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Determination of the Inductive Constant of the Succinimide Group from the Reaction Series of Thermolysis of Nitro Esters

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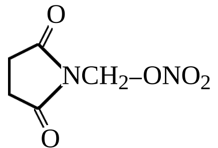
Abstract—The inductive constant σ* of the succinimide group was determined using the previously obtained equation correlating the rate constant k_1 ofliquid-phase homolysis of the O–NO_2 bond in nitro esters with the σ* constants of electronegative substituents. The kinetics of thermolysis of *N*-nitroxymethyl- and *N*-(2-nitroxyethyl)succinimide in the melt and solutions was studied manometrically. Adequate data for k_1 were obtained. The σ* constant of the succinimide group was determined to be 4.5. The σ* constants for the phthalimide group and some other imide substituents were determined by a similar procedure.

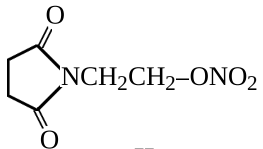
Analysis of extensive available data on the thermolysis of nitro esters, made in [1–3], showed that electronegative substituents accelerate the homolytic dissociation of the O–NO_2 bond; the major factor affecting the rate constant of liquid-phase decomposition of nitro esters (k_1) is the inductive effect of the substituent. The most representative data on the decomposition of nitro esters are available for 140°C [3]; for this temperature, the correlation between k_1 and the Taft aliphatic inductive constant σ* of substituents is as follows [4]:

$$\log k_1 = -5.994 + 1.220\Sigma\sigma^*,$$
$$r\ 0.9830,\ S\ 0.09326.$$

This relationship opens new prospects for determination of σ* for substituents of a complex structure. To determine the inductive constant of a group X, it is sufficient to prepare nitro esters $XCH_2CH_2ONO_2$ or XCH_2ONO_2 (if the latter exists) and determine for them k_1 at 140°C. A comparison of the inductive constants of a group X determined for both structures, taking into account the attenuation factor of 2.8 in the transfer of the inductive effect through the methylene group, will either confirm the purely inductive effect of the α-substituent and improve the reliability of the σ* constant thus obtained, or reveal an additional α-effect (e.g., steric). The goal of this study was to determine the σ* constant of the succinimide group, based on the above equation. Although numerous succinimide derivatives have been prepared, this constant is still unknown. As investigation objects we chose *N*-(nitroxymethyl)succinimide **I** (mp 68°C) and *N*-(2-nitroxyethyl)succinimide **II** (mp 114°C).



I



II

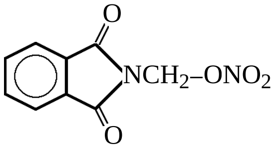
The succinimide group exhibits no base properties; therefore, aminolysis of **I** and **II**, occurring when a molecule contains even weakly basic functional groups [4], is impossible.

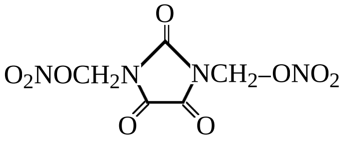
$$RCH_2ONO_2 + AmH \longrightarrow RCH_2Am + HONO_2.$$

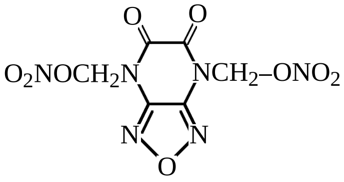
The ionic decomposition mechanism involving the heterolysis of the C–ONO_2 bond is also impossible. This mechanism is postulated [3] only for molecules containing donor substituents, such as, e.g., *tert*-butyl group [5]. Therefore, the only possible decomposition mechanism for **I** and **II** is the classical mechanism involving dissociation of the O–NO_2 bond.

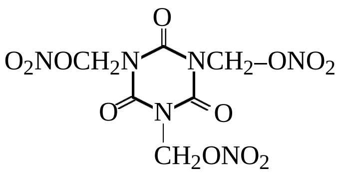
Determination of k_1 for nitro esters presents certain problems [3] because of the effect of secondary factors; in particular, the decomposition may occur faster through the gas phase, or the primary molecular reaction may be obscured by a strong autocatalytic process. An advantage of nitro esters derived from succinimide is their relatively low vapor pressure, which allows the decomposition to be performed in the liquid phase at low degrees of filling the vessel with the substance (*m*/*V*), when the catalytic processes induced by volatile products make a minor contribution and the contribution of the gas-phase decomposition is also insignificant, because the fraction of the vaporized substance is small.

Along with compounds **I** and **II**, we studied a series of other nitro esters with imide substituents: *N*-nitroxymethylphthalimide (**III**) (mp 102°C), *N,N*-bis(nitroxymethyl)triketoimidazole (**IV**) (mp 105°C), *N,N*-bis(nitroxymethyl)diketofurazanopiperazine (**V**) (mp 202°C), and 1,3,5-tris(nitroxymethyl) cyanurate (**VI**) (mp 148°C).


III


IV


V


VI

The vapor pressure of **I**, the most volatile compound among the nitro esters chosen, at 140°C is ~15 mm Hg, and the fraction of the vaporized substance at m/V 0.01 g cm^{-3} does not exceed 1%. Therefore, for all the compounds we determined k_1 at m/V 0.002–0.01 g cm^{-3}. Under these conditions, such factors as dissolution of gaseous products in the liquid phase and autocatalysis in early steps (up to 2% conversion) of the decomposition do no affect the initial gas evolution rate [3].

The kinetic curves of the gas evolution in the decomposition of **I**–**III** in the melt and in benzene solutions are compared in Fig. 1. It is seen that the kinetic curves for **I** and **III** coincide, whereas compound **II** decomposes considerably more slowly. The initial rate of decomposition of **II** in benzene is higher than that in the melt, unambiguously indicating that the contribution of autocatalysis to the initial rate is insignificant. The higher rate of the decomposition in benzene may be due to its lower viscosity and hence to weaker cage effect typical of nitro esters [3]. To check this assumption, we studied the decomposition of ester **II** (more stable than **I**) at 160°C in several structurally related solvents differing in the molecular weight and hence in the viscosity. Figure 2 and Table 1 show that the decomposition of **II** at 160°C in solutions is described by a first-order equation, and the rates vary in the order benzene > perfluoronaphthalene > nitrobenzene > melt ≈ naphthalene ≈ diphenyl. The cage effect rapidly gets saturated, and the maximal difference in the rates is approximately fivefold, which corresponds to a common decrease in the decomposition rate of nitro esters in going from the gas phase to a melt [3]. For compound **IV**, which is less stable than **I**, the rates

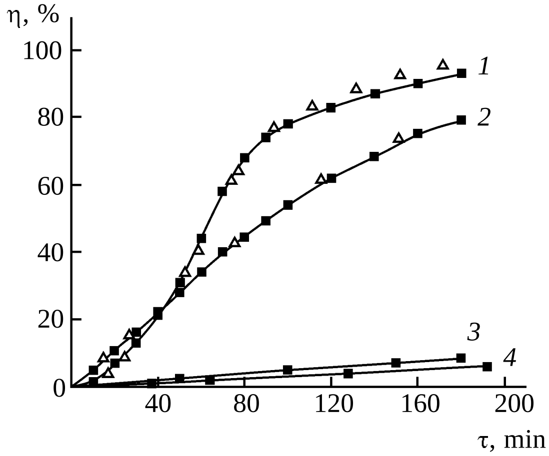


Fig. 1. Kinetic curves of decomposition at 140°C: (*1*) (squares) **I** and (triangles) **III** in a melt, (*2*) (squares) **I** and (triangles) **III** in benzene, (*3*) **II** in benzene, and (*4*) **II** in a melt; (η) conversion.

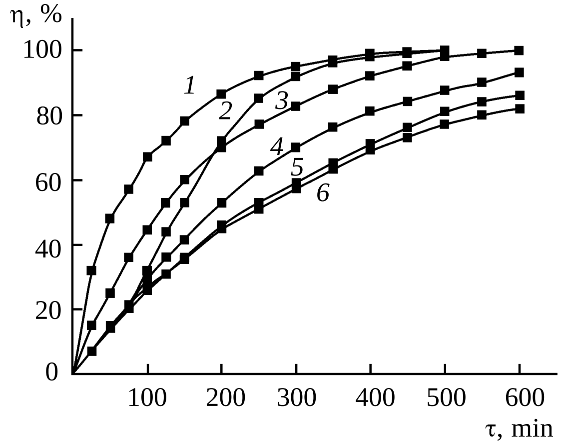


Fig. 2. Kinetic curves of decomposition of nitro ester **II** in various solvents at 160°C: (*1*) benzene, (*2*) melt, (*3*) perfluoronaphthalene, (*4*) nitrobenzene, (*5*) naphthalene, and (*6*) diphenyl; (η) conversion.

Table 1. Decomposition rates of nitro esters **I**–**VI**

Comp. no.	Medium	T, °C	k, s^{-1}
I	Melt	120	1.1×10^{-5}
	″	130	3.2×10^{-5}
	″	140	1.0×10^{-4}
	Benzene	140	1.3×10^{-4}
	″	150	4.9×10^{-4}
II	Melt	140	5.0×10^{-5}
	″	160	4.4×10^{-5}
	Benzene	140	1.5×10^{-5}
	″	160	2.3×10^{-4}
	Perfluoronaphthalene	160	1.0×10^{-4}
	Nitrobenzene	160	6.4×10^{-5}
	Naphthalene	160	4.5×10^{-5}
	Diphenyl	160	4.4×10^{-5}
III	Melt	140	1.0×10^{-4}
	Benzene	140	1.3×10^{-4}
IV	Melt	100	1.0×10^{-6}
	″	110	6.1×10^{-6}
	″	120	2.1×10^{-5}
	″	130	5.2×10^{-5}
	″	140	1.5×10^{-4}
	Naphthalene	140	1.5×10^{-4}
V	Solid phase	100	5.0×10^{-7}
	″	110	2.8×10^{-6}
	″	120	2.1×10^{-5}
	″	140	3.4×10^{-6}
	Naphthalene	140	2.4×10^{-4}
VI	Solid phase	120	5.0×10^{-6}
	″	140	5.1×10^{-5}
	Naphthalene	140	2.4×10^{-4}

Table 2. Inductive constant σ^* of substituents R in compounds $R–ONO_2$ (**I**–**VI**)

Comp. no.	k, s^{-1} (140°C)	σ^*	Comp. no.	k, s^{-1} (140°C)	σ^*
I	1.0×10^{-4}	1.634	**IV**	1.5×10^{-4}	1.780
II	5.0×10^{-6}	0.569	**V**	2.4×10^{-4}	1.947
III	1.0×10^{-4}	1.634	**VI**	2.4×10^{-4}	1.947

of decomposition in the melt and in a naphthalene solution at 140°C coincide (Table 1). These results show that k_l at 140°C for compounds that are solid at this temperature can be estimated by performing the reaction in naphthalene or diphenyl. Therefore, the decomposition of solid compounds **V** and **VI** was performed in 1% naphthalene solutions, and that of the other compounds, in the melt.

For **I**, **II** and **IV** in the melt and for **V** in the solid phase, we determined the Arrhenius parameters E (kJ mol^{-1}) and $\log A$ [s^{-1}]: 35.7 and 14.86; 38.8 and 15.20; 35.7 and 14.80; 32.8 and 13.53, respectively. These data show that an increase in the decomposition rate in foing from **II** to the other nitro esters is due to a decrease in the activation energy. From the rate constants at 140°C (Table 1), using the above-given equation, we calculated the inductive constants of the substituents (Table 2).

For the succinimide group, from data for **I**, we have $\sigma^* = 1.634 \times 2.8 = 4.57$, and from data for **II**, correspondingly, $0.569 \times 2.8 \times 2.8 = 4.46$. These results are well consistent taking into account possible errors. The mean value is close to 4.5. The inductive constant of the phthalimide group is equal to that of the succinimide group, as the rate constants of the noncatalytic steps of decomposition of **I** and **III** at 140°C virtually coincide. The σ^* constants of the other groups are somewhat higher than that of the succinimide group because of the presence of electron-withdrawing substituents, but the effect of these remote substituents is relatively weak. The closest analog of the imide group for which the inductive constant is known is the amide structure MeCONH, for which, according to the data from [6], $\sigma^* = 1.8$. At the same time, for the dialkylamino group Me_2N the σ^* constant is 0.61, i.e., it is lower by a factor of 3. An increase in σ^* to ~4.5 on addition of the second carbonyl group to the nitrogen atom seems quite reasonable.

EXPERIMENTAL

Compounds **I**, **II**, and **IV**–**VI** were prepared from the corresponding alcohols by a standard nitration procedure, and compound **III**, from the corresponding chloro derivative by the exchange with $AgNO_3$. All the compounds are solids and can be readily purified by recrystallization. The reaction kinetics were studied manometrically on an installation allowing measurement of pressures of up to 100 atm in 2–5 cm^3 glass reaction vessels. This procedure allows the reaction to be performed at various m/V and virtually in any solvent. In all the cases, we obtained the total kinetic curves of the gas release and calculated the rate constants either by a first-order equation always valid for solutions or by a first-order autocatalysis equation describing the decomposition in a melt or in the solid phase up to 70–80% conversion.

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