

THERMAL DECOMPOSITION OF 3-NITRO-1-NITROMETHYL- 1,2,4-1H-TRIAZOLE IN SOLUTION

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The thermal decomposition of 3-nitro-1-nitromethyl-1,2,4-1H-triazole in 1% solution in phenyl benzoate proceeds homolytically with initial rupture of the CH₂-NO₂ bond. Activation parameters of the process were $E_a = 172.6$ kJ/mol, $\log A = 14.25$. The initial basic pathway of fragmentation of the molecule under electron impact coincides with the first step of thermal decomposition, which is in agreement with X-ray structural and calculated quantum chemical data on bond stability in the molecule.

Keywords: heterocyclic nitro compounds, 3-nitro-1-nitromethyl-1,2,4-1H-triazole, thermal decomposition, energy-rich substances.

The problem of the reactivity of energy-rich nitro compounds in thermal decomposition reactions, in spite of significant advances [1], is still far from final resolution. First of all this concerns polyfunctional nitroheterocycles for which several pathways for thermal breakdown are possible.

In the present work the thermal decomposition of 3-nitro-1-nitromethyl-1,2,4-1H-triazole (**1**) has been studied [2]. If it is assumed that the breakdown of compound **1**, like that of other nitro compounds [1], proceeds homolytically with first the rupture of a C-NO₂ bond, then the problem of the choice of reaction center immediately arises. This might be either the C-NO₂ bond of the nitroalkyl fragment or the analogous bond of the heterocycle. In addition, it is possible to assume the breakdown of the C-N bond between the nitroalkane fragment and the triazole ring or the destruction of the actual heterocycle as the first stage. The present investigation is devoted to clarification of this problem.

Study of the thermal breakdown in dilute solution in an inert, low-polarity, aprotic solvent, when the inhibiting effect of the crystal lattice is not displayed and gas phase conditions are modeled to some extent, enables an idea of the real reactivity of the compound to be obtained. To study the thermal breakdown of compound **1** directly in the gas phase failed, due to the difficulty of transferring the substance into the gaseous state.

The kinetics of the thermal decomposition of compound **1** in a 1% solution of phenyl benzoate is described by a first order reaction up to 30-40% conversion. The concentration of the substance in solution within the limits of 1-10% (wt.) shows practically no effect on the rate constant for decomposition. Rate constants and activation parameters for the thermal breakdown are given in Table 1.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 699-703, May, 2003. Original article submitted July 20, 2000.

TABLE 1. Kinetic Parameters for the Thermal Breakdown of Compound **1** in Phenyl Benzoate Solution

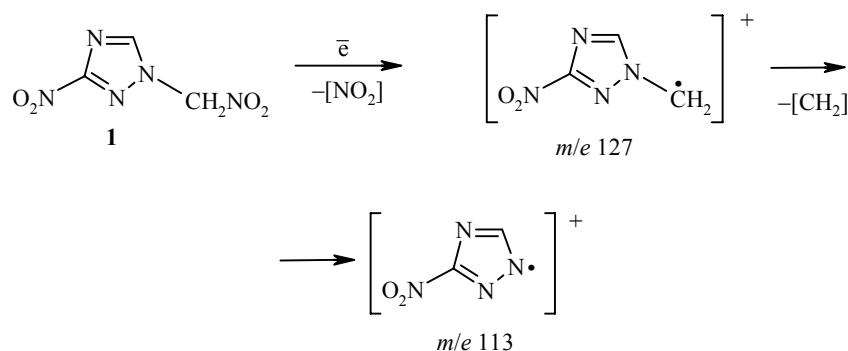
Concentration, %	Rate constants $k \cdot 10^5$ (sec ⁻¹), at temperature (°C)				E_a , kJ/mol	log A
	210	220	230	240		
1	4.14	8.64	21.39	49.98	172.6	14.25
10	—	—	25.30	—	—	—

Peaks for ions with m/z 44 (CO_2)⁺, (N_2O)⁺, 30 (NO)⁺, (CH_2O)⁺, 28 (CO)⁺, (N_2)⁺, and 27 (HCN)⁺ were recorded in the gas-phase breakdown products of compound **1** in a 1% solution at 230°C and a 20% degree of conversion.

The parameters of the optimum geometry of compound **1** have been calculated by the semiempirical quantum-chemical methods MNDO, AM1, and PM3 to assess the structure and reactivity of the substance on breakdown (Table 2). Analysis of the data of Table 2 indicates that the greatest C–NO₂ bond length is observed in the nitroalkyl fragment of the molecule. This enables a preliminary expectation of its lower stability and higher reactivity on breakdown compared with other variants of C–N bond fission. The calculated data obtained on the stability of bonds in the compound **1** molecule are in qualitative agreement with the results of an X-ray structural investigation carried out previously [2]. At the same time the calculated values for the bond lengths in the molecule are mainly overstated in comparison with the experimental data. In difference to the latter the semiempirical calculations show a largely hypothetical orthogonal disposition of the nitro group (bound to the triazole ring) relative to the plane of the heterocycle. In our view this deviation is linked not with the influence of the crystal lattice but with the underestimation by the semi-empirical methods of the effect of conjugation between the triazole ring and the nitro group.

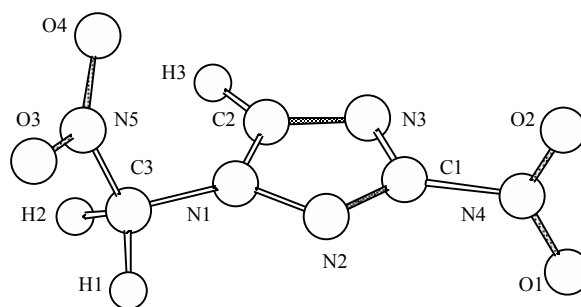
For many compounds the first step of homolytic thermal breakdown coincides with the main direction of dissociative ionization on electron impact [3]. The mass spectrum of compound **1** [m/z (I_{rel} , %)] consists of 127 (97.4) [$\text{M}-\text{NO}_2$]⁺, 113 (33), 100 (5.7), 86 (7.0), 73 (13.2), 69 (100), 58 (17.3), 53 (12.0), 52 (59.8), 46 (95.3) [NO_2]⁺. This indicates that electron impact fragmentation of the compound takes place with the initial rupture of a C–NO₂ bond. There is no molecular ion peak.

In principle the fragment ion with mass number 127 may be formed on removal of any nitro group from the **1** molecule. However, in our view, it is formed by rupture of the C–NO₂ bond in only the nitroalkyl function.



This is confirmed by the products of further destruction of the ion of m/z 127, and also by the mass spectrometric data for 3-nitro-1,2,4-triazole, which are 114 (100) M^+ , 98 (7.66) [$\text{M}-\text{O}$]⁺, 86 (30.0) [$\text{M}-\text{N}_2$]⁺, 69 (67.0), 68 (7.66) [$\text{M}-\text{NO}_2$]⁺, 55 (6.7), 53 (12.0), 46 (50.0) [NO_2]⁺. The high stability of the latter under similar mass spectrometric conditions, the composition of the fragmentation ions, and in particular, the absence of significant amounts of the ion with mass 68 [$\text{M}-\text{NO}_2$]⁺, probably indicates fragmentation of the triazole ring first.

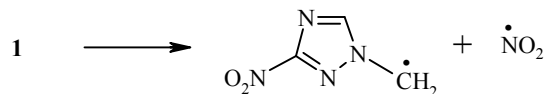
TABLE 2. Calculated Parameters of the Optimum Geometry of the Compound 1 Molecule*



	MNDO	AM1	PM3
Bond lengths, Å			
N ₍₂₎ -C ₍₁₎	1.343	1.369	1.345
N ₍₁₎ -N ₍₂₎	1.346	1.349	1.369
C ₍₁₎ -N ₍₃₎	1.394	1.428	1.395
C ₍₁₎ -N ₍₄₎	1.482	1.500	1.512
N ₍₃₎ -C ₍₂₎	1.336	1.339	1.342
C ₍₂₎ -N ₍₁₎	1.419	1.426	1.401
C ₍₂₎ -H ₍₃₎	1.086	1.098	1.096
N ₍₁₎ -C ₍₃₎	1.454	1.437	1.469
N ₍₄₎ -O ₍₁₎	1.207	1.193	1.208
N ₍₄₎ -O ₍₂₎	1.206	1.194	1.207
C ₍₃₎ -N ₍₅₎	1.571	1.553	1.562
C ₍₃₎ -H ₍₁₎	1.117	1.132	1.116
C ₍₃₎ -H ₍₂₎	1.118	1.130	1.112
N ₍₅₎ -O ₍₃₎	1.206	1.195	1.206
N ₍₅₎ -O ₍₄₎	1.209	1.196	1.209
Valence angles, ω, deg			
C ₍₁₎ -N ₍₂₎ -N ₍₁₎	103.4	103.7	105.8
N ₍₂₎ -C ₍₁₎ -N ₍₃₎	114.5	113.6	109.9
N ₍₂₎ -C ₍₁₎ -N ₍₄₎	123.7	124.3	125.9
N ₍₃₎ -C ₍₁₎ -N ₍₄₎	121.7	122.1	124.2
C ₍₁₎ -N ₍₃₎ -C ₍₂₎	103.6	102.9	108.1
N ₍₃₎ -C ₍₂₎ -N ₍₁₎	108.3	109.6	106.1
N ₍₃₎ -C ₍₂₎ -H ₍₃₎	127.3	127.3	126.2
N ₍₁₎ -C ₍₂₎ -H ₍₃₎	124.4	123.1	127.7
N ₍₂₎ -N ₍₁₎ -C ₍₂₎	110.1	110.1	110.1
N ₍₂₎ -N ₍₁₎ -C ₍₃₎	120.0	123.6	121.9
C ₍₂₎ -N ₍₁₎ -C ₍₃₎	129.9	125.6	128.0
C ₍₁₎ -N ₍₄₎ -O ₍₁₎	118.1	117.6	117.8
C ₍₁₎ -N ₍₄₎ -O ₍₂₎	118.4	117.6	118.1
O ₍₁₎ -N ₍₄₎ -O ₍₂₎	123.5	124.7	124.1
N ₍₁₎ -C ₍₃₎ -N ₍₅₎	108.3	114.6	112.7
N ₍₁₎ -C ₍₃₎ -H ₍₁₎	111.8	111.0	109.5
N ₍₁₎ -C ₍₃₎ -H ₍₂₎	110.9	108.6	108.6
N ₍₅₎ -C ₍₃₎ -H ₍₁₎	108.6	105.9	110.3
N ₍₅₎ -C ₍₃₎ -H ₍₂₎	107.2	104.9	109.3
H ₍₁₎ -C ₍₃₎ -H ₍₂₎	110.0	111.8	106.2
C ₍₃₎ -N ₍₅₎ -O ₍₃₎	118.9	116.9	117.3
C ₍₃₎ -N ₍₅₎ -O ₍₄₎	118.9	118.8	118.1
O ₍₃₎ -N ₍₅₎ -O ₍₄₎	122.2	124.2	124.5

* $\Delta H_f = 325.7$ (MNDO), 434.6 (AM1), 200.4 (kJ/mol).

The activation parameters for the decomposition of compound **1** (Table 1) are close to the parameters for homolytic thermal breakdown of phenylnitromethane ($E_a = 176.4$ kJ/mol, $\log A = 13.75$) [1] and differ significantly from those for 1-ethyl-3-nitro-1,2,4-triazole ($E_a = 272.6$ kJ/mol, $\log A = 16.81$) [4]. This forms a basis for supposing that the thermal decomposition of compound **1**, as in the case of phenylnitromethane [1], proceeds with the initial fission of the C–NO₂ bond in the nitroalkyl function.



The limiting stage in the thermal breakdown therefore coincides with the first step of fragmentation under electron impact, which is in full accord with the data on bond strengths in the molecule obtained by X-ray structural analysis and quantum-chemical calculations.

EXPERIMENTAL

Compound **1** was purified by triple recrystallization from a CHCl₃–CCl₄ mixture and according to GLC data contains 99.8% main substance. The kinetics of thermal breakdown were studied by a manometric method under isothermal conditions (± 0.2 to 0.3°C) using a Burdon type null manometer [5]. The rate constants were calculated for a reaction equation of the first order. The error in determining rate constants was less than 7%. The error of calculating the energies of activation did not exceed 0.5 kJ/mol, and the logarithm of the pre-exponential multiplier 0.05 logarithm units.

The mass spectra were obtained on Kratos MS 30 and MI 12-01-T instruments at a pressure in the ionization chamber of 10^{-5} – 10^{-7} torr, ionization energy was 70 eV, and accelerating voltage 5 kV.

The semiempirical quantum-chemical calculations were carried out with the CS MOPAC-93 set of programs.

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