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KINETICS OF THE N-NITRATION OF N-NITROSO (NITROALKYL) AMINES

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The reaction of N-nitroso(nitroalky1)amines with concentrated HNO₃ is a convenient method of obtained N-nitro(nitroalky1)amines [1]. A substantial difference in the reactions of N-nitrosoamines and N-nitroamines under the action of HNO₃ and peracids has been shown [2]. According to mass-spectral analysis, in the case of HNO₃ the electrophilic replacement of a nitrosonium cation by a nitronium cation, and no oxidation reaction, takes place. In order to determine the mechanism of the reaction more accurately, we have investigated the kinetics of the N-nitration of the N-nitroso(nitroalky1) amines (I)-(V) with nitric acid according to the scheme:

 $\begin{array}{cccc} R & R & R \\ R & N-NO + HNO_3 \rightarrow & N-NO_2 \\ R & R \\ R = CH_2C(NO_2)_3 \text{ (I);} & CH_2C(NO_2)_2F \text{ (II);} & CH_2C(NO_2)_2Me \text{ (III);} & CH_2C(NO_2)_2Et \text{ (IV);} \\ CH_2C(NO_2)Me_2 \text{ (V).} \end{array}$

At the present time, the kinetics of the N-nitration of secondary aromatic amines has been studied [3, 4], but there is no information whatever on the mechanism and kinetics of the conversion of N-nitroso(nitroalkyl)amines into N-nitro(nitroalkyl)amines.

EXPERIMENTAL

As the objects of investigation we selected the following nitroalkyl-substituted Nnitrosoamines: N-nitrosobis(2,2,2-trinitroethyl)amine (I), N-nitrosobis(2-fluoro-2,2-dinitroethyl)amine (II), N-nitrosobis(2,2-dinitropropyl)amine (III), N-nitrosobis(2,2-dinitrobutyl) amine (IV), and N-nitrosobis(2-nitroisobutyl)amine (V). The initial N-nitrosoamines were obtained as described previously [1, 5] and were purified by repeated recrystallization to constant melting point. The individuality of the substances was checked by TLC. Anhydrous HNO₃ containing no oxides of nitrogen was obtained by mixing one volume of concentrated HNO₃ (d 1.51 g/cm³) and two volumes of concentrated H₂SO₄ (d 1.86 g/cm³), followed by distillation

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TABLE 1. Rate Constants of the N-Nitration of N-Nitrosobis-(2,2-dinitrobutyl)amine (k_2) at Various Temperatures with Nitric Acid in the Presence of H_2SO_4 and in CF_3COOH

Nitrating mixture	Т, °К	$k_2 \cdot 10^4$, liters/ mole \cdot sec	E, kcal/mole	A, liter/ mole • sec
HNO ₃ -H ₂ SO ₄ (20:1)	274,65 278 284	0,17 0,28 0,42	$16,25 \pm 0,97$	1,48·10 ⁸
HNO₃ (23,63 M)	288 293 298	0,61 1,04 2,01		
HNO ₃ -CF ₃ COOH	275	1,38	$15,30 \pm 1,8$	2.79·10 ⁸
HNO3 (2,65 M)	278,30 284,25 288 293 298	2,86 5,62 7,35 8,68 14,53		

in the vacuum of a water pump. Trifluoroacetic acid was purified by fractional distillation over concentrated H_2SO_4 , bp 75.4°C. Aqueous solutions of HNO_3 of the necessary concentrations were prepared by weight.

Potassium hydrogen sulfate was obtained as described by Karyakin [6]. The rate of Nnitration of the N-nitroso(nitroalkyl)amines was measured from the increase in the optical density at v 29,000 cm⁻¹ on a Specord UV-VIS spectrophotometer in a quartz cell (d 1 cm) placed in a thermostated cell-holder. The temperature in the cell was maintained with an accuracy of ±0.1°C. It was shown preparatively that during the reaction and at the end of the experiment only one nitroamine is formed, and this in quantitative yield. At the beginning of the reaction we took the moment of adding the nitrating mixture to the cell containing the nitrosoamine. The concentration of nitrosoamine in the cell was $vl.3-2.6\cdot10^{-3}$ M; the concentrations of the aqueous HNO₃ solutions varied from 8.5 to 24 M; and the concentration of HNO₃ in CF₃CO₂H was 2.65 M.

The kinetic curves of the transformation of the nitrosoamines into nitroamine in an excess of HNO₃ are very satisfactorily described by a first-order equation up to 100% conversion. The effective pseudomonomolecular rate constant k_1 was calculated from the formula $k_1t = -\ln(D_{\infty} - D) + \text{const.}$ where D and D_{∞} are the optical densities during the experiment and at the end of the reaction, and t is the time. Then the effective bimolecular rate constant for nitration was calculated: $k_2 = k_1/C_{\text{HNO}_3}$. The value of k_1 (±3%) was obtained as the arithmetic mean of several parallel determinations. The rate constants k_1 did not depend on the concentration of the initial nitrosoamine.

The temperature dependence of the rate of conversion of the nitrosoamine (IV) into Nnitrobis(2,2-dinitrobutyl)amine (VI) under the action of HNO_3 in the presence of concentrated H_2SO_4 and in CF₃COOH satisfies the Arrenhius equation (Table 1). The activation parameters were calculated by the method of least squares. The observed activation energies in the presence of concentrated H_2SO_4 and CE₃COOH are, respectively, 16.3 \pm 0.97 and 15.3 \pm 1.8 kcal/mole, and the pre-exponential factors are, respectively, 1.48·10° and 2.79·10° liters/ mole·sec.

DISCUSSION OF RESULTS

In order to understand the mechanism of the transformation of N-nitroso(nitroalkyl)amines into N-nitro(nitroalkyl)amines under the action of HNO_3 , we checked the possibility of the deprotonation of the N-nitroso(nitroalkyl)amines in the presence of concentrated acids. It is known that dialkylnitrosoamines readily split out a nitroso group with the formation of amine salts under the action of mineral acids [7]. At the same time, as was shown by special experiments, the N-nitroso(nitroalkyl)amines (II) and (III) investigated are stable to the action of concentrated H₂SO₄ even on heating. Consequently the route to the formation of Nnitro(nitroalkyl) amines through a stage of the nitration of the amine is excluded.

$$\begin{array}{c} \mathbf{R}_{2}\mathbf{NNO} \xrightarrow{\mathbf{H}^{+}} \begin{bmatrix} \mathbf{R}_{2}^{+}\mathbf{N} - \mathbf{NO} \\ \\ \mathbf{I} \\ \mathbf{H} \end{bmatrix} \xrightarrow{- \times \rightarrow} \mathbf{R}_{2}\mathbf{NH} \xrightarrow{\mathbf{NO}_{2}^{+}} \mathbf{R}_{2}\mathbf{N} - \mathbf{NO}_{2} \ . \end{array}$$



Fig. 1. Dependence of the effective bimolecular rate constants of the N-nitration of N-nitroso-(nitroalkyl) amines k_2 on the acidity function H_0 (7°C). The numbering of the curves corresponds to Table 2.

Fig. 2. Dependence of the effective monomolecular rate constant of the N-nitration of N-nitro-sobis(2-nitroisobutyl)amine (V), k_1 , on the acidity function H_0 (7°C).

At the same time, the N-nitroso(nitroalkyl)amines are inert to the action of a powerful nitrating agent — nitronium tetrafluoroborate — in organic solvents but are nitrated in the presence of HF

$$\mathbf{R_2NNO} + \mathbf{NO_2}^+ \mathbf{BF_4}^- - \underbrace{\begin{vmatrix} -\times \rightarrow \\ \mathbf{HF} \end{vmatrix}}^{-\times \rightarrow} \mathbf{R_2NNO_2}$$

These facts permit the mechanism of the N-nitration of N-nitroso(nitroalkyl)amines to be regarded as a concerted electrophilic attack of the nitronium cation at the central N atom with the nucleophilic assistance of the anion of the acid (NO_3 , HSO_4 , or CF_3COO^-). A similar hypothetical mechanism of the N-nitration of N-nitroso(nitroalkyl)amines has been proposed previously [7].

$$\begin{array}{c} R & R \\ O_{2}^{+}N\cdots N \stackrel{!}{\longrightarrow} O \cdots H N O_{3} \rightarrow O_{2}N \leftarrow \cdots N \cdots \stackrel{!}{N} \stackrel{!}{\longrightarrow} O \cdots N O_{3}^{-} \cdots H^{+} \rightarrow \\ I \\ R & I \\ O_{2}N - N R_{2} + N \stackrel{!}{O} \cdot N O_{3}^{-} + H^{+} \end{array}$$

$$(A)$$

By analogy with the mechanism of the N-nitration of aromatic amines [3] it is impossible to exclude scheme (B) of the nitration of nitrosoamines

$$\begin{array}{c} HNO_{3} + HNO_{3} \stackrel{+1}{\longleftrightarrow} H_{2}NO_{3}^{+} + NO_{3}^{-} \\ H_{2}NO_{3}^{+} \stackrel{+2}{\longleftrightarrow} NO_{2}^{+} + H_{2}O \\ R_{2}N - NO + NO_{2}^{+} \stackrel{+3}{\longleftrightarrow} R_{2}\overset{-}{N} - NO_{2} \\ NO \end{array}$$

$$\begin{array}{c} R_{2}\overset{+}{N} - NO_{2} + NO_{3}^{-} \stackrel{+4}{\longleftrightarrow} R_{2}N - NO_{2} + \overset{+}{N}ONO_{3}^{-} \\ NO \end{array}$$

$$\begin{array}{c} (B) \\ R_{2}\overset{+}{N} - NO_{2} + NO_{3}^{-} \stackrel{+4}{\longleftrightarrow} R_{2}N - NO_{2} + \overset{+}{N}ONO_{3}^{-} \\ NO \end{array}$$

where the kinetic control of the whole process may apparently be effected by stage 3 or 4, depending on the conditions of performing the reaction.

Tables 2 and 3 and Figs. 1 and 2 show the results of measurements of the rate of nitration of the nitrosoamines (I)-(V) in media of different acidities. As can be seen, the dependence of the rate of nitration on the acidity of the medium has a fairly complex nature. The

Com- pound	R	$\bigcup_{k_2}^{\infty} \downarrow_{k_2}^{k_2} \cdot 10^4,$ liter/mole \cdot sec	Com- pound	R	C _{HNO3} , M	$ k_2 \cdot 10^4,$ liter/mole · sec
(I) (II)	CH2C (NO2) 3 CH2C (NO2) 2F	24,00 2,67 23,19 1,88 22,39 1,32 21,19 0,59 20,02 Decomposition 24,00 6,47 23,19 3,16 22,39 1,54 21,19 0,56 20,02 0,023 18,50 Cessation of the reaction	(III) (IV)	CH2C (NO2) 2Me CH2C (NO2) 2Et	24,00 23,19 22,39 21,19 20,02 18,50 24,00 23,19 22,39 21,19 20,02 18,50	0,48 0,41 0,37 0 30 Mixture of products Cessation of the reaction 0,42 0,44 0,34 0,22 Mixture of products Cessation of the reaction

TABLE 2. Kinetics of the N-Nitration of N-nitroso(nitroalkyl)amines R_2N -NO in aqueous HNO₃, 7°C

TABLE 3. Kinetics of the N-Nitration of N-Nitrosobis(2nitroisobuty1)amine (V) in Aqueous HNO₃ (C, M; $k_1 \cdot 10^3 \text{ sec}^{-1}$, 7°C)

C _{HNO3}	k1	C _{HNO3}	k _i	C _{HNO3}	k_1	C _{HNO³}	k ₁	$C_{\mathbf{HNO}_{3}}$	k ₁
24	1,58	22,39	1,19	21,19	0,81	20,02	0,32	18,5	0,16

nitration of the nitrosoamines (I)-(IV) takes place with 100% conversion in nitroamines down to 90% HNO_3 (21 M), while in 85% HNO_3 (20 M) a mixture of nitrosoamines and nitroamines is formed, and in 80% HNO_3 (18 M) nitration ceases completely.

It is known that an increase in the concentration of water in a nitrating mixture gives rise to the formation by the nitric acid of an H-bond with the H_2O and the formation of solvates or the ionization of the acid with the formation of nitrate ions [8, 9], which leads to a lowering of the concentration of active acid and, consequently, to the lowering of the equilibrium concentration of the main nitrating agent — the nitronium ion — and its complete disappearance in HNO_3 with a concentration <90% [9]. The cessation of the nitration of the nitrosoamine (I)-(IV) in HNO_3 with a concentration <20 M shows that it is precisely the nitronium cation that is the active nitrating particle with respect to N-nitroso(nitroalky1)amines. The unexpectedly high values of the rate constants for the nitration of (V) are apparently connected with a change in the mechanis of the N-nitration of (V) as compared with (I)-(IV), which is due to the difference in their electronic structures [10]. It is known that the correlation of the rate constants of C-nitration of aromatic compounds with the acidity function H_R or (H_R + log $a_{\rm H_2O}$) serves as a criterion of a mechanism with the participation of the nitronium cation in the rate-limiting stage - the stage of the formation of the intermediate complex - while the dependence of the effective second-order rate constant (k2) on the acidity of the medium in plots of log k_2 ($H_R + \log a_{H_2O}$) or of log k_2 versus H_R should be linear with a slope equal to -1 [11, 12]. Unfortunately, there is no information on the magnitude of the function HR for the concentrated solutions of HNO3 that we have considered, and therefore we investigated the dependence of the nitration rate constant k_2 on the acidity function H_o [13]. On the basis of results in the literature [12, 14], it was assumed that the angle of slope of the straight line in plots of log k_2 versus H_0 should be equal to or somewhat greater than -1.

As can be seen from Figs. 1 and 2, the dependence of the effective rate constants for the nitration of the nitrosoamines (I)-(V) on the acidity of the medium H₀ is linear. The angle of slope for (II) amounts to -1, for (I) it is somewhat less than -1, for (III) and (IV) it is -(0.25-0.34), and for (V) it is -0.8. It follows from Fig. 1 that the nitration rate constants of (I) and (II) depend to a high degree on the acidity of the medium and (III) and (IV) are nitrated at approximately the same rates in the range of acidity studied. These facts indi-



Fig. 3. Dependence of the effective bimolecular rate constants of the N-nitration of the N-nitroso(nitroalkyl)amines (I)-(III) by 90% HNO₃ on Taft's induction constants (7°C).

Fig. 4. Dependence of the rate of N-nitration of N-nitrosobis(2,2-dinitrobutyl)amine (IV) by HNO_3 (24 M) on the concentration of $KHSO_4$ (7°C). k_0 and k_1 are the nitration constants without the additive and in the presence of the additive, respectively.

cate that the rate of N-nitration of N-nitroso(nitroalkyl)amines rises more slowly with an increase in the acidity of the medium than the rate of C-nitration of aromatic compounds, which is in harmony with the results of an investigation of the N-nitration of secondary aromatic amines [4]. The low values of the angle of slope in plots of log k_2 versus H₀ may also mean that the rate-limiting stage of the N-nitration of N-nitroso(nitroalkyl)amines is not the stage of the addition of the nitronium cation (stage 3 in Scheme B) but stage 4 — the splitting out of a nitrosonium ion.

It can be seen from Tables 2 and 3 that the structure of the nitrosamine had a substantial influence on the rate of N-nitration. Nitrosoamines (I) and (II), containing powerful electron-accepting substituents, nitrated at similar rates, while nitrosoamines (III) and (IV), possessing almost the same structure nitrated at practically the same rates. The passage from (II) to (IV) lowered the rate of N-nitration in 100% HNO₃ 15-fold.

Attention is merited by the completely satisfactory linear dependence of the rate constants of the N-nitration of (I) and (III) on Taft's induction constants σ^* (Table 4 and Fig. 3), although because of the limited amount of experimental material no correlation analysis was performed and the value of σ^* was not calculated. Thus, the rate of N-nitration of N-nitroso(nitroalky1)amines rises with an increase in the electron-accepting properties of the substituent R.

To elucidate the possibility of the participation of the base (HSO₄) in the rate-limiting stage, we investigated the influence of added potassium hydrogen sulfate on the rate of nitration of (IV) in 100% HNO₃ (Table 5 and Fig. 4). It follows from Table 4 and Fig. 4 that with an increase in the concentration of KHSO₄ the rate constant of the nitration of (IV) fell linearly.

These results apparently cannot give an unambiguous answer to the question of the participation of the anion in the rate-limiting stage. It is known that additions of salts and of H_2O and H_2SO_4 affect the rate of N-nitration, changing both the acidity of the medium and the concentration of nitrating agent [16], and therefore an investigation of the independent influence of the concentration of the base is difficult.

A comparison of the rates of N-nitration of (IV) at various temperatures by HNO_3 in the

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TABLE 4. Quantitative Evaluation of the Influence of Substituents (σ *) on the Rate of N-Nitration of the N-Nitroso(nitro-alky1)amines (I)-(III) in 90% HNO₃, 7°C

R	σ*	$k_2 \cdot 10^4$, liters/ mole \cdot sec	- 10g k ₂
G (NO ₂) ₃	4,54 [15]	0,59	$\begin{array}{c} 4,2291 \\ 4,2518 \\ 4,6575 \end{array}$
C (NO ₂) ₂ F	4,38 ^a	0,56	
C (NO ₂) ₂ Me	2,76 [15]	0,22	

^aCalculated on the additivity principle.

TABLE 5. Influence of the Addition of KHSO₄ on the Rate of N-Nitration of N-Nitrosobis(2,2-dinitrobutyl)amino (k_1) in 100% HNO₃

C _{KHSO4} . 10 ²	k ₁ .104	$C_{\mathrm{KHSO_4}}$.10	$k_1 \cdot 10^4$	C _{KHSO4} .10	$k_1 \cdot 10^4$
0	10,30	0,69	9,93	1,14	7,38
C _{KHSO4} .10 ²	k1·104	C_{KHSO_4} . 10 ²	k1.104	C _{KHSO4} •10 ³	k1.104
2,29	5,01	3,44	2,62	4,59 -	1,41

presence of concentrated H_2SO_4 ($C_{\rm HNO_3} = 23.63$ M) and in CF_3COOH (see Table 1) shows that in the latter case nitration takes place with higher rates and lower concentrations of HNO_3 (2.65 M).

The kinetic results obtained do not permit an unambiguous conclusion to be drawn between the schemes of the N-nitration of N-nitroso(nitroalkyl)amines proposed above, but they do not contradict them. It is clear that the structure of the nitrosoamine has a substantial influence on the mechanism of N-nitration. It is known that the structure of nitrosoamines is described by the resonance forms [17]

$$\begin{array}{c} R_2 N - N = O \leftrightarrow R_2 N = N - O^- \\ (a) & (b) \end{array}$$

Electron-accepting substituents R increase the contribution of structure (a), and electrondonating substituents that of structure (b).

The nitrosoamines (I) and (II), having structure (a), must react more readily with the nitronium cation and more readily split out the nitroso group. In fact, (I) and (II) take part in the N-nitration reaction faster, as follows from the dependence of the rate constant of the magnitude σ^* . The fact that the dependences of the rate constant of N-nitration (k₂) on the acidity of the medium H₀ have slopes in no case exceeding -1, shows that both the attack of the substrate by the nitronium ion and also the splitting out of the nitroso group from the transition complex make a contribution to the rate-limiting stage of the reaction. At the same time, for (I) and (II) the slopes of the above-mentioned relations are greater for (III) and (IV), and therefore for three substrates the relative contribution of the attack of the nitronium ion is also greater and the relative contribution of the splitting out of the nitroso group is less.

SUMMARY

1. The kinetics of the conversion of a series of N-nitroso(nitroalkyl)amines into Nnitro(nitroalkyl)amines under the action of concentrated solutions of HNO₃ have been studied and the activation parameters have been determined.

2. The dependences of the rate constants on these reactions on the acidity of the

medium and on Taft's induction constants have been investigated.

3. A proposed mechanism has been given of the transformation of N-nitroso(nitroalkyl)amines into N-nitro(nitroalkyl)amines under the action of HNO₃.

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RELATIVE KINETICS IN THE TELOMERIZATION OF PROPYLENE WITH CC14

INITIATED BY COORDINATION INITIATORS BASED ON Cr(CO) 6

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In the telomerization of propylene with CCl₄ initiated by systems based on $Fe(CO)_5$ [1] nucleophilic additives (DMFA, i-CH₃H₇OH, CH₃OH) accelerate the transfer of a chlorine atom from CCl₄ to the growing telomer radicals and substantially increase the content of adduct in the reaction mixture. Acetonitrile, for which the donor properties are low, had no effect on the distribution of telomer homologs.

In a continuation of the study into the effect of the nature of metal carbonyls on the course of telomerization we have investigated the telomerization of propylene with CCl₄ initiated by $Cr(CO)_6$ in conjunction with HMPA, DMFA, CH₃OH, and CH₃CN in order to estimate by the method of relative kinetics the effect of nucleophilic additives on chlorine atom transfer in this reaction.

EXPERIMENTAL

GLC analysis was conducted with an LKhM-8MD instrument in a stream of He (6 liters/h) with a Katharometer, a steel column 2000 \times 3 mm containing 15% SKTFT-50 on Chromaton N-AW. The analysis temperature for the experiments in which HMPA, CH₃CN, and CH₃OH were present was 150°C; in the presence of DMFA the temperature programming was from 100 to 160°C (8 deg/min). The reactions were conducted with sealed glass 4-ml ampuls. The experimental procedure was

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