EFFECT OF THE POLARITY OF SUBSTITUENTS ON THE DECOMPOSITION RATE OF β-NITROAMINES

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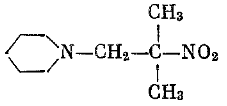
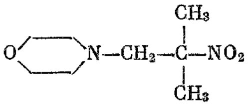
A quantitative study of the decomposition of β-nitroamines according to the scheme

$$R_2\overset{\oplus}{N}HCH_2CR_2'NO_2 \underset{}{\overset{K_a}{\rightleftarrows}} R_2NCH_2CR_2'NO_2 \xrightarrow{k_{\text{decompn}}} R_2\overset{\oplus}{N}{=}CH_2+\overset{\ominus}{C}R_2'NO_2$$

disclosed [1] that alkyl substituents on the nitrogen atom affect the decomposition rate mainly due to steric factors. In order to estimate the contribution made by the polar effect of substituents attached to nitrogen we studied the decomposition kinetics of β-nitroamines (I) and (II),

 (I) and  (II)

where the steric characteristics of the substituents attached to nitrogen are very close, while the induction effects differ markedly: the σ^* are respectively equal to –0.18 and 0.67.

EXPERIMENTAL

The KOH (analytical grade) solution was free of CO_3^{2-} ions.

1-Piperidyl-2-methyl-2-nitropropane (I). To 0.36 mole of piperidine, with cooling and stirring, was gradually added 0.12 mole of paraform, and the mixture was stirred at room temperature for 2 h. With stirring, the obtained mixture was added to a previously prepared solution of 2-nitropropane (0.12 mole) in 18.5 ml of a solution of 0.13 mole of KOH in water, after which CO_2 was passed in for approximately an hour. The product was extracted with ether, dried over $MgSO_4$, distilled twice from a glass vessel and once from a quartz vessel, and the fraction with bp 119-120° (8 mm), and n_D^{20} 1.4649, was collected. Found: C 57.50; 57.65; H 9.70; 9.70; N 15.47; 15.55%. $C_9H_{18}N_2O_2$. Calculated: C 58.04; H 9.74; N 15.04%.

1-Morpholyl-2-methyl-2-nitropropane (II) was synthesized in the same manner as (I) from morpholine, formaldehyde and 2-nitropropane; bp 73-76° (0.5 mm), mp 43-45° (hexane). From [2]: mp 43°.

The decomposition of (I) and (II) was studied in aqueous 0.1 N KOH solutions. The rate of the process was followed spectrophotometrically in the region of the absorption maximum of the 2-nitropropane anion (λ_{max} 223 nm) using a Hitachi EPS-3 instrument, in cells with a light path of 1 cm, placed in a thermostated cell holder. From the obtained kinetic curves was calculated the effective rate constant using the equation

$$k_{\text{eff}} = \frac{2,3}{t}\lg\frac{D_\infty - D_0}{D_\infty - D_x}$$

where D_∞ is the absorption of the solution at the end of experiment

TABLE 1. Decomposition of β-Nitroamines in 0.1 N KOH Solution

1-Piperidyl-2-methyl-2-nitropane		1-Morpholyl-2-methyl-2-nitropane	
T, °C	$k^*_{\text{eff}}\cdot 10^2$, sec^{-1}	T, °C	$k^*_{\text{eff}}\cdot 10^2$, sec^{-1}
10	0,41	25	0,44†
15	0,84	40	2,55
20	1,48	50	7,11
25	2,47	60	19,50

* Average value of 3-4 measurements.

†Calculated from the data on the activation energy.

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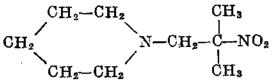
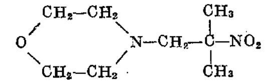
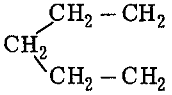
TABLE 2. Kinetic and Thermodynamic Characteristics of Decomposition of β-Nitroamines

Compound	K_a, M, 25°	$k_{decompn}$, sec^{-1}, 25°	$\Delta H^{\neq}$ kcal /mole	$\Delta S^{\neq}$, eu
	$6{,}76 \cdot 10^{-8}$	$(2{,}47 \pm 0{,}12) \cdot 10^{-2}$	$20{,}0 \pm 0{,}5$	0,0
	$(3{,}80 \pm 0{,}55) \cdot 10^{-5}$	$4{,}41 \cdot 10^{-4}$	$20{,}6 \pm 1{,}2$	−5,7

(in a time greater than 8 reaction half-periods), D_0 is the absorption of the solution at the start of experiment, and D_x is the absorption of the solution to time t. The results of studying the decomposition kinetics of (I) and (II) are given in Table 1. The constant remains constant up to 2/3 conversion.

Determination of Ionization Constants (K_a) for Conjugated Acids 1-Piperidyl-2-methyl-2-nitropropane (I) and 1-Morpholyl-2-methyl-2-nitropropane (II). In order to estimate the K_a of 1-piperidyl-2-methyl-2-nitropropane we used the correlation equation, which relates the ionization constants of conjugated acids of tertiary amines with the induction constants of the substituents [3].

$$pK_a = 9.61 - 3.3\Sigma\sigma^*$$

Previously we had found the value of σ^* for the substituent $CH_2C(CH_3)_2NO_2$ to be equal to 0.92 [4], and the value of σ^* for  to be equal to −0.18 [5], whence $K_a = 6.76 \cdot 10^{-8}$ M.

The ionization constant of conjugated acid (II) was determined by the potentiometric titration method. The given degree of neutralization of compound (II) was followed by the change in the pH with time. The obtained values were plotted on a graph relating the pH as a function of time (t), and extrapolated to t = 0. We obtained a value for the K_a of (II) equal to $(3.80 \pm 0.55) \cdot 10^{-5}$ M.

DISCUSSION OF RESULTS

The rate constant for the monomolecular decomposition of β-nitroamines is related to the effective rate constant by the equation given in [4]

$$k_{eff} = \frac{K_a k_{decompn}}{K_a + a_{H_3O^{\oplus}}}.$$

From this equation it follows that when the pH > 8 for (I) and (II) the k_{eff} is equal to $k_{decompn}$. The data on the decomposition of compounds (I) and (II) are given in Table 2.

From the obtained values of the decomposition constants of compounds (I) and (II), the parameter ρ of the equation of the Hammett – Taft type is equal to −2.1. A negative value for ρ testifies to the fact that an increase of the electron density in the reaction center favors the reaction. This was to be expected, since partial separation of the charges occurs in the transition state of the decomposition, with the subsequent formation of the carbonium ion. The low value of parameter ρ testifies to the slight sensitivity of the given reaction to the induction effect of the substituents. It is interesting to mention that, when calculated on the basis of the Hammett equation, the decomposition rates of compounds, containing alkyl substituents on the nitrogen atom, of 1-N-dimethylamino-2-methyl-2-nitropropane and 1-N-diisopropylamino-2-methyl-2-nitropropane, should differ by a factor of 7, whereas actually an increase of 2500 times in the rate is observed.

As a result, the obtained data again corroborate the fact that the polar effects cannot be the reason for the increase in the decomposition rates of β-nitroamines with increase in the size of the alkyl substituents attached to the nitrogen atom.

CONCLUSIONS

1. A study was made of the decomposition kinetics of 1-piperidyl-2-methyl-2-nitropropane and 1-morpholyl-2-methyl-2-nitropropane in 0.1 N KOH solution.

2. The constants of the true decomposition rates of these compounds at 25° were determined, as well as the enthalpy and activation entropy for cleavage of the C – C bond.

3. The ionization constant of the conjugated acid 1-morpholyl-2-methyl-2-nitropropane was determined; on the basis of correlation equations, the value of the ionization constant of 1-piperidyl-2-methyl-2-nitropropane was estimated.

4. The contribution made by the polar effect to the previously observed change in the decomposition rates of N-alkyl-β-nitroamines is slight.

LITERATURE CITED

1. M. M. Dolgaya, Yu. N. Belokon', and V. M. Belikov, Izv. Akad. Nauk SSSR, Ser. Khim., 74 (1969).
2. H. Johnson, J. Am. Chem. Soc., 68, 12 (1946).
3. H. K. Hall, J. Am. Chem. Soc., 79, 5441 (1957).
4. M. M. Dolgaya, Yu. N. Belokon' N. S. Martinkova, and V. M. Belikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2234 (1967).
5. Yu. A. Zhdanov and V. I. Minkin, Correlation Analysis in Organic Chemistry [in Russian], Izd. Rostov. Univ. (1966).