending along the reaction coordinate toward the starting compound and the reaction products. The results are shown in Table 1. The most energy advantageous process is isomerization to the aci form of methylnitramine, while a nitro–nitrite rearrangement requires overcoming a maximum energy barrier. Difference in energy barriers of radical decomposition and HNO_2 elimination is small. The data obtained allow us to exclude the radical mechanism being the principal pathway of gas-phase decomposition of methylnitramine. In fact, the energy barrier of radical decomposition exceeds that of aci form formation by 45.8 or 41.0 kJ mol^{-1} [B3LYP/6-31G(d) or B3LYP/6-311++G(df,p), respectively]; thus, at 250 to 350 °C (the usual range for investigating the kinetics of thermal decomposition of nitramines in a gas state[3]), isomerization into the aci form proceeds faster than radical decomposition. The above statement is also confirmed by a rough evaluation of the reaction pre-exponential factor for methylnitramine isomerization into its aci form: $\lg A \sim 13.4$ s^{-1}. Note that this assumption is also proved by evaluation of energy barriers for steps (1) and (4) using the G2 method (220.1 and 149.2 kJ mol^{-1}, respectively).

According to our calculations, the most favourable pathway of the reaction primary event involves rearrangement. The study

Table 1 Geometrical parameters of *N*-methylnitramine for the ground state, transition states of the monomolecular decomposition reactions and energy barriers.

Compound, reaction	Bond length/pm [B3LYP/6-31G(d)]					Energy barrier/kJ mol^{-1}			
	C–N	N–N	N–O	N–H	O–H	B3LYP/6-31G(d)	B3LYP/6-311++G(df,p)	MP2/6-31G(d)	MP2/6-311++G(df,p)
$MeNHNO_2$	145.6	138.5	122.9	101.4	—	—	—	—	—
1	145.6	—	122.9	101.4	—	195.2	189.0	217.4	239.1
2	134.4	212.5	126.8	102.5	129.8	198.6	191.3	227.2	219.0
3	143.3	218.2	220.5	102.6	—	342.3	338.0	391.2	403.2
4	145.0	131.1	132.6	130.6	131.6	149.4	148.0	152.3	147.0

showed that aci form radical decomposition [reaction (5)][†] is energy forbidden due to the fact that the activation enthalpy of reaction (5) is equal to 247.5 kJ mol^{-1}, which is considerably higher than the D(N–N) value and the activation energy of radical decomposition. Among the alternative pathways of *N*-methylnitramine aci form decomposition is water elimination, which proceeds *via* a minimal energy barrier (6). Khrapkovskii *et al.*[6] used nitromethane and dinitromethane as model substances. According to the B3LYP/6-31G(d) method, the barrier of such a reaction of methylnitramine exceeds the activation enthalpy of its aci form formation but is considerably lower than that of radical decomposition. The evaluation of the pre-exponential factor (lg A ~ 13.1) at medium decomposition temperatures (< 700 K) allows us to ascertain that this reaction pathway is preferable in comparison with radical mechanism. Note that activation enthalpies for water elimination obtained using the other above methods are lower than the barrier of aci form formation.

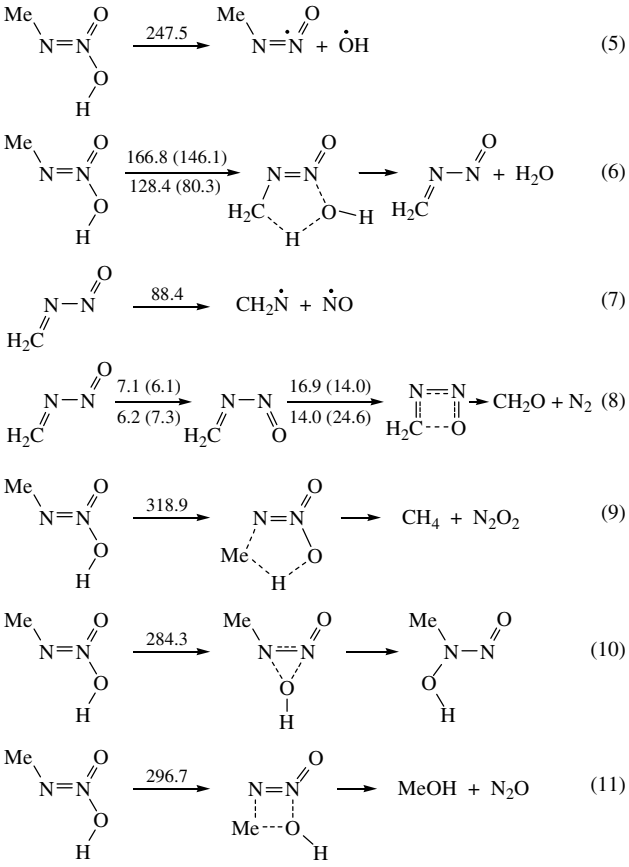
We found two energy-favourable pathways for the subsequent transformation: reactions (7) and (8), more energy-favourable pathway being reaction (8). Formation of TS in reaction (8) is followed by a conformation transition.

Great expenditures of energy are required for reactions (9) and (10) (methane elimination and hydroxyl transfer, respectively) to proceed; in fact, the activation barrier of reaction (9) is the greatest one among all the test reactions. Reaction (11), which seems possible, was found energy-forbidden: corresponding products were found in liquid-phase decomposition of *N*-nitramines.[15] Our results allowed us to rule out the above mechanism from aci form decomposition, at least from the gas-phase unimolecular decomposition process.

Thus, a theoretical study allowed us to find a new, more energy-favourable pathway of gas-phase unimolecular decomposition of *N*-methylnitramine. The reaction starts with isomerization of *N*-methylnitramine into its aci form *via* intramolecular hydrogen transfer from amine nitrogen to the nitro group. Then, the cyclic intermediate eliminates water [reaction (6)] followed by reaction (8) to form formaldehyde and nitrogen.

Arrhenius's parameters of the primary event of *N*-methylnitramine gas-phase decomposition (E = 171.0 kJ mol^{-1}, lg A = = 13.65 s^{-1}) were published previously[9] and explained in accordance with a radical reaction mechanism. However, we do not believe that the reaction proceeds *via* the homolytical disruption of the N–NO_2 bond. Quantum-chemical (Table 1) and thermochemical (207.5 kJ mol^{-1})[16] evaluations of D(N–N) value exceed the effective activation energy considerably. The value of lg A for the *N*-methylnitramine radical decomposition appeared to be noticeably underestimated in comparison with similar values obtained for gas-phase radical decomposition of other simple aliphatic nitro compounds (*N*,*N*-dimethylnitramine, *N*-methylnitramine and nitromethane[3]). Our quantum-chemical calculations showed that lg A for radical decomposition should be at least equal to 14.5 s^{-1}.

Meanwhile, the experimental values for E and lg A are in satisfactory agreement with the reaction mechanism and parameters of its principal steps [reactions (4), (6) and (8)]. Depending upon experimental conditions, a radical reaction can compete



with isomerization into the aci form followed by its subsequent decomposition, which was proposed in this work. Published data[9] and our calculations indicate that a non-radical mechanism prevails under gas-phase conditions. The liquid-phase decomposition of *N*-methylnitramine is known[17] to proceed with greater velocity than similar decomposition in a gaseous phase, which can be explained by heterolytic processes. However, experimental conditions[9] excluded a noticeable influence of a heterolytic mechanism upon kinetic parameters.

The results obtained are valuable not only for understanding the mechanisms of *N*-nitramine thermal decomposition but also for comprehension of general regularities governing the gas-phase decomposition of nitro compounds.

[†] For this step and other secondary reactions of *N*-methylnitramine aci form decomposition, the activation enthalpies obtained with the B3LYP/6-31G(d) method (kJ mol^{-1}) are shown above the arrows in the reaction schemes, while the corresponding values obtained with the B3LYP/6-311++G(df,p) method are given in parentheses. For the main step (6) of the process proposed the activation enthalpies (in parentheses) of the corresponding reactions obtained with MP2/6-31G(d) and MP2/6-311++G(df,p) methods taking into account zero-point oscillation energy are given under the arrows.

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