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Kinetics and Mechanism of the Thermal Decomposition of 1-Bromo-4-Nitroxymethylcubane

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Abstract—The thermal decomposition kinetics of 1-bromo-4-nitroxymethylcubane in the liquid phase is typical of C–ONO_2 bond heterolysis, which occurs if the nitro ester has a strong donor substituent. A comparison between 1-bromo-4-nitroxymethylcubane and *tert*-butyl nitrate shows that bromocubyl is close to the *tert*-butyl group in induction properties and cubyl itself is a stronger donor than this group.

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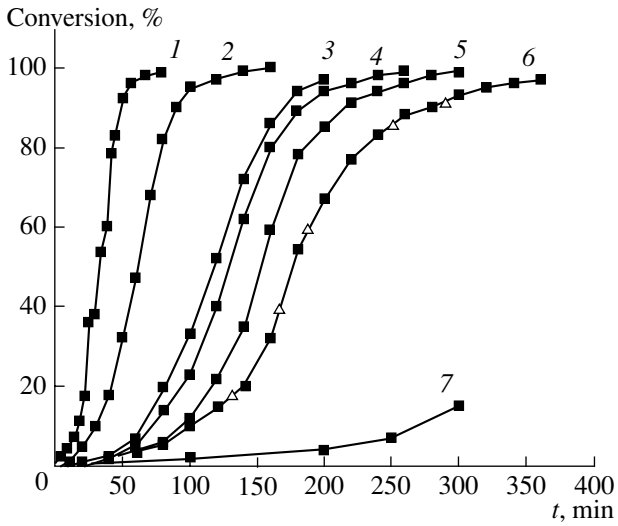
The inductive effect of the substituent is the main factor determining the structure effect on the thermal stability of organic nitro esters [1–3]. Both donor and acceptor substituents increase the decomposition rate of methyl nitrate, which is the most stable among the nitro esters. For electronegative groups (R), there is an equation correlating the decomposition rate constant of the nitro ester $RONO_2$ in the liquid phase and the Taft induction constant σ^* [3]. The magnitude of this effect at 140°C is characterized by the reaction constant ρ = 1.22. As σ^* changes by 0.1, the rate constant increases by 30%. The relative influence of the donor substituents is approximately three times as strong as that of the acceptor substituents [4]. Furthermore, already at σ^* = –0.3 (i.e., for *tert*-butyl nitrate), the decomposition mechanism changes so that the homolytic cleavage of the O–NO_2 bond gives way to C–ONO_2 bond ionization with nitrate ion formation, particularly in polar solvents [5]. The present kinetic study of the thermal decomposition of 1-bromo-4-nitroxymethylcubane (**I**) allowed us to determine the hitherto unknown induction properties of the cubane moiety and the reaction mechanism. For this purpose, it was necessary to correctly measure the rate constant of the initial, noncatalytic reaction step and to compare the kinetic data for compound **I** to the kinetic data for nitro esters whose decomposition rates are closest to that of cubane **I** and whose Taft induction constants and decomposition mechanism are known. A comparison between the decomposition rates of 1,4-dibromocubane [6] and alkyl nitrates [4] demonstrated that, at 140°C, these rates differ by several orders of magnitude. Therefore, the reaction site of cubane **I** is undoubtedly in the nitro ester group and bromocubyl acts as a substituent in the β position. Along with cubane **I**, 1,4-bis(nitroxymethyl)cubane (**II**) was studied as an auxiliary object for reactions in solutions.

EXPERIMENTAL

The decomposition kinetics was studied by manometric and calorimetric methods. In the former case, we used a setup designed for balanced pressure measurements in glass reactors up to a pressure of 100 atm. This procedure makes it possible to perform the reaction in volatile solvents and to record complete kinetic curves provided that the vessel is filled with a sufficiently large amount of the substance (the m/V ratio is high). The heat release rate was determined on a differential microcalorimeter with a sensitivity of 10^{-6} W capable of operating in the scanning and isothermal modes. The design of the calorimeter combined the advantages of a rather large metallic ampoule (1.4 cm^3) with a rather small time constant (~50 s). The transition from the scanning to the isothermal mode took 5 min. These characteristics allowed heat release rates to be measured with a high accuracy for 5- to 20-mg samples, the baseline to be checked quickly, and the isothermal increment method to be used efficiently in the determination of rate constants.

RESULTS AND DISCUSSION

The decomposition of cubane **I** in the liquid phase proceeds according to the first-order autocatalysis law (figure). The experimental conditions and the characteristics measured for the reactions are given in Table 1. The rate constant of the initial, noncatalytic step is independent of m/V (g/cm^3) in the 0.002–0.1 interval, and the extent of autocatalysis increases with an increase in m/V, as can be seen from the comparison of the 1 and 10% conversion times. The decomposition of cubane **I** is characterized by a low yield (φ, mol) of gaseous products and by a weak dependence of this yield on m/V. It can be seen from the data in Table 1 that, at m/V = 0.002, at most 1 mol of gaseous products is formed from 1 mol of the substance decomposed and



Decomposition kinetics of nitro ester **I** measured by the (*1–3*) manometric and (*4–7*) calorimetric methods: (*1*) 130°C, m/V = 0.002; (*2*) 125°C, m/V = 0.002; (*3*) 112.6°C, m/V = 0.1; (*4*) 110°C, m/V = 0.1; (*5*) 110°C, m/V = 0.01; (*6*) 110°C, m/V = 0.002 and 0.04 (Δ); (*7*) 105°C, m/V = 0.002.

this value decreases to 0.35 mol as m/V is increased to 0.1. The yield of gaseous products for the decomposition of mononitro esters is usually 2 moles per mole of ester, and this value does not decrease with increasing m/V [4].

Along with the low yield of the gaseous products, another specific feature of the decomposition of cubane **I** is a low activation energy (31.6 kcal/mol), which is unnatural for O–NO_2 bond homolysis [4]. This suggests that some other mechanism, probably bond heterolysis as in *tert*-butyl nitrate, can contribute to the decomposition rate.

The decomposition of cubane **I** in dilute (1–2%) solutions was studied to obtain additional data on the reaction mechanism. Several polar and nonpolar solvents were used. The polarity of a solvent was roughly characterized by its dielectric constant ε. The decomposition of pentaerythritol tetranitrate (PETN) was studied in the same solvents for comparison. This compound contains only electron-acceptor substituents, and the heterolytic mechanism of spontaneous decomposition is excluded for PETN in any medium. The tests were carried out at 160°C. At this temperature, cubane **I** and PETN show equal decomposition rates. In solutions, the reactions proceed according to a first-order rate equation. The results are presented in Table 2. The decomposition rate of compound **I** increases with increasing medium polarity, whereas the decomposition rate of PETN is independent of the solvent polarity. The activation energy of cubane **I** decomposition was measured in several solvents between 100 and 130°C. The activation energy data are listed in Table 3. The data reported for the decomposition of *tert*-butyl nitrate in acetonitrile [5] are presented in Table 3 for comparison. The activation energy decreases dramatically with an increase in the solvent polarity. The kinetic parameters measured in acetonitrile are similar to those for *tert*-butyl nitrate. These data on the solvent effect on the decomposition rate are evidence of the ion mechanism of cubane **I** decomposition and of the donor character of the bromocubyl group as a substituent. In the framework of this mechanism, the low yield of the gaseous products can be attributed to HNO_3 consumption for the nitration of the intermediate carbocation, which has

Table 1. Characteristics of the decomposition of nitro ester **I**

T, °C	m/V, g/cm^3	φ, mol/mol	Time of 1% conversion (τ(1%)), min	τ (10%), min	k, s^{-1}
130	0.002	1.00	2.8	21	6.0×10^{-5}
125	0.002	0.88	4.4	30	3.8×10^{-5}
110	0.0016	0.89	20	100	8.3×10^{-6}
110	0.004	0.85	21.3	98	7.8×10^{-6}
110	0.01	0.63	20.8	90	8.0×10^{-6}
110	0.1	0.35	19.5	70	8.5×10^{-6}
112.6*	0.1	–	12	65	1.4×10^{-5}
113.5*	0.1	–	26.9	70	6.2×10^{-6}
105	0.002	0.85	41	270	4.0×10^{-6}
90	0.002	0.90	410	5000	4.0×10^{-7}
80	0.003	0.8	1500	–	1.1×10^{-7}
80	0.03	0.8	1433	–	1.2×10^{-7}
70	0.03	0.8	5500	–	3.0×10^{-8}

* Calorimetric method.

Table 2. Decomposition half-lives of compounds **I**, **II**, and PETN in solutions

Solvent	ε	$\tau_{1/2}$, min		
		I (160°C)	**II** (150°C)	PETN (160°C)
Chloroform	4.7	50	42	40
Benzene	2.28	50	35	38
Naphthalene	2.54	45	42	41
ortho-Dichlorobenzene	9.93	50	40	37
Nitrobenzene	30.0	14	14	35
Benzonitrile	25.2	10	11	40
Nitromethane	38.6	9	10	38
Acetonitrile	36.2	<5	<5	32

to undergo isomerization with C–C bond cleavage before proton abstraction and, hence, can be relatively long-lived. The small preexponential factor is a consequence of the reversibility of the first ionization step. At 100°C, the decomposition rates of cubane **I** and *tert*-butyl nitrate differ by a factor of 20. However, since the bromine added directly to the cubane moiety decreases its donor properties and the influence of bromocubyl on the nitro-ester group is weakened by the methylene bridge, it seems likely that cubyl itself considerably excels the *tert*-butyl group in donor properties.

The solvent effect on the decomposition rate of dinitrate **II** is similar to the effect observed for cubane **I** (Tables 2, 3). The rate constants are several times larger for **II** than for **I**. This is likely due to the fact that the nitroxymethyl group has a considerably lower electronegativity than the bromine atom and weakens the donor capacity of the cubyl group to a lesser extent.

Table 3. Kinetic parameters of the decomposition of compounds **I** and **II**

Compound	Medium	E, kcal/mol	$\log A$ [s^{-1}]
I	Melt	31.6	12.92
	Naphthalene	34.4	13.77
	ortho-Dichlorobenzene	30.4	11.66
	Benzonitrile	26.2	10.25
	Nitromethane	25.2	10.50
	Acetonitrile	24.0	10.40
II	Naphthalene	33.9	14.00
	Benzonitrile	20.9	8.00
tert-Butyl nitrate	Acetonitrile	22.5	11.78

Thus, the study of the thermal decomposition of compound **I** indicates that an ion mechanism is possible for this reaction and that bromocubyl is an electron donor comparable in strength to the *tert*-butyl group rather than an electronegative substituent, such as primary and secondary bromoalkyl groups.

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