ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 6, pp. 1071–1076. © Pleiades Publishing, Ltd., 2013.
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Relation Between the N–NO_2 Bond Length and Stability of the Secondary Nitramines

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Received May 15, 2012

Abstract—The fact of the constancy of activation entropy of N–NO_2 bond homolysis in a series of secondary nitramines was utilized for correction of the experimental values of activation energy E of this process proceeding from the reliable data for the rate constants of the nitramines decomposition in solutions. When comparing the refined values of E (kJ mol^{-1}) with the N–N bond length $d_{N–N}$ (Å) the following correlations were obtained: for cyclic and framework nitramines $E = 663 - 356d_{N–N}$, and for the aromatic nitramines $E = 1810 - 1227d_{N–N}$. A linear relationship between E and d is observed in the series of similar compounds. It depends on the electronic and steric effects of substituents.

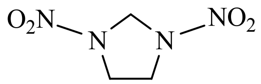
DOI: 10.1134/S107036321306011X

The purpose of this study was to determine the relationship between the stability of secondary aliphatic and aromatic nitramines and the N–N bond length $d_{N–N}$. The reason for such a study is the fact that the dependence of the stability of the secondary nitramines on their structure is determined mainly by the changing activation energy E of the N–N bond homolysis, which is directly related to the dissociation energy of bond and its length. The preexponential factor A, as first noted in [1], relatively weakly depends on the structure of secondary nitramines. For example, for a series of aliphatic compounds, the most data obtained both for the liquid phase or solution satisfy the equality $\log A = 14.5\pm0.5$ [1]. Thus, in terms of correlation analysis, the decay of secondary nitramines is an isentropic series. The constancy of A opens a possibility to correlate $d_{N–N}$ not only with the activation energy, but also with the rate constants of decomposition k, measured at the same temperature, and also allows finding the E values from the relation $E = (\log k – \log A)RT$ at A = Const. The E values calculated in this way can be used to refine the experimental data and to quickly find the E in the new conditions of the reaction. Due to the high melting temperatures and high rates of decomposition at the temperatures above the melting point, the data on the decomposition of secondary nitramines in the liquid phase are rather limited. The basic research has been carried most often in solutions in the nonvolatile solvent inert with respect to the secondary nitramines, e.g., dinitrobenzene, trinitrobenzene, dicyclohexyl phthalate, and dibutyl phthalate. However, in these relatively viscous solvents, as well as in the liquid phase, the kinetic influence of cage effect is observed, and therefore the apparent decay rate is lower than in the lighter solvents such as isooctane or benzene [2, 3]. The influence of the solvent and the possibility to recalculate the data on the rate at changing solvent was described in [2]. In solvents like toluene containing the C–H bonds of lower strength, the decomposition of secondary nitramines results in the development of the chain processes accelerating the decay. The experiments in these solvents should be excluded from consideration. Apparently, the rate of thermal decomposition of nitramines by the pathway of the N–NO_2 bond homolysis the least distorted by side effects can be obtained using benzene as a solvent.

Attempting to establish a direct correlation of experimental E values with $d_{N–N}$ failed [4], possibly because of the strong scatter of experimental data. At the same time, the use of rate constants measured in the same solvent at the same temperature allowed us obtaining a satisfactory correlation for a series of cyclic and framework nitramines in dibutyl phthalate [5] and benzene [6]. It seems useful to summarize these data, to adjust *E* values in correspondence with the rate constants, and to find a correlation of *E* in benzene, the most informative quantity for the estimation of the stability at different temperatures and in different environments.

In addition to cyclic and framework nitramines, we included in the review the aromatic nitramines, analogs of tetryl. While for the compounds of the first two types there are quite complete literature data and only processing of the latter is necessary, aromatic compounds require further structural and kinetic measurements.

A series of nitramines whose data are available on the kinetics of decomposition and the structure of the molecule consists of the following compounds: 1,3-dinitro-1,3-diazacyclopentane (**I**), *N,N*'-dinitropiperazine (**II**), hexogen (**III**), octogen (**IV**), CL-20 (**V**), ketohexogen (**VI**), 4,8,10,12-tetranitro-2,6-dioxa-4,8,10,12-tetraazatetracyclo$(5.5.0^{03,11}.0^{5,9})$dodecane (**VII**), 4,6,10,12-tetranitro-2,8-dioxa-4,6,10,12-tetraazatetracyclo-$(5.5.0^{03,11}.0^{5,9})$dodecane (**VIII**), *cis*-2,4,6,8-tetranitro-1*H*,5*H*-2,4,6,8-tetraazabicyclo(3.3.0)octane (**IX**), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-$(5.5.0^{03,11}.0^{5,9})$dodecane (**X**), tetryl (**XI**), *N*-nitro-*N*-ethyl-2,4,6-trinitroaniline (**XII**), and *N*-nitro-*N*-methyl-4-nitroaniline (**XIII**).



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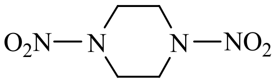

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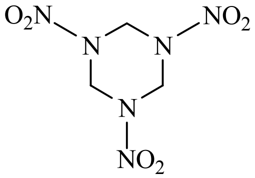

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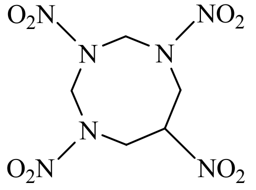

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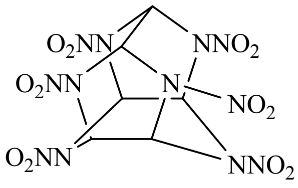

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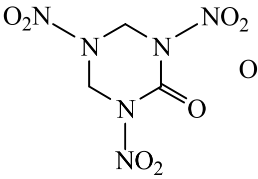

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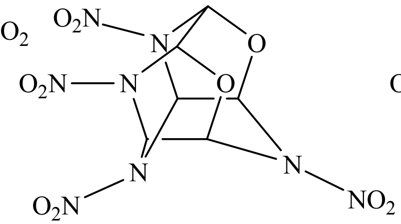

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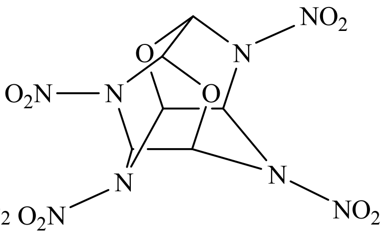

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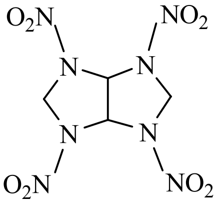

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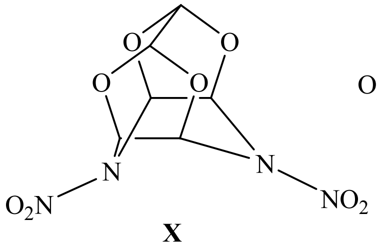

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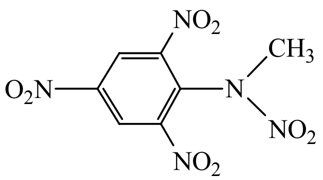

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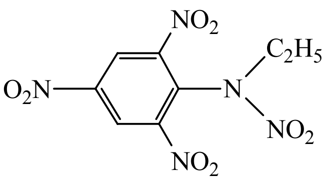

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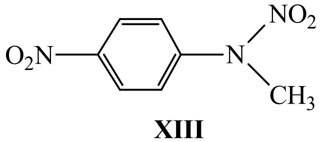


XIII

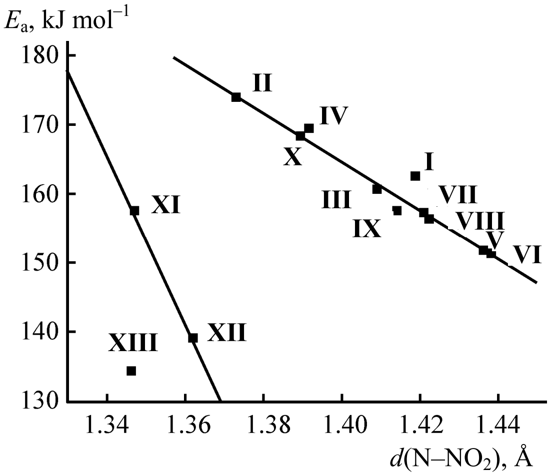
All data on these compounds and references to original publications are collected in [3, 5, 6], which we used to obtain the necessary information. Most of the results on the measurement of reaction rates is given in the literature as the kinetic parameters *E* and *A*. Therefore, the desired values of the activation energy in benzene E_{bz} were found as follows. For the average temperature T_{av} of the temperature range in which the value of *E*

The kinetic characteristics of decomposition of nitramines, and the N–NO_2 bond lengths

Comp. no.	Environment	ΔT, °C	E, kJ mol^{-1}	log (A/s^{-1})	k_{obs} (s^{-1}) at T_{av}	σ	S	k_{bz} (s^{-1}) at T_{av}	E_{bz}, kJ mol^{-1}	$E_{a,av}$	d(N–N), Å
I	Dinitrobenzene [3]	170–210	156.3	13.6	8.7×10^{-5}	2	2	8.7×10^{-5}	164.5	162.5	1.419
	Trinitrobenzene [3]	120–210	158.6	14.0	1.2×10^{-5}	2	2	1.2×10^{-5}	162.8		
	Melt [3]	135–200	155.3	13.9	3.1×10^{-5}	2	2	3.1×10^{-5}	160.3		
II	Nitrobenzene [3]	225–245	155.8	12.0	1.1×10^{-4}	1	2	2.2×10^{-4}	177.1	174.1	1.373
	Trinitrobenzene [3]	230–235	191.7	15.7	1.2×10^{-4}	1	2	2.4×10^{-4}	177.0		
	Liquid phase [31]	216–250	198.4	17.3	6.8×10^{-4}	1	2	1.4×10^{-3}	168.3		
III	Dinitrobenzene [3]	160–200	166.1	14.3	1.7×10^{-5}	1	2	3.4×10^{-5}	164.5	160.7	1.409
	Trinitrotoluene [3]	166–184	154.4	13.9	1.2×10^{-4}	1	2	2.4×10^{-4}	157.0		
	Trinitrotoluene [3]	195–280	171.6	15.5	8.9×10^{-3}	1	2	1.8×10^{-2}	158.7		
	Dicyclohexyl phthalate [3]	201–280	173.7	15.4	5.0×10^{-4}	1	2	1.0×10^{-3}	161.9		
	Benzene [2]	180			5.5×10^{-5}	1	1	5.5×10^{-5}	166.9		
	Liquid phase [3]	213–299	198.8	18.5	7.4×10^{-2}	1	2	1.5×10^{-1}	155.3		
IV	Dinitrobenzene [3]	171–215	187.9	16.0	8.6×10^{-6}	2	2	8.6×10^{-6}	174.5	169.4	1.392
	Liquid phase [3]	271–314	220.6	19.7	2.1×10^{-1}	2	2	2.1×10^{-1}	164.3		
V	Dinitrobenzene [5]	150–190	45.3	18.6	5.4×10^{-5}	2	2	5.4×10^{-5}	151.2	151.8	1.436
	Dibutyl phthalate [5]	160–190	43.86	17.98	3.8×10^{-4}	2	2	3.8×10^{-4}	152.4		
VI	Benzene [2]	180	–	–	1.1×10^{-3}	1	1	1.1×10^{-3}	151.4		1.438
VII	Dibutyl phthalate [5]	150–180	162.9	15.23	2.8×10^{-5}	1	2	5.6×10^{-5}	157.2		1.421
VIII	Dibutyl phthalate [5]	150–190	166.6	15.68	2.2×10^{-5}	2	2	2.2×10^{-5}	156.5		1.422
IX	Dinitrobenzene [5]	145–190	170.0	15.77	5.4×10^{-4}	1	2	1.1×10^{-4}	156.7	157.6	1.414
	Dibutyl phthalate [5]	140–185	165.0	14.96		1	2		158.6		
	Benzene [6]	180	–	–	2.3×10^{-4}	1	1	2.3×10^{-4}	157.4		
X	Dibutyl phthalate [5]	210–250	158.1	13.15		1	2		168.4		1.39
XI	Liquid phase [3]	211–260	160.7	15.4	7.5×10^{-2}	1	2	1.5×10^{-3}	144.0	157.6	1.347
		132–164	146.1	12.9	6.0×10^{-6}	1	2	1.2×10^{-5}	152.4		
		131–155	150.7	13.8	7.6×10^{-6}	1	2	1.5×10^{-5}	149.9		
		140–160	147.3	13.5	2.02×10^{-5}	1	2	4.0×10^{-5}	149.0		
		140–165	167.4	16.0	2.9×10^{-5}	1	2	5.8×10^{-5}	148.6		
		150–175	150.3	13.5	2.4×10^{-5}	1	2	4.8×10^{-5}	151.9		
		130–139	254.9	27.3	4.2×10^{-6}	1	2	8.4×10^{-6}	148.8		
		140–150	232.3	24.5	3.0×10^{-5}	1	2	6.0×10^{-5}	145.9		
	Dinitrobenzene [3]	150–175	150.3	13.5	2.4×10^{-5}	1	2	4.8×10^{-5}	151.2		
XII	Dinitrobenzene [3]	144–165	139.4	13.9	7.7×10^{-4}	1	2	1.5×10^{-3}	137.8	139.2	1.362
	Benzene	140	–	–	1.7×10^{-4}	1	1	1.7×10^{-4}	140.5		
XIII	Benzene	120	–	–	1.3×10^{-4}	1	1	1.3×10^{-4}	134.5		1.346

was determined we calculated the observed rate constant k_{obs} and then transformed it into the rate constant in benzene according to the formula: $k_{bz} = k_{obs}S/\sigma$, where $S = k_{bz}/k_{obs}$ is kinetic cage effect, which reduces the rate in a viscous solvent, and σ is a statistical factor of the reaction, which must be considered in the case of multifunctional nitramines.

The cage effect is due to the reduction of the starting compound at the recombination of aminyl radical $R_2N^{\bullet}$ and NO_2 particles emerging in the first stage of decay. The value of *S*, which is observed in solvents like dinitrobenzene, takes a value within 2–3 range [2]. In fact, it is equal to the limiting magnitude of the cage effect, which is defined as a ratio of the rate constants of recombination and disproportionation (into R_2NO and NO) of the primary particles. Both the reactions proceed with low activation energy and differ only in the probability of aminyl radical to react with NO_2 at either oxygen or nitrogen atoms. A similar situation occurs in the recombination of NO_2 with alkyl radicals. Thus, at the recombination of methyl radical with NO_2 the yield ratio CH_3ONO/CH_3NO_2 is 2 [7], that is, in this case the disproportionation is exactly 2 times faster than the recombination. Further in the calculations of k_{bz}, $S = 2$ is taken, with no great loss in accuracy at the calculation of E_{bz}.



The dependence of the activation energy of thermal decomposition of secondary nitramines in benzene E_{bz} on the N–N bond length.

The statistical factor σ is determined from the structural data, and, except for the case of stepwise decay, it is equal to the number of nitramine groups with a maximum $N–NO_2$ bond length. Use of σ makes it possible to eliminate the difference in the nitramines due to the number of the nitramine groups and to assign k_{bz} to a single reaction group NNO_2. In determining σ, the possibility should be considered of a stepwise mechanism of decomposition of secondary nitramines. If the nitramine groups are separated by one methylene group, then splitting of one of them with a rate constant k_1 leads to a rapid decomposition of the whole molecule to the final product without the formation of stable intermediates. In this case, the parameter σ is equal to the number of the most reactive groups. If the NNO_2 groups are separated by two methylene groups, at the decomposition of one of them a stable intermediate is formed, which comprises the second nitramine group that then decomposes at about the same rate constant as the first one. When the decay rate is measured by the formation of the end products (manometric, colorimetric, and gravimetric methods), then the stepwise mechanism results in the first order reaction with the rate constant k_1 [8]. For this reason, in the case of dinitropiperazine **II**, which has two groups with the same value of $d(N–NO_2)$, σ = 1.

After calculating k_{bz} we find $E_{bz} = (k_{bz} - \log A)RT_{av}$. According to the most reliable published data we can establish that log *A* is 14.5 and 14.0 for aliphatic and aromatic nitramines, respectively [3]. To calculate E_{bz} we used all the data obtained under isothermal conditions. In almost all cases, the reaction kinetics was measured by the manometric method. The table lists the input data and results of E_{bz} calculation, as well as the values of $d_{N–N}$. The information on the bond length was taken from the Cambridge Structural Database [9]. At the inconsistence of the literature data the $d_{N–N}$ values were taken from the more recent publications. All references to primary sources, corresponding to the selected $d_{N–N}$, are given in [5, 6].

The structure of nitramine **XII** was investigated by XRD method, and it was found that the N–N bond length in this compound is 1.362 Å. Comparison of E_{bz} (kJ mol^{-1}) with $d_{N–N}$ (Å) shows that the data for the cyclic and framework nitramines are collinear (see the figure), in correspondence with the regression equation

$$E_{bz} = (663\pm43) - (356\pm30)d(N–NO_2), \quad (1)$$

$$r = 0.938;\ S_{Ebz} = 29;\ n = 10.$$

At the increase in bond length by 0.01 Å the activation energy decreases by 3.56 kJ mol^{-1}. The main reason for the increase in the N–N bond length of cyclic nitramines is, as noted in [5], the conformational strain, which forces the nitramine group to acquire a pyramidal structure reducing the resonance conjugation within the nitramine group.

In the aromatic compounds another type of electronic interaction occurs between the nitramine group and the substituent. As a result of conjugation of the nitro group with the benzene ring the N–N bond length is reduced, and simultaneously due to even stronger conjugation with the ring of the free valence of aminyl radical the strength of this bond decreases. A straight line drawn through the points for compounds **XI–XII** reflects a stronger dependence of E on d than the cyclic nitramines.

$$E_{bz} = 1810 - 1227d(N\text{–}NO_2).$$

The point for the compound **XIII** drops out of this dependence due to a decrease in the steric shielding, which leads to increased conjugation and further reduction of the N–N bond strength.

Thus, in the series of such compounds having the same type of electronic and steric interactions with substituents, there is a correlation between the activation energy of decomposition and the N–N bond length.

The existence of relation (1) allows us to estimate approximately the thermal stability of the new compounds from the results of the XRD studies. A quantitative measure of thermal stability of compounds is the rate constant for the initial stage of non-catalytic decomposition. To find this value for each compound, first we calculated E_{bz} by Eq. (1) and then k_{bz} for any temperature. Dividing k_{bz} by 2 we may find the approximate value of the rate constants of decomposition of nitramine in the liquid state k_{liquid}, and based on this value, to estimate according to certain rules [10] the rate constant for the initial stage of decomposition in the solid phase k_{solid}, which is the ultimate goal of the forecast. The maximum error in going from a k_{solid} to k_{liquid} is no more than 5% [10].

EXPERIMENTAL

Compound **XII** was synthesized according to [11] by the nitration of 4-nitro-*N*-methylaniline with nitric acid in acetic anhydride, and recrystallized from isopropanol, mp 144–145°C. Compound **XIII** was prepared in a procedure similar to that described in [12], recrystallized from hexane-ethyl acetate (2:1), mp 95–96°C, purity according to ^{1}H NMR was not less than 98%.

Kinetic measurements were performed using a manometric setup designed for pressures up to 100 at. The reactor was a glass 0.5–5.0 ml ampule equipped with a crescent-like membrane with a pointer, placed in a metal enclosure with a window to observe the deflection. The pressure was measured by the compensation method. This technique allows to perform experiments at high temperatures in almost all solvents, and to measure the kinetics of decomposition at high degrees of filling the container with the material.

X-ray diffraction study of compound XII. Colorless bulky crystals, empirical formula $C_8H_7N_5O_8$, belonging to the monoclinic type: a = 15.052(1), b = 7.504(1), c = 10.661(1) Å, β = 93.160(10)°, V = 1202.3(2) Å^3, M = 301.19, d_{calc} = 1.664 g cm^{-3}, Z = 4, space group P21/c. A set of experimental reflections was obtained with an automatic 4-circle diffractometer KM-4 (KUMA DIFFRACTION) with χ-geometry, by the method of ω/2θ scanning using monochromatic MoK_α-radiation (2θ ≤ 50°).In total 2873 reflections were measured, of which 2115 were independent (R_{int} = 0.0191). No correction for extinction was applied (μ = 0.151 mm^{-1}). The structure was determined by the direct method with SIR92 software [13], followed by a series of calculations of electron density maps. Hydrogen atoms were localized objectively from the difference electron density synthesis and refined in an isotropic approximation. Full-anisotropic (nonhydrogen atoms) refinement was carried out by the mean square method with the SHELXL-97 software [14] and completed at R_1 = 0.0367 for 1873 reflections with $I \geq 2\sigma(I)$ and R_1 = 0.0422 for all 2115 reflexes. The number of refined parameters is 219, *GOOF* 1.041. The maximum peak in the difference synthesis of electron density is equal to 0.245 Å^3. A CIF file containing full information on the investigated structure is deposited in Cambridge Crystallographic Data Centre, no. 876381, and can be freely obtained on the website: www.ccdc.cam.ac.uk/data_request/cif.

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