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LETTERS TO THE EDITOR

Effect of Structure on the Rate and Mechanism of Thermolysis of Some 4-Substituted 3-Methylfuroxans

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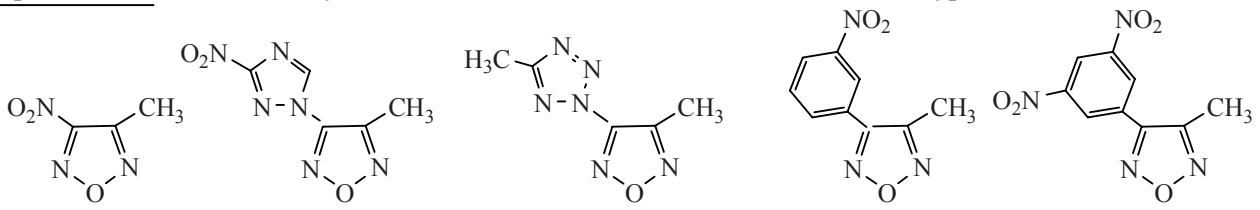
In extension of [1] the thermolysis kinetics of compounds **I–V** was studied by manometric method in a vacuum (10^{-1}–10^{-2} mm Hg) using compensation manometer of Burdon type [2].

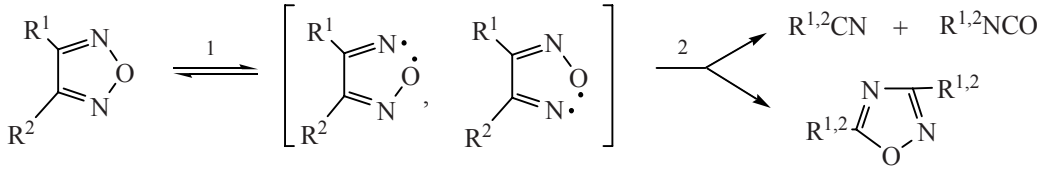


I **II** **III** **IV** **V**

Compounds **I–V** were prepared by known methods [3] and purified by recrystallization from suitable solvents. They were chromatographically pure and contained 98.8–99.4% of the basic substance.

The gas-phase thermolysis of **I** proceeds as a unimolecular process and is independent of the initial vapor pressure of the substance (over 190 mm Hg) and of the ratio of the reaction vessel surface to its volume (S/V = 0.55–4.62 cm^{-1}). In the melt and in solution in an inert solvent dibutylphtalate (DBP) the furazans decompose according to the first-order reaction law to the conversion level of 30–45 %. The substance content in the solution (1–10 %) does not affect the reaction rate.

The limiting stage, according to [3], can be represented by the following scheme:



(1)

The ring opening reaction at the N–O and C–C bonds results in the intermediate nitriles and nitrile oxides. The nitrile oxides are consumed both in the irreversible isomerization to form isocyanate and in 1,3-dipolar cycloaddition to nitriles to form 1,2,4-oxadiazoles.

Thermolysis activation parameters of the studied furazans except **III** can be ascribed to the limiting stage (1). They are close for all compounds, and the rate constant differences can be easily attributed to the inductive effect of the 4-substituent

$$\log k_{220^\circ C} = -0.19\sigma^* - 5.63,\ r\ 0.999;\ S_{st}\ 0.01;\ n\ 6. \quad (2)$$

Kinetic parameters of thermolysis of furasans **I–VI**

Comp. no.	Thermolysis conditions	Temperature range,°C	E_a, kJ mol^{-1}	log A	–log $k_{220°C}$
I	Gas [4]	260–320	195.5	14.30	6.411
	Gas	240–280	193.8	14.20	6.331
II	DBP solution	220–270	195.0	14.57	6.088
	Melt	200–250	194.7	14.65	5.976
III	DBP solution	200–240	176.3	15.12	3.557
IV	Melt	210–240	192.9	14.74	5.695
	DBP solution	210–250	193.5	14.73	5.769
V	DBP solution	210–250	193.8	14.65	5.881
VI[a]	Gas [4]	240–300	193.0	14.83	5.616

[a] 3-methyl-4-ethylfurazan.

The low value of ρ-constant in (2) indicates that the substituent weakly affects the reaction center of reaction (1), where the N–O bond rupture is activated.

Compound **III** do not fit relationship (2) most likely due to another decomposition mechanism. We emphasize that tetrazole ring is less heat-resistant [4] than 1,2,4-triazole and furazan rings (see table). This fact suggests an alternative thermolysis mechanism for compound **III** involving an initial cleavage of the N–N bond in the tetrazole ring. Activation parameters for **III** are in good agreement with this mechanism.

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