2. It has been shown that the phosphinocarborane complexes of rhodium(I) have high activities in the hydrogenation and isomerization of olefins and diolefins.

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REACTIONS OF ORGANIC HYDROTRIOXIDES WITH TERTIARY AMINES

V. V. Shereshovets, L. A. Bachanova,
U. M. Dzhemilev, V. D. Komissarov,
and G. A. Tolstikov

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Low-temperature (−80 to −40°C) ozonization of aldehydes, ethers, acetals, alcohols, and alkylaromatic hydrocarbons leads to the corresponding hydrotrioxides ROOOH [1-4]. It was shown in [5, 6] that ROOOH reacts with secondary and tertiary amines. In the present work, the catalytic effect of amines on the decomposition of hydrotrioxides has been discovered, and the kinetic regularities of this process have been investigated.

EXPERIMENTAL

Hydrotrioxides of 2-propanol $Me_2C(OH)OOOH$ (I), benzaldehyde $PhC(O)OOOH$ (II), diisopropyl ether $Me_2CH(O)C(OOOH)Me_2$ (III), and 1,1-diethoxyethane $MeC(OEt)_2OOOH$ (IV) were prepared and analyzed according to [1-4].

Oxidation of Tertiary Amines R_3N into the Corresponding N-Oxides. The required amount of R_3N was added at −55°C in an argon atmosphere to a freshly prepared solution of $\sim 5 \cdot 10^{-3}$– $5 \cdot 10^{-2}$ moles of (I), and the mixture was left to stand for 12 h at −55°C. To separate the reaction mixture, the solution was passed through a column with Al_2O_3 (100 g per g of amine), using a benzene–methanol mixture in the required ratio as the eluent.

The Kinetics of Decomposition of ROOOH in Presence of Amines was studied by the chemiluminescence method (CL) in the temperature range of −30 to +3°C [7]. A solution of hydrotrioxide ([ROOOH] $\sim 10^{-2}$–10^{-1} mole/liter) was placed in a ~ 50-ml thermostated reactor containing R_3N in 2-propanol, diisopropyl ether, 1,1-diethoxyethane, or benzaldehyde in an Ar atmosphere, and the CL attenuation was recorded. In some experiments, the decomposition kinetics of ROOOH was studied by the PMR method according to [1-4]. The two methods for studying the decomposition kinetics of ROOOH lead to the same results.

The purification of 2-propanol, diisopropyl ether, 1,1-diethoxyethane, benzaldehyde, benzene, and methanol is described in [8, 9]. Triethylamine (V), pyridine (VI), 2-methyl- (VII), 3-methyl- (VIII), 4-methyl- (IX), 2-bromo- (X), 2,6-dimethylpyridine (XI), and quinoline (XII) were purified by the methods in [9, 10].

Compounds (VI), (X), (XII) were analyzed by the GLC method (flame ionization detector). Compounds (X) and (XII) were analyzed on a column ($\ell = 1$ m, $d = 3.5$ mm) with SE-30 at 50-230°C); in the case of (VI) the column ($\ell = 3.7$ m, $d = 3.5$ mm) was filled with 15% Carbowax on Chromaton N-AW, at an analysis temperature of 120°C. The pyridine N-oxide content in

TABLE 1. Decomposition of $Me_2C(OH)OOOH$ in the Presence of Pyridine, 2-Bromopyridine, Quinoline (solvent 2-propanol, 0°C)

$[ROOOH]_0 \cdot 10^2$	$[R_3N]_0 \cdot 10^2$	$\Delta[R_3N] \cdot 10^2$	$[ROOOH]_0/[R_3N]_0$	$\Delta[ROOOH]*/\Delta[R_3N]$
mole/liter			mole/mole	
Pyridine				
60,0	71,0	20,0 †	0,84	3,0
17,1	2,4	0	7,1	–
18,0	0,85	0	21,2	–
26,0	0,42	0	61,9	–
2-Bromopyridine				
33,7	132,9	42,2	0,25	0,80
34,3	27,4	1,3	1,6	26,4
Quinoline				
30,8	7,3	1,9	4,22	16,2
34,8	4,2	0,8	8,3	43,5
39,5	1,3	0,30	30,4	132

*$\Delta ROOOH = [ROOOH]_0$.
†—55°C. The yield of pyridine N-oxide isolated was 0.21 mole/liter.

the oxidate was determined by IR spectroscopy after prelminary distillation of the decomposition products of (I). The measurements were carried out on a UR-20 spectrophotometer at ~ 1250 cm^{-1}, cuvette thickness 0.037 mm, $\varepsilon = 198$ liter/mole·cm.

DISCUSSION OF RESULTS

As noted in [5], tertiary amines react with ROOOH and convert into the corresponding N-oxides. The latter were identified by IR spectroscopy by the presence of a characteristic band in the 1250 cm^{-1} region, and by comparison with known samples. The boiling and melting points found in the present work for pyridine-, 2-methylpyridine-, and 2,6-dimethylpyridine-1-oxides are equal to 138-140 (15 mm) and 66°C; 127 (12 mm) and 91°C; 115-118°C (18 mm), respectively, and agree well with the data in [11].

The yield of N-oxide based on ROOOH ($\Delta[R_3NO]/[ROOOH]_0$) depends on the substrate:oxidizing agent ratio $[R_3N]_0/[ROOOH]_0$ ($[R_3N]_0$ and $[ROOOH]_0$ are the initial concentrations of the amine and hydrotrioxide). In oxidation of (VI) by (I) (−55°C), $\Delta[R_3NO]/[ROOOH]_0 = 0.17, 0.38, 0.55$ mole/mole for $[R_3N]_0/[ROOOH]_0 = 2.06, 18.35, 20.00$ mole/mole. The yield of N-oxide based on amine is quantitative (Table 1). It was also found that $\Delta[R_3NO]/[ROOOH]_0$ depends on the structure of the amine: $\Delta[R_3NO]/[ROOOH]_0 = 0.40, 0.26, 0.14$ mole/mole for the reaction of (I) with (VI), (VII), (XI) ($\Delta[R_3N]_0/[ROOOH]_0 \approx 6.0$ mole/mole, −55°C).

Data are given in Table 1 on the stoichiometry of the process ($\Delta ROOOH/\Delta R_3N$) for the decomposition of (I) in the presence of (VI), (X), (XII); it is seen that $\Delta ROOOH/\Delta R_3N > 1$ and increases with increase in the $[ROOOH]_0/\Delta[R_3N]_6$ ratio. It can be assumed that in the presence of amines there is a catalytic decomposition of ROOOH. The conclusion on the catalytic character of the process also follows from the data on the kinetic experiments carried out at $[ROOOH]_0 \gg [R_3N]_0$ for (V)-(IX), (XII); in the case of (VI) (−26°C) and (X), the conditions $[ROOOH]_0 \ll [R_3N]_0$ were used. It was found that in the case of excess of both hydrotrioxide and amine, the kinetics of consumption of ROOOH is described by a first-order equation with a rate constant k' (Fig. 1). Table 2 gives the k' values for decomposition of (I) on addition of different amines: k' increases in the presence of R_3N. A similar effect is observed on addition of (V) and (VI) to $PhC(O)OOOH$. For example, the rate constant of the decomposition of (II) in the absence of R_3N is equal to $8.58 \cdot 10^{-4}$ sec^{-1} (0°C). In the presence of (V) ($4.1 \cdot 10^{-3}$ mole/liter) and (VI) ($4.2 \cdot 10^{-3}$ mole/liter) (II) decomposes with a rate constant of $14.8 \cdot 10^{-3}$ and $4.3 \cdot 10^{-3}$ sec^{-1}, respectively. It is interesting to note that the addition of up to $4.5-26 \cdot 10^{-3}$ mole/liter of (VI) does not have any accelerating effect on the decomposition of $Me_2C(OOOH)OCHMe_2$ (0°C) and $MeC(OOOH)(OEt)_2$ (−30°C).

Analysis of the experimental data shows that the dependence of k' on the R_3N concentration is described by an empirical equation (Fig. 2)
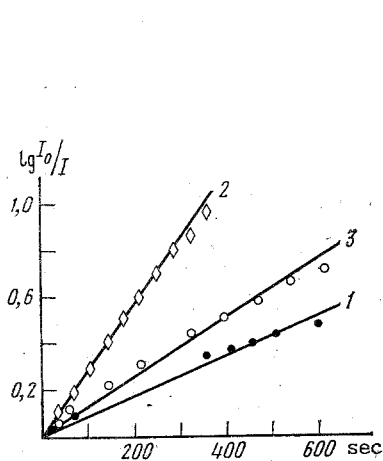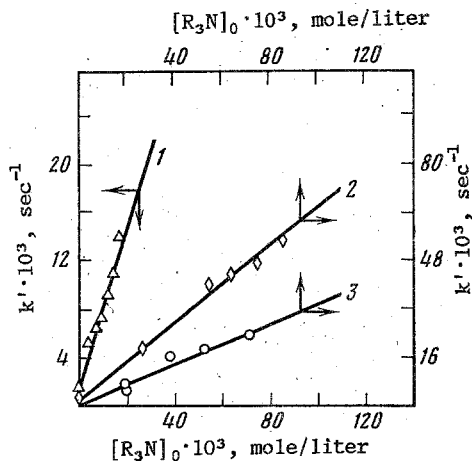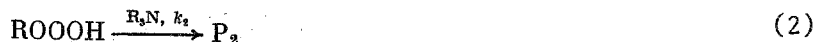
Fig. 1. Kinetics of CL attenuation during the decomposition of 2-propanol hydrotrioxide ($-2 \pm 1°C$): 1) in absence of R_3N, $[ROOOH]_0 = 8.3 \cdot 10^{-2}$ mole/liter; 2) in presence of pyridine $[R_3N] = 7.5 \cdot 10^{-3}$, $[ROOOH]_0 = 27 \cdot 10^{-2}$ mole/liter; 3) in presence of 3-bromopyridine, $[R_3N] = 2.19$, $[ROOOH]_0 = 25 \cdot 10^{-2}$ mole/liter.

Fig. 2. Dependence of effective first-order rate constant k' on the amine concentration in the decomposition reaction of $Me_2C(OH)OOOH$ in the presence of pyridine: 1) $-1°C$, $[ROOOH]_0 = 0.1$ mole/liter; 2) $-14°C$, $[ROOOH]_0 = 0.1$ mole/liter; 3) $-26°C$, $[ROOOH]_0 = 0.001$ mole/liter.

$$k' = a + b\,[R_3N]_0$$

where a and b are constant values at given temperature. The values of a, b are given in Table 2. From the temperature dependence of k' for the decomposition of (I) in the presence of (VI), it was found that: $\log a = (7.93 + 1.80) - (13{,}400 \pm 1100)/\theta$; $\log b = (12.60 \pm 1.10) - (15{,}900 \pm 2000)/\theta$, where $\theta = 2.303\ RT$ cal/mole.

The catalytic decomposition of the peroxide compounds by the action of amines apparently proceeds by a complex mechanism [12-15]. On the other hand, the principal paths of the ROOOH and amine consumption can be described by a simple scheme

$$ROOOH \xrightarrow{k_1} P_1 \tag{1}$$

$$ROOOH \xrightarrow{R_3N,\ k_2} P_2 \tag{2}$$

$$ROOOH + R_3N \xrightarrow{k_3} R_3N \rightarrow O \tag{3}$$

where P_1, P_2 are products of thermal and catalytic decomposition of ROOOH; k_1-k_3 are rate constants of the corresponding net stages.

According to the above scheme, the rate of consumption of ROOOH is described by the expression

$$-d[ROOOH]/dt = k'[ROOOH]$$

where

$$k' = k_1 + (k_2 + k_3)\,[R_3N]_0$$

At $k_1 = a$, $(k_2 + k_3) = b$, the last expression coincides with the empirically derived expression for the rate of consumption of ROOOH.

As already mentioned, in experiments with low R_3N concentrations there is practically no consumption of amine and no formation of N-oxide under these conditions. It follows from the experiments that $k_2 \gg k_3$, and hence

$$k' = k_1 + k_2\,[R_3N]_0$$

TABLE 2. Kinetic Data for Decomposition of $Me_2C(OH)OOOH$ in the Presence of Amines

T, °C	$[R_3N]_0 \cdot 10^3$, mole/liter	$k' \cdot 10^3$, c⁻¹	a^*, c⁻¹	b^*, liter/mole·sec
		Pyridine		
-1 ± 1	0	1,45	$1{,}45 \cdot 10^{-3}$	0,69
	3,8	5,24		
	7,5	6,39		
	10,0	7,19		
	12,6	9,21		
	15,1	10,94		
	17,6	14,0		
		Pyridine		
-26 ± 2	0	0,177	$1{,}17 \cdot 10^{-4}$	0,03
	18,9	7,67		
	380	16,40		
	520,8	17,97		
	710,2	23,52		
		2-Methylpyridine		
-2 ± 1	0	1,32	$1{,}32 \cdot 10^{-3}$	0,93
	5,4	8,96		
	11,0	12,30		
	23,0	21,30		
		2-Bromopyridine		
-2 ± 1	0	1,32	$1{,}32 \cdot 10^{-3}$	$0{,}5 \cdot 10^{-3}$
	21,70	0,69		
	508,00	1,28		
	2190	2,92		
	29400	2,74		

T, °C	$[R_3N]_0 \cdot 10^3$, mole/liter	$k' \cdot 10^3$, c⁻¹	a^*, c⁻¹	b^*, liter/mole·sec
		Pyridine		
-14 ± 1	0	0,447	$4{,}17 \cdot 10^{-4}$	0,16
	26,5	4,72		
	36,0	7,84		
	45,5	12,79		
	55,0	9,71		
	64,6	10,65		
	74,8	11,98		
	85,7	13,69		
		3-Methylpyridine		
-2 ± 1	0	1,32	$1{,}32 \cdot 10^{-3}$	0,95
	3,75	6,60		
	7,49	11,50		
	11,20	12,50		
	14,98	12,80		
	18,73	19,50		
		4-Methylpyridine		
-1 ± 1	0	1,45	$1{,}45 \cdot 10^{-3}$	1,34
	4,15	12,30		
	10,80	18,70		
	16,62	24,00		
	24,93	35,10		
		Quinoline		
-2 ± 1	0	1,32	$1{,}32 \cdot 10^{-3}$	0,33
	15,00	6,72		
	31,00	10,70		
	47,60	18,40		

*At $[R_3N]_0 = 0$, $k' = a = k_1$. If $[R_3N]_0 \ll [ROOOH]_0$, we have $b = k_2$.

Fig. 3. Influence of pK_a of amine on decomposition of $Me_2C(OH)OOOH$ at $-2 \pm 1°C$: a) pyridine; b) 2-methylpyridine; 3) 3-methylpyridine; d) 4-methylpyridine; e) 2-bromopyridine; f) quinoline. The pK_a values for (VI)-(XIII) were taken from [16].

This equation can be used to determine separately the rate constant of the thermal k_1 and catalytic k_2 decomposition of ROOOH (see Table 2). It is interesting to note that an almost linear dependence is observed between log b and pK_a of amines (Fig. 3); increase in the basicity of R_3N increases the rate of catalytic decomposition of ROOOH. Thus the low yields of N-oxides during oxidation of R_3N by ROOOH can be explained by the fact that besides the consumption of ROOOH in the oxidation reaction, there are other paths of its transformation. With increase in the basicity of R_3N, the rate constant of the catalytic process increases, with simultaneous decrease in the yield of the corresponding N-oxide.

CONCLUSIONS

1. The catalytic effect of tertiary amines on the decomposition of hydrotrioxides was discovered using $Me_2C(OH)OOOH$ and $PhC(O)OOOH$ as examples.

2. Increase in the basicity of the amine intensifies its catalytic effect on the decomposition of hydrotrioxides.

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