

KINETICS AND MECHANISM OF PRODUCT FORMATION
IN THERMAL DECOMPOSITION OF TETRAPHENYLHYDRAZINE

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Tetraphenylhydrazine (TPH) is a labile compound that decomposes upon heating to form active diphenylaminyl radicals $\text{Ph}_2\text{N}^\cdot$ [1]. The stable products from the decomposition of TPH in inert solvents (boiling toluene [2], chlorobenzene [3]) are diphenylamine (DPA) and oligomeric semidines $\text{Ph}_2\text{N}[-\text{C}_6\text{H}_4-\text{NPh}]_{i-2}-\text{C}_6\text{H}_4-\text{NH}-\text{Ph}$. The mechanism of their formation is discussed in [3-5], but this mechanism is based solely on the composition of the final reaction products, without any supporting kinetic data. Mechanistic studies of this reaction are of particular interest for the theory of inhibited oxidation, since the primary product from decomposition of TPH, the $\text{Ph}_2\text{N}^\cdot$, is also the primary product in the conversion of diphenylamine when that amine is used as an antioxidant [6].

Formal kinetic relationships in the decomposition of TPH in inert solvents were set forth in [7]. The present work has been aimed at studying the kinetics of accumulation of TPH decomposition products when there is no acceptor of the $\text{Ph}_2\text{N}^\cdot$ radicals, and at comparing the results that are obtained with the hypothetical mechanism of their formation that has been suggested in the literature.

EXPERIMENTAL

The decomposition of TPH was studied at $348 \pm 0.15^\circ\text{K}$ in CCl_4 and n-heptadecane in an argon atmosphere. The reaction mixture was analyzed by means of liquid chromatography and IR spectrophotometry [7]. The reaction products were identified on the basis of the sequence of their elution from the chromatographic column [3] and the UV absorption spectra [2]. The DPA concentrations were determined from the IR spectra on the basis of the intensity of the band at 3432 cm^{-1} (νNH). The ebullioscopic measurements were performed in an ÉP-68 instrument.

DISCUSSION OF RESULTS

Regardless of the degree of reaction, the only products from the TPH decomposition in any of the experiments were DPA and o- and p-semidines (o- and p- In_iH , where i is the number of $\text{Ph}_2\text{N}^\cdot$ radicals going into

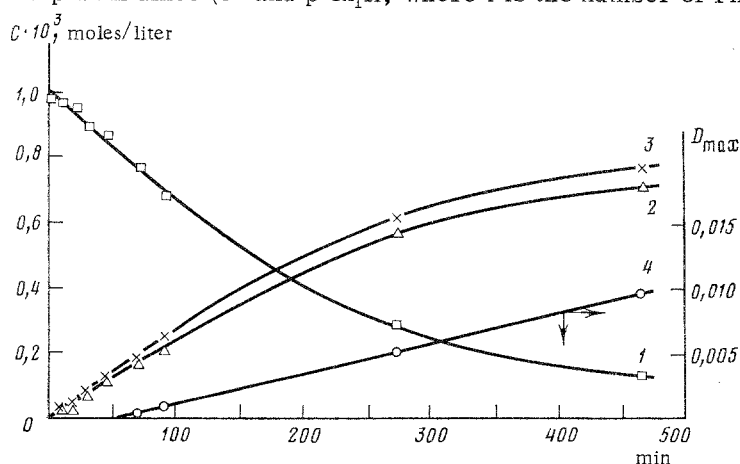


Fig. 1. Kinetic curves for decomposition of TPH (1), accumulation of DPA (curve 2 for chromatographic analysis, curve 3 for IR analysis), and accumulation of p-semidine dimer (4). Heights of chromatographic peaks are given in optical density units with detection at $\lambda = 285 \text{ nm}$. Decomposition reaction was carried out in CCl_4 solvent with $[\text{TPH}]_0 = 1 \cdot 10^{-3} \text{ mole/liter}$.

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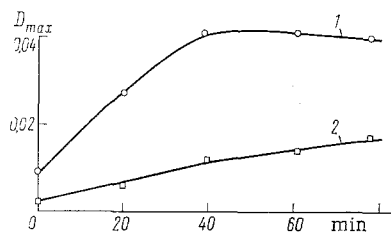


Fig. 2. Formation of o-semidine dimer (1) and o-semidine oligomers (2) in TPH decomposition, expressed in units of optical density at maximum of chromatographic peak with detection at $\lambda = 260$ nm. Decomposition reaction was carried out in CCl_4 solvent with $[\text{TPH}]_0 = 5 \cdot 10^{-3}$ mole/liter.

the formation of one molecule of the semidine). Thus, the qualitative composition of the products does not change whether the TPH is decomposed in boiling chlorobenzene or toluene, under which conditions the reaction is completed in a few minutes, or in CCl_4 or $n\text{-C}_{17}\text{H}_{36}$ at lower temperatures, such that the TPH decomposition extends over a period of hours. From the kinetic curves for the product accumulation (Figs. 1 and 2), it can be seen that the DPA and o-semidines ($i \geq 2$) are the primary reaction products, but the p-semidine dimer (p- In_2H) begins to be accumulated only after a certain time. It can also be seen from Fig. 1 that the DPA accumulation curve plotted from the chromatographic data does not coincide with the curve plotted from the IR data. This divergence is observed from the very start of the reaction, and it is explained by the parallel formation of DPA and semidines (the semidines also have an NH bond, and this leads to fictitiously high values from the IR analysis for DPA). The yield of DPA relative to the TPH decomposed is always less than 50%; the yield does not change with increasing degree of reaction, and it is independent of the initial TPH concentration (Table 1). In the presence of diphenyl ether (DPE), the DPA yield is lower; the decomposition of TPH in $n\text{-C}_{17}\text{H}_{36}$ gives a higher yield of DPA. If the TPH decomposition is carried out in the presence of DPA, the yield of DPA is much lower, but the yield gradually increases with increasing degree of reaction (Table 1 and Fig. 3). Thus, even though the medium does not influence the qualitative composition of the TPH decomposition products, the quantitative ratios among the products do change when the solvent is changed; a similar relationship was observed in [8] for the formation of products from the recombination of N-phenyl-2-naphthyl-aminyl radicals.

Starting from the product composition, we can write for any moment of time t the following balance equations with respect to the Ph_2N fragments and H atoms:

$$2([\text{TPH}]_0 - [\text{TPH}]_t) = [\text{DPA}]_t + \sum_{i=2}^{\max} i[o-, p\text{-In}_i\text{H}] \quad (1)$$

$$[\text{DPA}]_t = \sum_{i=2}^{\max} (i - 2)[o-, p\text{-In}_i\text{H}] \quad (2)$$

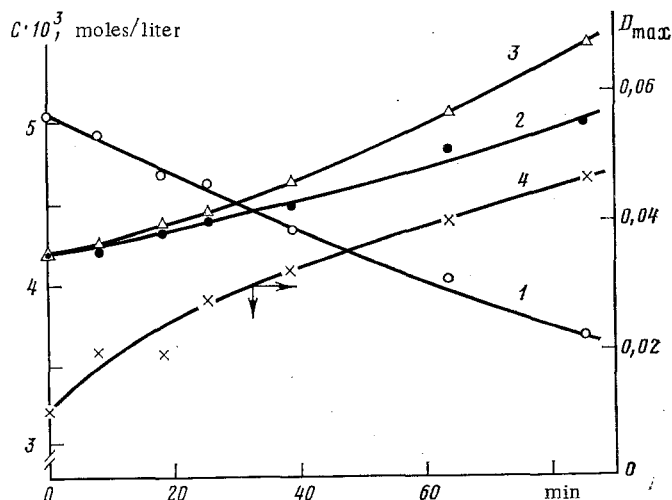


Fig. 3. Decomposition of TPH ($[\text{TPH}]_0 = 5 \cdot 10^{-3}$ mole/liter) in the presence of DPA ($4.21 \cdot 10^{-3}$ mole/liter): 1) consumption of TPH; 2, 3) accumulation of DPA as determined by chromatography and IR analysis, respectively; 4) accumulation of p-semidine dimer (height of chromatographic peak, detection at $\lambda = 285$ nm).

TABLE I. DPA Yield on TPH Decomposed, as Influenced by the Medium and the Degree of Reaction at 348°K, and Calculated Average Degree of Polymerization \bar{P}_n of Semidines Formed*

CCl ₄											
$[\text{TPH}]_0 = 1 \cdot 10^{-3}$		$[\text{TPH}]_0 = 5 \cdot 10^{-3}$		$[\text{TPH}]_0 = 5 \cdot 10^{-3}$, $[\text{DPE}]_0 = 4.2 \cdot 10^{-3}$		$[\text{TPH}]_0 = 5 \cdot 10^{-3}$, $[\text{DPE}]_0 = 0.79$		$[\text{TPH}]_0 = 5 \cdot 10^{-3}$, $[\text{DPA}]_0 = 4.2 \cdot 10^{-3}$		$[\text{TPH}]_0 = 1 \cdot 10^{-3}$	
I	II	I	II	I	II	I	II	I	II	I	II
0.598	0.0294	0.785	0.11	0.497	0.038	0.372	0.080	0.386	0.023	0.83	0.088
0.620	0.0982	0.772	0.118	0.595	0.0877	0.720	0.112	0.371	0.076	0.864	0.140
4.006	0.116	0.812	0.32	0.596	0.139	0.571	0.224	0.429	0.0815	0.929	0.184
0.744	0.218	0.798	0.428	0.601	0.175	0.558	0.335	0.415	0.139	0.897	0.252
0.675	0.309			0.642	0.473			0.602	0.199	0.894	0.322
0.824	0.707							0.591	0.270	0.834	0.398
0.845	0.863									0.832	0.476
Average 0.76±0.12		Average 0.79±0.02		Average 0.57±0.05		Average 0.62±0.07		Average 0.58 at $t = (\dots)$		Average 0.87±0.04	
$\bar{P}_n = 5.17 \pm 1.70$		$\bar{P}_n = 5.76 \pm 0.29$		$\bar{P}_n = 3.33 \pm 0.58$		$\bar{P}_n = 3.63 \pm 0.82$		$\bar{P}_n = 2.51 \pm 0.14$		$\bar{P}_n = 8.69 \pm 0.80$	

* Values in column I are for the molar yield of DPA, equal to $[\text{DPA}]_t / \Delta[\text{TPH}]_t$; values in column II are for the degree of reaction, $\Delta[\text{TPH}]_t / [\text{TPH}]_0$.

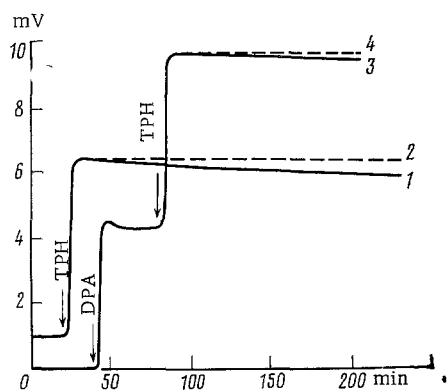


Fig. 4. Ebullioscopic curves for change of \bar{M}_n in TPH decomposition ($[\text{TPH}]_0 = 4.78 \cdot 10^{-3}$ mole/liter) in CCl_4 : 1) experimental curve; 2) theoretical calculation. Experimental (3) and theoretical (4) curves for the change in \bar{M}_n in experiments with DPA added at start of experiment ($[\text{TPH}]_0 = 4.89 \cdot 10^{-3}$ mole/liter, $[\text{DPA}]_0 = 4.08 \cdot 10^{-3}$ mole/liter; CCl_4). Arrows indicate moment of injection.

It follows from (2) that the formation of one molecule of the semidine (o- or p- In_iH) is accompanied by the formation of $(i-2)$ molecules of DPA; e. i., the DPA yield depends on the degree of polymerization of the semidines that are formed. After combining (1) and (2), we have

$$\Delta [\text{TPH}]_t = [\text{TPH}]_0 - [\text{TPH}]_t = [\text{DPA}]_t + \sum_{i=2}^{\max} [o-, p-\text{In}_i\text{H}] \quad (3)$$

Differentiating (3) with respect to time, we obtain

$$v^{\text{TPH}} = v^{\text{DPA}} + \sum_{i=2}^{\max} v^{\text{In}_i\text{H}}$$

from which it follows that $v^{\text{TPH}} > v^{\text{DPA}}$, since $\sum_{i=2}^{\max} v^{\text{In}_i\text{H}} > 0$ (see Figs. 1 and 2). This means that the DPA

yield relative to the TPH decomposed is always less than 50%, and this is in full agreement with data reported in [2, 3] and our data. It also follows from (3) that the decomposition of TPH under these particular conditions is not accompanied by any change in the number of particles in the system. This conclusion can be further supported by direct calculation; it is found that during the course of the process, the number-average molecular weight $\bar{M}_n = \text{const} = 2M$, where M is the molecular weight of the Ph_2N fragment. The results from the ebullioscopic experiments (Fig. 4) generally confirm the correctness of this conclusion. The main reason for the slight increase in \bar{M}_n is apparently the association of the highly polar p-semidines, leading to a decrease in the effective number of particles in the system (the decomposition of TPH in boiling toluene leads also to precipitation of p-semidines [3]). Further evidence in favor of this hypothesis can be found in the ebulliogram for the decomposition of TPH in the presence of DPA (Fig. 4); the change in \bar{M}_n is substantially smaller in this case. It will be shown below that in the presence of DPA, semidines with shorter chains are formed, with polarities substantially lower than the long-chain semidines [3].

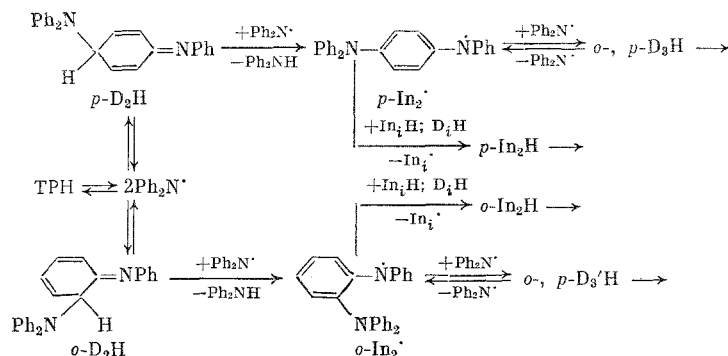
The results we have obtained, i. e., the lack of any change in the number of particles, the constancy of the DPA yield relative to TPH decomposed during the course of the reaction (Table 1), and the relationship between the DPA yield and the degree of polymerization of the semidines as indicated in Eq. (2), provide grounds for the conclusion that the average degree of polymerization \bar{P}_n of all the semidines that are formed remains unchanged in the course of the TPH decomposition. If we assume in calculating \bar{P}_n that the reaction proceeds with the formation of DPA and a semidine with an average degree of polymerization \bar{P}_n , and if we

then set up the expression for $\bar{M}_n = M_{\text{TPH}} = \text{const} = \sum_i M_i n_i / \sum_i n_i$ and use Eqs. (1)-(3), we obtain $\bar{P}_n = 2 + \alpha /$

$(1 - \alpha)$, where $\alpha = [\text{DPA}]_t / \Delta[\text{TPH}]_t$ is the molar yield of DPA relative to TPH decomposed. It can be seen from Table 1 that the values of \bar{P}_n vary from 2.6 to 8.7, depending on the conditions of experiment. The values of \bar{P}_n that we have calculated are close to the experimental values given in [2].

A correlation of the data of [3-5, 7-10] makes it possible to formulate the following mechanism for the formation of products in the thermal decomposition of TPH. Spontaneous decomposition of the TPH molecule forms two $\text{Ph}_2\text{N}^\cdot$ radicals, which, owing to the high spin density on the N atom and in the p- and o-positions

of the benzene rings, recombine with each other in the bulk to form both the original TPH (N-N bond) and unstable molecules with the iminoquinolide structure *o*-, *p*-D₂H (C-N bond). The new radical abstracts an H atom from the *o*-, *p*-D₂H, forming DPA and a radical of the semidine *o*-, *p*-In₂'. The latter can then abstract an H atom from any hydrogen atom donor, being converted to the stable semidine molecule *o*-, *p*-In₂H, or it can react with the Ph₂N' radicals that are constantly being generated, forming a new iminoquinolide structure *o*-, *p*-D₃H. The process is then repeated.

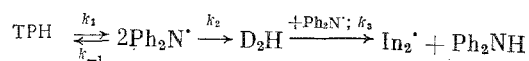


According to such a scheme, the sole path for DPA formation in the initial stages is the reaction of the Ph₂N' radical with labile molecules of *o*-, *p*-D₂H. The primary stable products of TPH decomposition in these stages should be DPA and long-chain semidines *o*-, *p*-In₂H (under conditions of constant generation of Ph₂N' radicals and the lack of a sufficient quantity of hydrogen donors). According to Eq. (2), this means that the DPA yield should drop off as the reaction progresses, and this is contradictory to experiment. Also inconsistent with these views is the curve for accumulation of the *o*-semidine dimer (Fig. 2), which, in contrast to the *p*-isomer, is a primary product of the TPH decomposition. These inconsistencies can be eliminated, while staying within the framework of the scheme under consideration, only on the assumption that the *o*-D₂H is rearranged to the corresponding *o*-In₂H for the most part intramolecularly. Since the *o*-semidines are formed in substantially smaller quantities than the *p*-isomers [3], the particular features of the *o*-semidine formation have little influence on the character of accumulation of DPA (the primary stable product of the reaction) and *p*-semidines.

The kinetics of DPA accumulation can be used to evaluate the rate constant for reaction of the Ph₂N' radical with unstable D_iH molecules. When TPH is prepared by the commonly accepted method [11], we found that it contains oligomeric *p*-semidines as impurities (THF purity ≤ 97%), and these are H atom donors.

In order to obtain the required purity (99.8%), the TPH was purified by rapid passage of a TPH solution in acetone through a column with silica gel, after which the TPH was recrystallized at 205°K (the operation was repeated three times). When this purified TPH was used, the accumulation of DPA (CCl₄, [TPH]₀ = 1.10⁻³ mole/liter) began at τ ≈ 30 sec after the start of the experiment, with v₀^{DPA} = 0.77 v₀^{TPH}.

According to the scheme under consideration, at such a degree of reaction, the DPA is formed solely through the interaction of Ph₂N' with the D₂H molecules that had accumulated during the induction period τ,



Let us assume that in the course of the induction period τ ≈ 30 sec, all of the TPH that is decomposed is converted to D₂H and that v_{demp}^{D₂H} ≈ v_{demp}^{TPH}; then, [D₂H]_τ ≈ k₂^{TPH} / k_{demp}^{TPH} [TPH]₀τ. The rate of TPH decomposition v_{demp}^{TPH} = k_{demp}^{TPH} [TPH]₀ = k₁ [TPH]₀ - k₋₁ [Ph₂N']², whence, in the initial reaction period, [Ph₂N'] = (k₁ - k_{demp}^{TPH})^{1/2} [TPH]₀^{1/2} · k₋₁^{-1/2}. Using for k₁ and k_{demp}^{TPH} the respective values 15 · 10⁻⁵ and 6.2 · 10⁻⁵ sec⁻¹ [7], we have

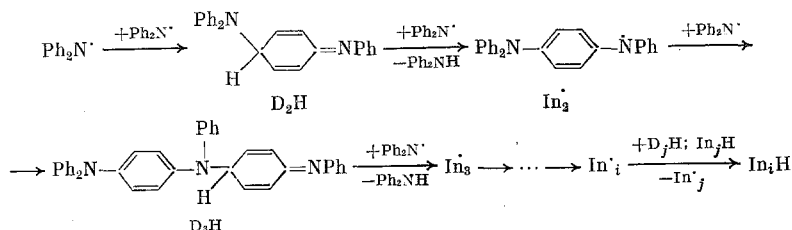
$$k_3 \sim \frac{v_0^{\text{DPA}}}{[\text{D}_2\text{H}]_\tau [\text{Ph}_2\text{N}']} = \frac{0.77 \sqrt{k_{-1}}}{\tau \sqrt{[\text{TPH}]_0 (k_1 - k_{\text{demp}}^{\text{TPH}})}} \approx 0.8 \cdot 10^2 \sqrt{k_{-1}}$$

The value of k₋₁ is unknown, but we can assume that it is close to the value of the rate constant of a diffusion-controlled reaction (~ 10⁹ liters/mole · sec). An indication in favor of this assumption is the extremely low concentration of Ph₂N' radicals in the decomposition of TPH, which cannot be determined even by means of

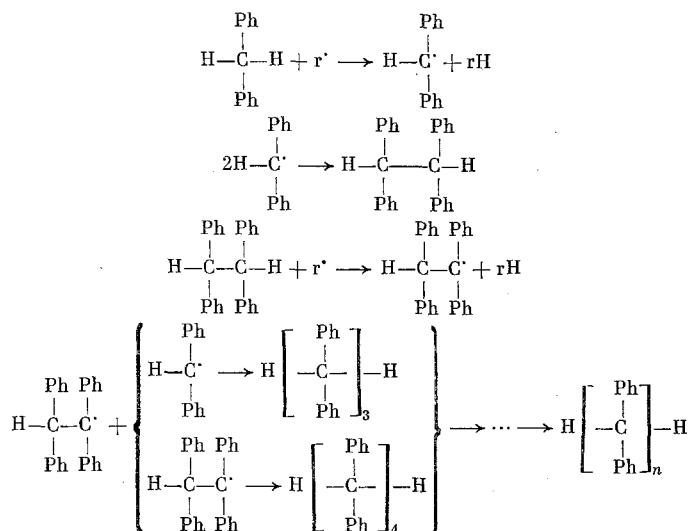
ESR [9]. Whence, we obtain $k_3 \approx 10^6$ liters/mole·sec. We should emphasize that this value is only a very rough estimate. Nonetheless, the estimate of k_3 that we have obtained does indicate a very high activity of the iminoquinolidine structures as H atom donors; such activity of quinolide structures has been observed for carbon* radicals [8, 12].

Thus, the mechanism that has been proposed in the literature for the formation of products from the thermal decomposition of TPH in inert solvents, when we factor in the additional possibility of intramolecular isomerization of $o\text{-D}_1\text{H}$ to $o\text{-In}_1\text{H}$, does not contradict the kinetic data we have obtained, on the assumption of a very high activity of iminoquinolide structures as H-atom donors.

The accumulation of p-semidine oligomers proceeds as follows:



The mechanism of formation of the p-semidines has general features in common with the mechanism of polyrecombination polymerization [13]; this can be illustrated in the example of polymer formation from diphenylmethane under the influence of a peroxide (source of primary radicals r^\cdot):



However, the product from the recombination of $p\text{-In}_1^\cdot$ with $\text{Ph}_2\text{N}^\cdot$ is not a stable compound that might be isolated in the individual state, but rather a labile molecule D_{i+1}H with the iminoquinolide structure. Correspondingly, the polymerization of diphenylaminyl radicals can be termed an intermediate polyrecombination polymerization. The recombination of the In_1^\cdot radicals with the $\text{Ph}_2\text{N}^\cdot$ is concluded with the formation of not a bifunctional compound but rather a monofunctional compound D_{i+1}H with a single mobile H atom. It is also important that each act of recombination of the growing radical In_1^\cdot with a $\text{Ph}_2\text{N}^\cdot$ radical is accompanied by regeneration of this mobile H atom. Thus, in the decomposition of TPH in inert solvents, there is a polymerization of diphenylaminyl radicals that proceeds as a new type of recombination polymerization.

The author wishes to express his thanks to E. T. Denisov for valuable advice in the writing of this article.

CONCLUSIONS

1. The stable products from the decomposition of tetraphenylhydrazine in inert solvents at 348–400°K are diphenylamine and a mixture of *o*- and *p*-semidine oligomers. The diphenylamine yield depends on the medium, but is no greater than 50% of the tetraphenylhydrazine decomposed.

2. The formation of stable reaction products is preceded by a stage of formation of labile intermediates with the iminoquinolide structure as a result of recombination of aminyl radicals.

*As in Russian original; possibly a misprint for "hydrocarbon" — Translator.

3. o-Semidines are formed as a result of intramolecular rearrangement of the corresponding o-iminoquinolide structures.

4. p-Semidines and diphenylamine are the products of intermediate polyrecombination polymerization with the participation of aminyl radicals and iminoquinolide structures.

LITERATURE CITED

1. H. Wieland, *Liebigs Ann. Chem.*, **381**, 200 (1911).
2. H. Musso, *Chem. Ber.*, **92**, 2881 (1959).
3. P. Welzel, *Chem. Ber.*, **103**, 1318 (1970).
4. P. Welzel, L. Günther and G. Eckhardt, *Chem. Ber.*, **107**, 3624 (1974).
5. P. Welzel, Ch. Dietz, and G. Eckhardt, *Chem. Ber.*, **108**, 3550 (1975).
6. N. M. Emanuel, E. T. Denisov, and Z. K. Maizus, *Liquid-Phase Oxidation of Hydrocarbons*, Plenum Press, New York (1967).
7. V. T. Varlamov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1629 (1982).
8. R. F. Bridger, *J. Am. Chem. Soc.*, **94**, 3124 (1972).
9. F. A. Neugebauer and St. Bamberger, *Chem. Ber.*, **107**, 2362 (1974).
10. F. A. Neugebauer, H. Fischer, St. Bamberger, and H. O. Smith, *Chem. Ber.*, **105**, 2694 (1972).
11. L. Gatterman and H. Wieland, *Practical Studies in Organic Chemistry [Russian translation]*, NKhTI VSNKh SSR, Leningrad (1930), p. 263.
12. J. A. Kampmeier, R. P. Geer, A. J. Meskin, and R. M. D'Silva, *J. Am. Chem. Soc.*, **88**, 1257 (1966).
13. V. V. Korshak, S. L. Sosin, and M. M. Chistyakova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1271 (1957).

KINETICS OF N-NITRATION OF N-(NITROSO)- NITROALKYLAMINES BY CONCENTRATED DNO₃

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The present work represents a continuation of a study of the kinetics of N-nitration of N-(nitroso)nitroalkylamines by concentrated HNO₃ [1]; in the present work, we investigated the kinetics of N-nitration of certain N-(nitroso)nitroalkylamines by concentrated DNO₃ with the aim of refining the mechanism of their conversion to N-(nitro)nitroalkylamines and elucidating the role of the proton in the limiting stage of the reaction.

As objects of investigation we selected bis(2,2,2-trinitroethyl)-N-nitrosoamine (I), bis(2-fluoro-2,2-dinitroethyl)-N-nitrosoamine (II), bis(2,2-dinitropropyl)-N-nitrosoamine (III), bis(2,2-dinitrobutyl)-N-nitrosoamine (IV), and bis(2-nitroisobutyl)-N-nitrosoamine (V).

EXPERIMENTAL

The compounds to be nitrated were synthesized and purified as described in [1-3]. The individuality of the compounds was confirmed by means of TLC. Anhydrous DNO₃, free of nitrogen oxides, was obtained by mixing 1 volume of 98.5% DNO₃ (content of isotope 98.8%) and 2 volumes of 99% D₂SO₄ (content of isotope 99.7%), with subsequent distillation under vacuum from a water-jet aspirator. The course of the reaction was followed on the basis of the change in the UV spectrum as determined in a Specord UV-VIS spectrophotometer. The reaction was carried out in a quartz cuvette (d 1 cm) mounted in a thermostated cuvette holder. The reaction kinetics were observed on the basis of the increase in optical density at $\nu = 30,000 \text{ cm}^{-1}$. It was shown preparatively that during the course of the reaction and at the end of the experiment, the nitramine is formed quantitatively. The concentration of the nitrosoamine in the optical cuvette was $1.3-2.6 \cdot 10^3$ mmoles/liter; the DNO₃ concentration was 24 moles/liter. The kinetic curves for the conversion of the N-nitrosoamines to N-nitroamines

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