Kinetics of 2,4-Dihydro-1,2,4-triazol-3-one Nitration in Nitric Acid

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Abstract—The kinetics and mechanism of 2,4-dihydro-1,2,4-triazol-3-one nitration in nitric acid have been studied. The role of 2-nitro-2,4-dihydro-1,2,4-triazol-3-one as an intermediate has been determined.

INTRODUCTION

2,4-Dihydro-1,2,4-triazol-3-one (TO) nitration is presently used in the production of the energetic low-sensitivity compound 5-nitro-2,4-dihydro-1,2,4-triazol-3-one (NTO) [1]. Although many publications have been devoted to the kinetics and mechanism of the nitration of azoles, the kinetics of TO nitration is still obscure. The present study is devoted to the study of TO nitration in 70–100% nitric acid.

EXPERIMENTAL

The kinetics of the process was studied using a Specord M-40 spectrophotometer. Nitration was carried out in a temperature-controlled cell with sampling. The samples were diluted with a 100-fold amount of water to terminate the process. Absorbance was measured at 250–330 nm in 1–1.5% nitric acid. For these solutions, the absorbance maximum of NTO lies at 316 nm ($\varepsilon = 4100\ \mathrm{l\ mol^{-1}\ cm^{-1}}$) and that of 2-nitro-1,2,4-triazol-3-one (N-NTO) is at 276 nm ($\varepsilon = 3700\ \mathrm{l\ mol^{-1}\ cm^{-1}}$). No absorption due to TO is observed in this wavelength range. The concentrations of the components in the system were calculated by the Firordt method [2]. Under the experimental conditions examined, the TO concentration was $(1–3) \times 10^{-2}$ mol/l, 500–2000 times lower than the concentration of nitric acid. The semilogarithmic anamorphoses of kinetic curves were fitted to linear functions with a high correlation coefficient of at least 0.99, indicating that the reaction is first-order.

RESULTS AND DISCUSSION

The study of NTO accumulation kinetics during TO nitration in 70–100% nitric acid has revealed that, at HNO$_3$ concentrations above 77%, a product giving rise to an absorbance peak at 276 nm appears in the reaction mixture a few minutes after the beginning of the experiment. This peak is due to the recently synthesized compound N-NTO [3]. Furthermore, in 96–100%

HNO$_3$, the NTO yield is as low as 25–30%, and this effect cannot be explained by the acidic decomposition of NTO. The rate constants of this process are 5.37×10^{-5} and 2.46×10^{-6} s^{-1} in 94.4 and 99.6% HNO$_3$, respectively, implying a ~10% decrease in the NTO yield in anhydrous nitric acid. All these facts point to a complicated mechanism of TO nitration.

Indeed, a distinct peak of N-NTO, whose intensity increases with an increase in the HNO$_3$ concentration, and only an insignificant NTO absorption are observed at the beginning of the process. However, the absorption characteristic of N-NTO disappears in a short time (Fig. 1).

We studied the behavior of N-NTO in a wide acidity range (see Table 1) for the reason that C-nitroazoles can form by both direct nitration and the rearrangement of the corresponding N-nitro compounds in acidic media
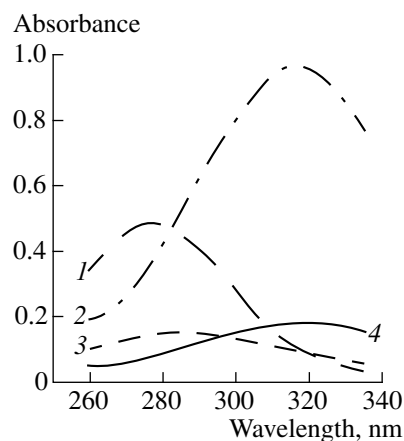

Fig. 1. Absorbance of reaction solutions in TO nitration versus reaction time and HNO$_3$ concentration: (*1*) 87.4% HNO$_3$, 1 min; (*2*) 87.4% HNO$_3$, 180 min; (*3*) 99.9% HNO$_3$, 4 min; (*4*) 99.9% HNO$_3$, 180 min.
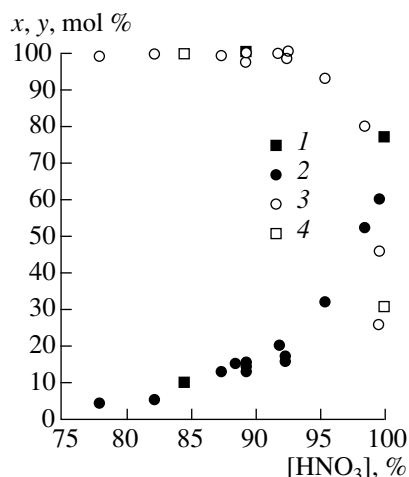
Fig. 2. Formation of NTO from TO and N-NTO in nitric acid at 25°C: (*1*) N-NTO percentage (*x*) in the N-NTO–TO mixture 1 min after N-NTO dissolution in nitric acid, (*2*) N-NTO percentage in the N-NTO–TO mixture 1 min after TO dissolution in nitric acid, (*3*) NTO yield (*y*) from TO, and (*4*) NTO yield from N-NTO.

Fig. 3. Apparent first-order rate constants of NTO formation from (*1*) N-NTO and (*2*) TO in nitric acid at 25°C.

[4]. We have found that denitration occurs at $H_0 < -1$, yielding TO.

At pH > 1, complete destruction occurs, resulting in the breaking of the ring and in the evolution of a gaseous product consisting of carbon dioxide, nitrogen, and nitrous oxide, whereas TO is virtually absent in the hydrolysis products. In 99% trifluoroacetic and 94% sulfuric acids, N-NTO disappears immediately after mixing and then NTO forms very slowly. No intramolecular rearrangement is observed.

In order to determine the true role of N-NTO in the overall process, we studied the transformations of TO and N-NTO into NTO. The results are presented in Fig. 2.

The N-NTO concentrations in these processes at a given reaction time are almost the same and are determined by the HNO$_3$ concentration only. This indicates a high rate of equilibration between TO and N-NTO. Note that, at –30°C, the maximum concentration of N-NTO is reached within 10–15 min. The ultimate NTO yield data (Fig. 2) provide evidence that the processes in question are identical. For instance, in 84.5% HNO$_3$, N-NTO disappears almost completely 1 min after mixing and the ultimate NTO yield is 98% (in 180 min) and is identical to the yield obtained by TO nitration. The rate constants of NTO formation from TO and N-NTO at [HNO$_3$] = const (Fig. 3) almost coincide. It can be stated that N-NTO is not an intermediate product and NTO results from N-NTO denitration followed by the nitration of the resulting TO.
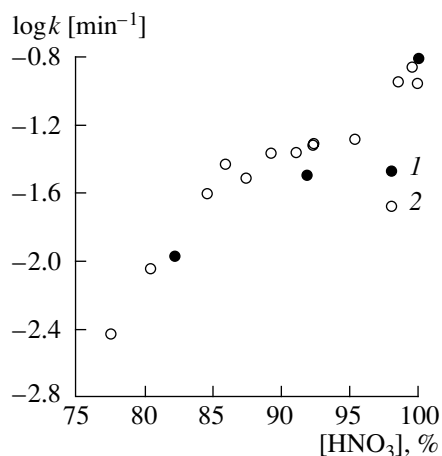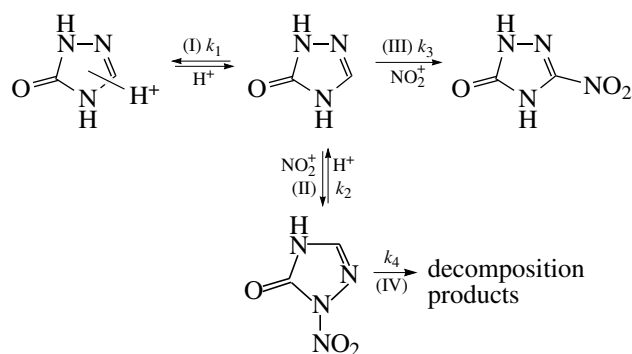
Our data (including the decrease in the NTO yield in 98–100% HNO$_3$) suggest the following mechanism for triazolone nitration:

The rate constants k_3 and k_4 were calculated using a method conventional for systems with parallel reac-

Table 1. Rate constant of N-NTO decomposition as a function of the acidity of the medium

Experiment no.	Medium	H_o	pH	k_1, min^{-1}
1	58.1% H$_2$SO$_4$	–4.0		0.00820
2	44.9% H$_2$SO$_4$	–2.9		0.00070
3	27.72% H$_2$SO$_4$	–1.6		0.00050
4	0.1 N HCl		1.0	0.00328
5	0.1 N CF$_3$COOH		1.0	0.00409
6	0.238 N HNO$_3$		1.1	0.00670
7	0.01 N HCl		2.0	0.0105
8	0.01 N CH$_3$COOH		3.4	0.100

Note: In experiments 1–3, TO is formed; in experiments 4–8, N-NTO is destroyed.
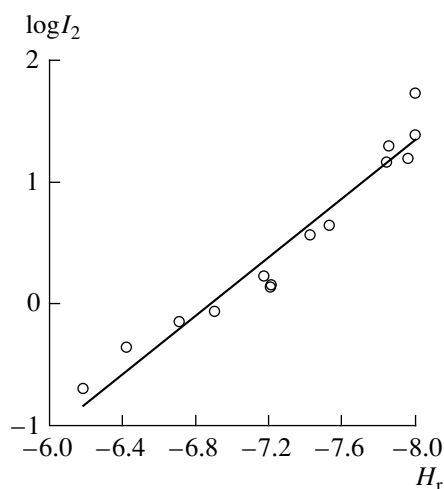
Fig. 4. $\log I_2$ versus the acidity function H_r.

Fig. 5. Apparent rate constants of (*1*) NTO formation (k_3') and (*2*) N-NTO decomposition (k_4') as functions of the HNO$_3$ concentration.

tions and equilibrium [5]. The pK_1 value is equal to -2.01 ($H_0^{1/2} = -3.98$, $m = 0.5$) [6].

$$K_1 = \frac{[\text{TOH}^+]}{[\text{TO}][\text{H}^+]}, \quad K_2 = \frac{[\text{N-NTO}][\text{H}^+]}{[\text{TO}][\text{NO}_2^+]},$$

$$\frac{[\text{TOH}^+]}{[\text{TO}]} = K_1[\text{H}^+] = I_1, \quad \frac{[\text{N-NTO}]}{[\text{TO}]} = K_2\frac{[\text{NO}_2^+]}{[\text{H}^+]} = I_2,$$

$$\log I_2 = \text{p}K_2 + \log\frac{[\text{NO}_2^+]}{[\text{H}^+]} = \text{p}K_2 + A,$$

where *A* is a function depending on the nitric acid concentration and related to the concentration of the nitronium ion.

In order to calculate I_2, let us use a formula derived from the material balance equation for the initial moment of the reaction:

$$I_2 = \frac{1 + I_1}{\dfrac{[\text{TO}]_0}{[\text{N-NTO}]} - 1}.$$

If the function *A* is appropriately prescribed, the slope of the $\log I_2$ versus *A* line will be close to unity (Fig. 4). The best results are obtained with the function H_r (slope 1.19, correlation coefficient 0.9665), whereas the $H_r + \log a_{\text{H}_2\text{O}}$ function is less appropriate (slope 0.63, correction coefficient 0.9795) [7, 8]. In the case of
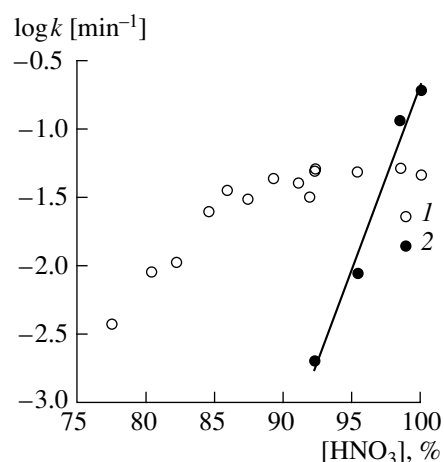
two parallel processes, the first-order rate equations appear as

$$[\text{NTO}] = [\text{TO}]_0\frac{k_3'}{k_3' + k_4'}(1 - e^{(k_3' + k_4')\tau}),$$

$$[\text{N-NTO}] = [\text{TO}]_0\frac{k_3'}{k_3' + k_4'}e^{(k_3' + k_4')\tau},$$

$$[\text{TO}]_0\frac{k_3'}{k_3' + k_4'} = [\text{NTO}]_{\text{fin}},$$

$$\frac{[\text{NTO}]_{\text{fin}}}{[\text{TO}]_0} = \omega_{\text{NTO}},$$

where ω is the NTO yield and k_3' and k_4' are the apparent rate constants of reactions (III) and (IV), respectively.

It is clear from the plots shown in Fig. 5 that the N-NTO decomposition rate exceeds the NTO formation rate at nitric acid concentrations of 98–100%. As mentioned above, as the nitric acid concentration is raised above 85%, the apparent rate constant of TO nitration stops increasing because of a rapid decrease in the concentration of TO in the form of a free base. In order to explain this result, we took into account the TO protonation and N-nitration equilibria and calculated the true rate constants k_3 and k_4 (Fig. 6)

$$\log k_3 = \log k_3' + \log(1 + I_1 + I_2),$$

$$\log k_4 = \log k_4' + \log((1 + I_1 + I_2)/I_2).$$

In this case, the first-order rate constant of TO nitration increases monotonically with an increase in the nitric acid concentration. Thus, TO nitration with nitric
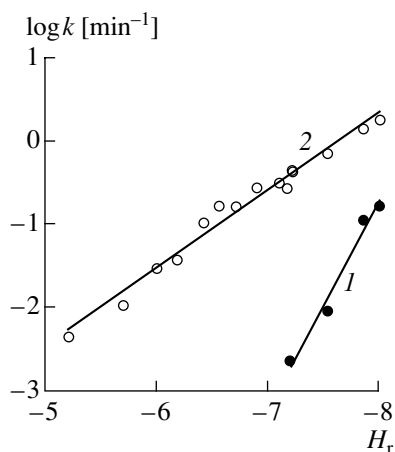
Fig. 6. True rate constants (*1*) k_3 and (*2*) k_4 versus the acidity function H_r.

mine the parameters of the Arrhenius equation (Table 2). The activation energy of N-NTO decomposition in 100% HNO_3 is higher than that of TO nitration, and this is the reason why the NTO yield decreases with increasing temperature. The activation energy of TO nitration decreases with an increase in the nitric acid concentration—a trend usual for nitration with nitric acid [8].

Thus, the nitration of TO with nitric acid is a complicated process. Both C- and N-nitro derivatives form simultaneously in the reaction system, and N-NTO is in fast equilibrium with the starting triazolone. This differentiates TO from 1,2,4-triazole and pyrazole, whose nitration with nitric acid yields no N-nitro derivatives. The kinetics of the process is substantially affected by substrate protonation. This process, along with N-nitration, are responsible for the fact that the apparent rate of NTO formation in nitric acid does not increase starting at an acid concentration of 85%.

acid involves "free" triazolone and the cessation of the increase of the apparent rate constant of the process in 85–100% nitric acid is caused by a decrease in the triazolone concentration due to equilibria (I) and (II).

Furthermore, we studied the temperature effect on TO nitration. The kinetic data obtained were used to calculate the rate constants of TO nitration and N-NTO decomposition (k_3' and k_4', respectively) and to deter-

Table 2. Parameters of the Arrhenius equation for TO nitration and decomposition

Process	HNO_3, %	A	E, kJ/mol
Nitration	77.9	1.06×10^{13}	86.0
Nitration	89.27	1.13×10^{12}	76.5
Nitration	100	2.02×10^{10}	66.8
Decomposition	100	6.89×10^{12}	78.5

REFERENCES

1. Zhilin, V.F. and Zbarskii, V.L., *Khim. Tekhnol.*, 2001, no. 5, p. 6.
2. Bershtein, I.Ya. and Kaminskii, Yu.L., *Spektrofotometricheskii analiz v organicheskoi khimii* (Spectrophotometric Analysis in Organic Chemistry), Leningrad: Khimiya, 1975.
3. Zbarskii, V.L., Kuz'min, V.V., and Yudin, N.V., *Zh. Org. Khim.*, 2004, vol. 40, no. 7, p. 1110.
4. Pevzner, M.S., *Ross. Khim. Zh.*, 1997, vol. 41, no. 2, p. 73.
5. Emmanuel', N.M. and Knorre, D.G., *Kurs khimicheskoi kinetiki* (Chemical Kinetics), Moscow: Vysshaya Shkola, 1974.
6. Katritzky, A.R. and Ögretir, C., *Chim. Acta Turcica*, 1982, vol. 10, no. 2, p. 137.
7. Belson, D.J. and Strachan, A.N., *J. Chem. Soc., Perkin Trans. 2*, 1989, p. 15.
8. Veretennikov, E.A., Lebedev, B.A., and Tselinskii, I.V., *Zh. Org. Khim.*, 2001, no. 7, p. 1016.