THERMAL DECOMPOSITION RATE OF TETRAPHENYLHYDRAZINE IN INERT SOLVENTS

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When tetraphenylhydrazine (TPH) is heated, it decomposes to diphenylaminyl radicals [1]. The decomposition rate of TPH in the presence of acceptors of $Ph_2N^{\cdot}$ radicals was studied in [2-4]. Since TPH is frequently used as a source of $Ph_2N^{\cdot}$ radicals [5], it is necessary to know the decomposition rate of TPH under conditions where the acceptance of these radicals is absent. The kinetic rules for the decomposition of TPH in inert solvents, like CCl_4 and n-heptadecane, were studied in the present paper.

EXPERIMENTAL

The crystalline TPH was synthesized by the oxidation of diphenylamine (DPA) with $KMnO_4$ in acetone [6]. The CCl_4 (very pure) was purified by passage through an Al_2O_3 column and subsequent distillation in argon. The diphenyl ether (DPE) and DPA were recrystallized from hexane (208°C) and toluene, respectively.

The decomposition of TPH was studied at 348 ± 0.15°K in glass ampul reactors in an argon atmosphere. The chromatographic analysis for THP was run on a 30 × 0.8 cm glass column packed with silica gel (Chemapol, 65 ± 5 μ). Ether–hexane mixtures were used as the eluant. The eluate escaping from the column passed through a continuous-flow cell (40 μl), which was mounted in the cell assembly of an SFD-2 spectrophotometer that was connected to an automatic recorder. The eluate was collected in suspended receivers, the volume of the escaping zone was determined (based on the density of the eluant) and the UV absorption spectra were recorded on a Specord UV-VIS instrument (the cell thickness was varied from 10 to 40 mm). The analysis error was ±3%. When the [TPH] exceeded 0.005 mole/liter, the analysis was run on a Specord 75 IR spectrophotometer, using for this the intensity of the narrow band at 599 cm^{-1}, and here the analysis error was ±5%.

DISCUSSION OF RESULTS

The TPH decomposition rate is described by the rule for a first-order reaction (Fig. 1)., and the constant for the decomposition rate in CCl_4 is independent of the initial TPH concentration in the range $(1-50)\cdot 10^{-3}$ mole/liter. The decomposition of TPH is somewhat more rapid in $n\text{-}C_{17}H_{36}$ than in CCl_4, and the decomposition is also accelerated in the presence of DPE; the addition of DPA to the starting system has no effect on the TPH decomposition rate (Table 1). The decomposition of TPH in either n-heptadecane or CCl_4 in the presence of DPE is not accompanied by the formation of the amine $Ph_2N-C_{17}H_{35}$ or by the consumption of DPE (shown by

TABLE 1. Dependence of k and k_2/k_{-1} on the Medium, Initial TPH Concentration, and Presence of Acceptors of Diphenylaminyl Radicals (348°K)

Medium	Additive	$[TPH]_0$	$k\cdot 10^5$, sec^{-1}	k_2/k_{-1}
	mole/liter			
CCl_4	—	$1\cdot 10^{-3}$	6,36±0,95	0,75
CCl_4	—	$5\cdot 10^{-3}$	5,90±0,77	0,66
CCl_4	—	$4{,}90\cdot 10^{-2}$	6,60±0,58	0,78
CCl_4	$[DPE]_0 = 4{,}21\cdot 10^{-3}$	$5\cdot 10^{-3}$	7,01±0,33	0,90
CCl_4	$[DPE]_0 = 0{,}79$	$5\cdot 10^{-3}$	7,91±0,77	1,15
CCl_4	$[DPA]_0 = 4{,}21\cdot 10^{-3}$	$5\cdot 10^{-3}$	6,22±0,53	0,72
$n\text{-}C_{17}H_{36}$	—	$1\cdot 10^{-3}$	8,64±0,35	1,40
CCl_4	$[\text{Neozone-D}]_0 = 4{,}0\cdot 10^{-3}$	$5\cdot 10^{-3}$	14,8±0,37	
C_6H_6	$[\text{DPPH-H}]_0 = (5-50)\cdot 10^{-4}$	$1\cdot 10^{-4}$	15,0 [2]	
$C_6H_5CH_3$	$[\text{DPPH-H}]_0 = (1{,}9-12)\cdot 10^{-4}$	$(1-3)\cdot 10^{-4}$	20,05 [3]	
$o\text{-}C_6H_4Cl_2$	NO; $p_{NO} = 0{,}1-1$ atm	$(2-4{,}5)\cdot 10^{-2}$	20 [4]	

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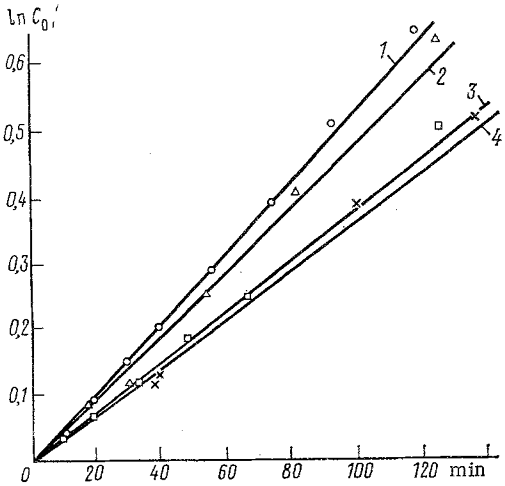

Fig. 1. Kinetic curves for consumption of TPH in inert solvents at 348°K in semilogarithmic coordinates: 1) heptadecane, $[TPH]_0=1\cdot10^{-3}$ mole/liter; 2) DPE (0.79 mole/liter) in CCl_4, $[TPH]_0=5\cdot10^{-3}$ mole/liter; 3) CCl_4, $[TPH]_0=4.90\cdot10^{-2}$ mole/liter; 4) CCl_4, $[TPH]_0=5\cdot10^{-3}$ mole/liter.

chromatography), and hence it follows that reaction between the $Ph_2N^{\cdot}$ radical and these compounds is absent at 348°K.

The addition of a free-radical acceptor to the solution greatly accelerates the TPH decomposition; for example, the addition of 0.004 mole/liter of N-phenyl-2-naphthylamine (Neozone D) increases the decomposition rate constant (k) up to $14.8\cdot10^{-5}$ instead of $6.3\cdot10^{-5}$ sec^{-1} without the acceptor (see Table 1). Apparently, a part of the $Ph_2N^{\cdot}$ radicals recombines with the formation of TPH, while the addition of an acceptor of these radicals prevents the recombination, which also accelerates the TPH decomposition. As a first approximation the decomposition of TPH in inert solvents can be depicted by the following scheme:

$$Ph_2NNPh_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2Ph_2N^{\cdot} \xrightarrow{k_2} \text{Products}$$

According to this scheme, the experimentally measured rate constant for the decomposition of TPH is $k=k_1k_2/(k_{-1}+k_2)$, from which can be found the ratio $k_2/k_{-1}=k(k_1-k)$. In the calculations it is assumed that $k_1=15\cdot10^{-5}$ sec^{-1} (see Table 1). This value was obtained in the presence of a radical acceptor, where the recombination of the $Ph_2N^{\cdot}$ radicals is suppressed. The k_2/k_{-1} values are given in Table 1, from which it can be seen that these constants are commensurate. The k_2 value should be regarded as being an empirical characteristic for the consumption of the $Ph_2N^{\cdot}$ radicals by various reactions, except recombination with the formation of TPH.

The obtained kinetic data are not in agreement with the concepts of the induced decomposition of TPH [7]. It can be shown that if the decomposition of TPH proceeds by the mechanism of radical substitution on the N atom [7], while destruction of the radicals proceeds via their squared recombination, then the initial decomposition rate should depend in the following manner on the initial TPH concentration:

$$v_0^{TPH} \simeq k_3 \sqrt{\frac{k_1}{k_{-1}}} [TPH]_0^{3/2}$$

where k_3 refers to the reaction $TPH+Ph_2N^{\cdot} \rightarrow Ph_2N^{\cdot}+\text{products}$.

Our data show that $v_0^{TPH} \sim [TPH]_0$. In addition, in induced decomposition the addition of an acceptor of $Ph_2N^{\cdot}$ radicals should lower the TPH decomposition rate, whereas the opposite effect is observed experimentally (see Table 1).

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CONCLUSIONS

The decomposition of tetraphenylhydrazine in inert media at 348°K proceeds not as an induced, but instead as a pseudomonomolecular process, with decomposition rate constants of $6.3 \cdot 10^{-5}$ and $8.6 \cdot 10^{-5}$ sec^{-1} in CCl_4 and n-heptadecane, respectively.

LITERATURE CITED

1. H. Wieland, Ann. Chem., 381, 200 (1911).
2. F. Tyudesh and M. Azori, Acta Chim. Acad. Sci. Hung., 34, 61 (1962).
3. L. A. Zhivechkova, B. S. Tanaseichuk, and A. Yu. Ermishov, Zh. Org. Khim., 7, 2397 (1971).
4. C. K. Cain and F. Y. Wiselogle, J. Am. Chem. Soc., 62, 1163 (1940).
5. M. Ya. Meskina, G. V. Karpukhina, and Z. K. Maizus, Izv. Akad. Nauk SSSR, Ser. Khim., 1974, 1755.
6. L. Gatterman and H. Wieland, Laboratory Guide in Organic Chemistry [Russian translation], NKhTIVSNKh SSR, Leningrad (1930), p. 263.
7. J. Hollaender, W. P. Neumann, and H. Lind, Chem. Ber., 106, 2395 (1973)

REACTION OF FORMALDEHYDE WITH HYDROGEN SULFIDE

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The reaction of formaldehyde with H_2S has received little study. Patent data mainly exist, in which it is indicated that polymethylene sulfide is formed in 92-98% yield [1, 2].

We found that the rate of the uncatalyzed reaction of formaldehyde with H_2S is very close to that of the reaction that proceeds in the presence of an alkaline catalyst (Fig. 1), with a substantial difference in the yield of the polymer (16 and 83%, respectively). This can be explained by the participation of the intermediate compounds in the reaction and their subsequent catalytic conversion to polymethylene sulfide. To verify this assumption, we isolated and studied the products of the uncatalyzed reaction of CH_2O with H_2S. The treatment of an H_2S-saturated solution of CH_2O with ether gave dimercapto sulfide and a high yield of formthional, while the reaction of a saturated CH_2O solution with amines gave a complex mixture of aminomethyl derivatives, on the basis of whose formation it could be judged that oligosulfides with $-(-CH_2SCH_2SCH_2-)-$ and $-(-CH_2SCH_2 \cdot OCH_2SCH_2-)-$fragments also take part in the reaction.

To ascertain the characteristics of the reaction, we studied the polycondensation of formthional. H_2S is not liberated when formthional is condensed in the presence of NaSH, but the concentration of the mercapto groups in solution steadily decreases, with a constant increase in the yield of the insoluble polymethylene sulfide (amount of S = 65.3 wt. %). H_2S is also absent in both the gas phase and the reaction mass when the condensation is run as a melt (120°, 5-10 h), but the liberation of water was observed, the amount of which was inversely proportional to the concentration of the thiyl groups. The presented data permit proposing the following scheme for the reaction of formaldehyde with hydrogen sulfide:

$$CH_2O + H_2S \rightarrow HOCH_2SH \rightarrow HOCH_2SCH_2SH \quad (1)$$

$$n\,HOCH_2SCH_2SH \xrightarrow{\text{cat}} n\,H_2O + {\sim}({\sim}CH_2S{\sim}){\sim}_n \quad (2)$$

A kinetic study of the polycondensation of formthional disclosed a linear relationship between the initial reaction rate and the formthional concentration (Fig. 2, line 1), which testifies that the reaction is first order in monomer. The relation between the reaction rate and the concentration of OH^- ions is also linear (see Fig. 2, line 2), which indicates that the reaction is first order in catalyst.

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