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Kinetics of the Decomposition of α-Phenylethyl Hydroperoxide in the Presence of *N*,*N*,*N*',*N*'-Tetramethyl-*para*-Phenylenediamine

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Abstract—It is found that the tertiary amine *N*,*N*,*N*',*N*'-tetramethyl-*para*-phenylenediamine (TMPD) causes the decomposition of α-phenylethyl hydroperoxide (ROOH), and the interaction between the components occurs in accordance with a complicated rate law. It is demonstrated that more than 30 hydroperoxide molecules (n) can be degraded at a molecule of TMPD; this fact suggests that the amine has a catalytic effect on the process. The value of n increases with the $[ROOH]_0/[TMPD]_0$ ratio. The initial rates of consumption of ROOH and TMPD linearly increase with the initial concentrations of both of the reactants. The apparent rate constant of the reaction is $k = 0.4\ l\ mol^{-1}\ s^{-1}$ (393 K), as calculated from the initial rates of ROOH consumption. As a result of the interaction, TMPD is converted into an inhibitor. The rate constant of the reaction of this inhibitor with ethylbenzene peroxy radicals is about $2 \times 10^4\ l\ mol^{-1}\ s^{-1}$.

INTRODUCTION

Aromatic amines are widely used as antioxidants. Among them, secondary *N*,*N*'-substituted *para*-phenylenediamines are the most effective antioxidants [1, 2]. In accordance with the well-known mechanisms of the action of inhibitors [3], tertiary amines from this series would not be expected to exhibit inhibiting activity because the molecules of these compounds do not contain a hydrogen atom in the amino group. However, it was found experimentally that *N*,*N*,*N*',*N*'-tetraalkyl-substituted *para*-phenylenediamines inhibited the processes of the low-temperature [4] and high-temperature degenerated branched oxidation of hydrocarbons, and they were effective components of synergetic antioxidant mixtures under these conditions [5]. To study the mechanism of inhibition, we examined the reaction of *N*,*N*,*N*',*N*'-tetramethyl-*para*-phenylenediamine (TMPD) with α-phenylethyl hydroperoxide, which is the primary ethylbenzene oxidation product responsible for chain branching.

EXPERIMENTAL

The decomposition of α-phenylethyl hydroperoxide was studied at 333 and 393 K in an argon atmosphere. The hydroperoxide (ROOH) was prepared by the oxidation of ethylbenzene with oxygen at 393 K in the presence of azobisisobutyronitrile (AIBN) additives for 3.5 h. Ethylbenzene or a mixture of ethylbenzene with chlorobenzene was used as a solvent. The concentrations of ROOH and TMPD and the ratio between the components of the ethylbenzene–chlorobenzene mixture were varied in the experiments.

The concentration of ROOH was determined by iodometric titration. The kinetics of TMPD consumption was monitored by measuring a decrease in the absorbance of the Wurster cation generated from TMPD in the absorption spectra [6]. The spectra of a test sample in solution containing acetic acid were recorded after a fixed exposure time. The concentration of TMPD was calculated using a calibration line obtained under the same conditions.

To evaluate the inhibiting effect of the reaction products of ROOH with TMPD, we used a model reaction of ethylbenzene oxidation initiated by AIBN (333 K). Before measurements, ethylbenzene with the dissolved initiator was thermostated; then, the reaction mixture was added in a 10% amount based on the total solution volume.

RESULTS AND DISCUSSION

The thermal decomposition of α-phenylethyl hydroperoxide at 393 K occurs with the rate constant $k = 6.7 \times 10^{-6}\ s^{-1}$ [7]. At this value of the rate constant, the hydroperoxide concentration in an inert gas atmosphere decreased by no more than 5% in a reaction time equal to 120 min (Fig. 1, dashed line). The additives of TMPD resulted in the detectable consumption of ROOH (Fig. 1). The initial rate of ROOH consumption (w_{ROOH}), which was calculated from data shown in Fig. 1, increased in direct proportion to an increase in the initial concentrations of both of the reactants (Fig. 2, straight line *1* and Table 1).

In the course of reaction, the consumption of the tertiary amine occurred along with the decomposition of the hydroperoxide. The initial rate of TMPD consumption (w_{TMPD}) was also proportional to the product of the initial concentrations of the hydroperoxide and TMPD (Fig. 2, straight line *2*).

On the assumption of a 1 : 1 reaction stoichiometry, it would be expected that the initial rates of consump-

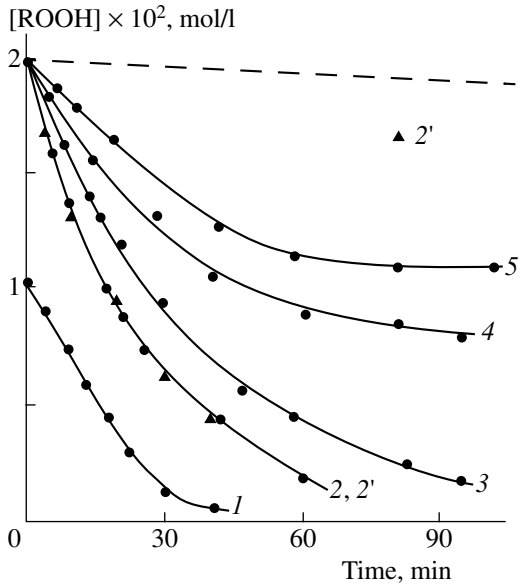

Fig. 1. Kinetic curves of ROOH consumption at $[TMPD]_0$, mol/l: (*1*, *2*) 2×10^{-3}, (*3*) 1×10^{-3}, (*4*) 5.6×10^{-4}, and (*5*) 2.7×10^{-4}. (*2'*) The same as *2* but with the addition of ionol (2×10^{-3} mol/l). T = 393 K; argon; chlorobenzene–ethylbenzene, 2 : 1. The dashed line indicates the thermal decomposition of ROOH, 393 K.

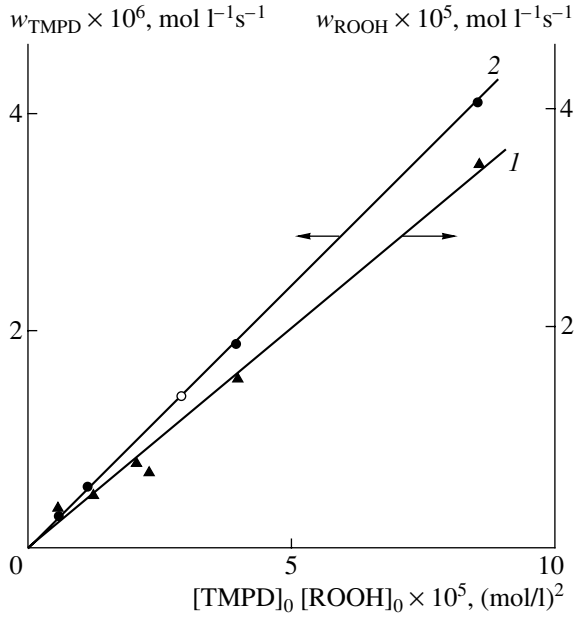

Fig. 2. Dependence of the initial rates of consumption of (*1*) ROOH and (*2*) TMPD on the product $[TMPD]_0 [ROOH]_0$. T = 393 K; argon; chlorobenzene–ethylbenzene, 2 : 1. An open circle in straight line *2* corresponds to w_{TMPD} in an experiment performed in oxygen.

tion of the reactants would be equal, and a decrease in the concentration of ROOH, which was taken in an excess, would be equal to a decrease in the initial concentration of TMPD, which was taken in a deficiency. However, an analysis of the reaction kinetics of ROOH decomposition under the action of TMPD demonstrated that the reaction mechanism is more complicated. Thus, the initial rates of ROOH and TMPD consumption (Table 1) differed by almost one order of magnitude. This suggests that several ROOH molecules underwent decomposition at one molecule of TMPD. Depending on the ratio between the initial concentrations of the hydroperoxide and TMPD (Fig. 1), either ROOH was almost completely decomposed (curves *1–3*) or the reaction was stopped (curves *4*, *5*). In the latter case, the concentration of TMPD was close to zero by the point in time after which the concentration of ROOH remained unchanged.

With the use of data shown in Fig. 1 (curves *4*, *5*) and experimental data obtained at the initial reactant concentrations $[ROOH]_0 = 4.3 \times 10^{-2}$ mol/l and $[TMPD]_0 = 2 \times 10^{-3}$ mol/l, we calculated the total number of hydroperoxide molecules degraded at one TMPD molecule ($n = \Delta[ROOH]/[TMPD]_0$, where $\Delta[ROOH]$ is a decrease in the hydroperoxide concentration during the experiment time). As can be seen in Table 2, the value of n depends on the initial concentrations of the reactants and increases with the $[ROOH]_0/[TMPD]_0$ ratio.

The apparent rate constant of ROOH decomposition in the reaction with TMPD is $k = 0.4$ l mol^{-1} s^{-1} (393 K), as calculated from data in Fig. 2 (straight line *1*). The estimated activation energy (E_a) is close to 75 kJ/mol.

For comparison, the secondary aromatic amine *N*,*N*'-di-β-naphthyl-*para*-phenylenediamine (like TMPD, it also belongs to *para*-phenylenediamine derivatives) reacts with *tert*-butyl hydroperoxide in chlorobenzene with a rate constant similar to that obtained in this work and equal to $k = 0.42$ l mol^{-1} s^{-1} (395 K); $E_a = 41.8$ kJ/mol [8]. Secondary and primary aromatic amines (diphenylamine and α-naphthylamine, respectively) having one amino group react with hydroperoxides with much lower

Table 1. Initial rates of consumption of ROOH and TMPD at various initial reactant concentrations

$[TMPD]_0 \times 10^3$, mol/l	0.27	0.56	1.0	2.0	2.0	2.0
$[ROOH]_0 \times 10^2$, mol/l	2.0	2.0	2.0	1.05	2.0	4.3
$w_{ROOH} \times 10^5$, mol l^{-1} s^{-1}	0.3	0.49	0.67	0.55	1.5	3.5
$w_{TMPD} \times 10^6$, mol l^{-1} s^{-1}	0.29	0.52	–	–	1.8	4.1

Note: Argon; 393 K; chlorobenzene–ethylbenzene, 2 : 1.

Table 2. Total number (n) of hydroperoxide molecules degraded at one molecule of TMPD at various initial concentrations of TMPD and ROOH

$[ROOH]_0 \times 10^2$, mol/l	$[TMPD]_0 \times 10^3$, mol/l	$[ROOH]_0/[TMPD]_0$	$\Delta[ROOH] \times 10^2$, mol/l	n
2.0	0.27	74.1	0.9	35.1
2.0	0.56	35.7	1.2	21.4
4.3	2	21.5	2.1	15.5

Note: Argon; 393 K.

rate constants than in the case of *para*-phenylenediamine derivatives. Thus, the rate constant of the reaction of diphenylamine with α-phenylethyl hydroperoxide is $k = 1.6 \times 10^{-4}$ l mol^{-1} s^{-1} (393 K) [9], whereas the rate constant of the reaction of α-naphthylamine with cumyl hydroperoxide is 4.2×10^{-4} l mol^{-1} s^{-1} (393 K) and E_a = 53.1 kJ/mol [10].

In special experiments, we found that a change in the solvent composition from pure ethylbenzene to an ethylbenzene–chlorobenzene mixture (1 : 2) had almost no effect on the initial rate of ROOH consumption.

It is well known that the reactions of amines with peroxides are of a chain character in a number of cases [11]. For eliminating such a mechanism from the reaction of TMPD with ROOH, we considered the effect of 2,6-di-*tert*-butyl-4-methylphenol (ionol), which is an inhibitor of free-radical reactions, on the rate of the reaction. We found that the kinetic curves of both TMPD consumption and hydroperoxide decomposition catalyzed by the tertiary amine in the presence (Fig. 1, curve 2') and in the absence (Fig. 1, curve *2*) of ionol were practically coincident. This result suggests that the process is a nonchain reaction, unlike, for example, the reaction of *N*,*N*'-dimethylaniline with benzoyl peroxide [11].

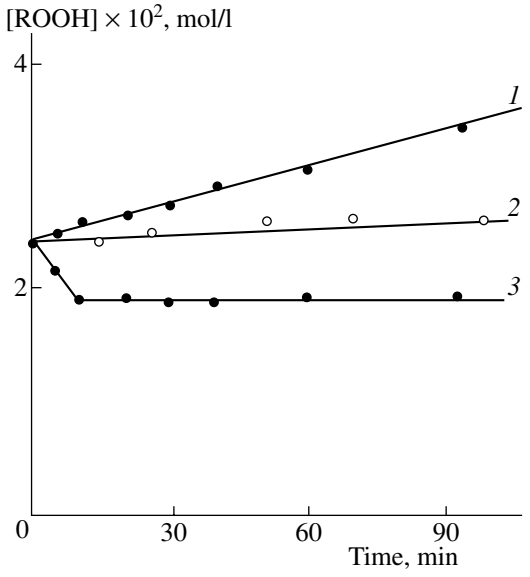

Fig. 3. Changes in the concentration of ROOH (*1*) in the absence of additives and in the presence of (*2*) ionol (2×10^{-3} mol/l) or (*3*) TMPD. T = 393 K; oxygen; chlorobenzene–ethylbenzene, 2 : 1; $[ROOH]_0 = 2.4 \times 10^{-2}$ mol/l.

To study in detail the mechanism of the reaction of ROOH with TMPD, we examined the effect of this reaction on the degenerated branched oxidation of ethylbenzene at 393 K (Fig. 3). In a control experiment on ethylbenzene oxidation with the initial concentration $[ROOH]_0 = 2.4 \times 10^{-2}$ mol/l in the absence of TMPD, the hydroperoxide concentration increased in the course of oxidation (Fig. 3, curve *1*). In the presence of TMPD (curve *3*), ROOH was consumed in the first 10 min; then, the concentration of the hydroperoxide remained almost unchanged for at least 2 h. Analysis for TMPD demonstrated that its concentration was practically equal to zero 30 min after the onset of the experiment. Thus, although TMPD was completely consumed, the oxidation was completely inhibited. The experimental results suggest that an oxidation inhibitor is formed in the course of the reaction of ROOH with TMPD; this inhibitor reacts with peroxy radicals to terminate chains. This was supported by the complete inhibition of the buildup of ROOH (Fig. 3, curve *2*) upon the addition of a known antioxidant (ionol) at the beginning of an experiment performed under conditions analogous to the conditions of an experiment described by curve *1*. Note that the kinetics of the reaction of TMPD with the hydroperoxide in oxygen and argon atmospheres seems identical, as evidenced by data in Fig. 2 (straight line *2*).

We considered two conceivable reaction paths of inhibitor formation from ROOH and TMPD. The formation of an inhibitor (phenol) from α-phenylethyl hydroperoxide under the action of sulfur-containing compounds was observed previously [12]. In this case, the amount of phenol formed was 50–80% of the reacted hydroperoxide. With the use of chromatographic analysis, we found that phenol was absent from the reaction products in our system, whereas ROOH was mainly converted into acetophenone. Thus, it is likely that the inhibitor (InH) formed in the reaction is a product of TMPD conversion.

To determine the concentration of the inhibitor formed in the ROOH + TMPD reaction, we performed a model reaction of initiated ethylbenzene oxidation. In this experiment (Fig. 4), we used reaction mixtures after ROOH decomposition in the presence of TMPD in

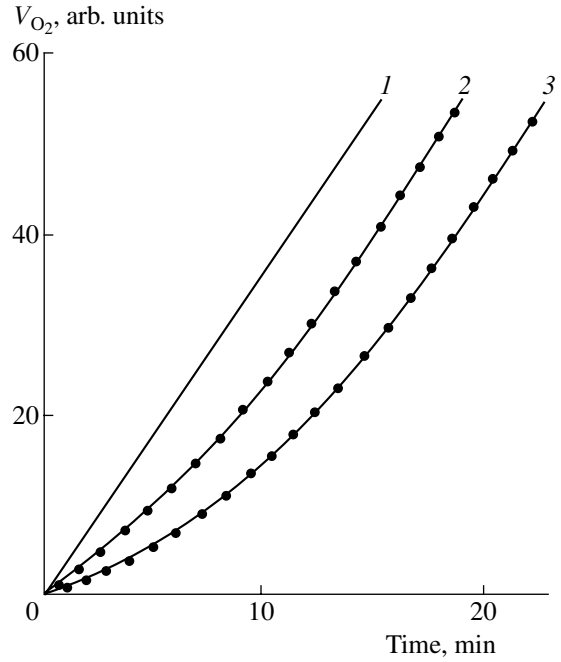

Fig. 4. Kinetic curves of oxygen consumption in the oxidation of ethylbenzene (*1*) without additives and in the presence of (*2*, *3*) 10 vol % of the reaction mixture taken after ROOH decomposition in the presence of TMPD: (*2*) the mixture from an experiment illustrated in Fig. 1, curve *3* and (*3*) the mixture from an experiment illustrated in Fig. 1, curve *1*. $T = 333$ K; $w_i = 5 \times 10^{-7}$ mol l^{-1} s^{-1}.

an argon atmosphere (Fig. 1, curves *1*, *3*) with different initial concentrations of the hydroperoxide and TMPD. It can be seen that the reaction mixture additives decreased the rate of oxygen consumption (Fig. 4); this fact provides support for the presence of an antioxidant in these additives. The efficiency of inhibition increased proportionally to the initial concentration of TMPD in the starting reaction mixture (Fig. 4, curves *2*, *3*). The parameter $f[\mathrm{InH}]_0 = \tau w_i$, where f is the stoichiometric factor of inhibition, τ is the inhibition period, and w_i is the rate of initiation, was calculated from the kinetic curves of oxygen consumption. The value of τ was determined in accordance with a published procedure [13]. Taking into account dilution and assuming $f = 2$, the inhibitor concentrations were $[\mathrm{InH}]_0 = 9 \times 10^{-4}$ (curve *2*) and 2×10^{-3} mol/l (curve *3*), which are practically equal to the initial concentrations of TMPD in the corresponding experiments (Fig. 1, curves *3* and *1*). Thus, the experimental results indicate that InH is a product of TMPD conversion.

To characterize the antiradical activity of InH, we evaluated the reaction rate constant $k_7 \sim 2 \times 10^4$ l mol^{-1} s^{-1} (333 K) from the kinetic curves of oxygen consumption (Fig. 4, curves *2*, *3*) using the initial rates of oxidation. In the calculation, we used the following equation:

$$w_0/w - w/w_0 = fk_7[\mathrm{InH}]/(w_i k_6)^{0.5},$$

where w_0 and w are the rates of oxidation without additives and in the presence of an inhibitor, respectively; k_6 is the rate constant of quadratic recombination equal to 1.9×10^7 l mol^{-1} s^{-1} [14] for α-phenylethyl peroxy radicals.

Among antioxidants from the class of aromatic amines, primary α-naphthylamine exhibited the most similar antiradical activity, $k_7 = 1.4 \times 10^4$ l mol^{-1} s^{-1} (333 K) [15].

Thus, we found that the tertiary amine TMPD induces the nonchain decomposition of ROOH. The high stoichiometric factor of ROOH decomposition ($n > 30$) is indicative of a complex reaction mechanism. A product of TMPD conversion formed in the course of the reaction is an inhibitor, which reacts with peroxyl radicals. Consequently, the role of the test reaction in the mechanism of the inhibition of hydrocarbon oxidation reactions can consist in both the decomposition of the hydroperoxide as a chain-branching product and the termination of oxidation chains. The occurrence of a new inhibitor (InH) does not allow us to draw the unambiguous conclusion that the decomposition of ROOH in the presence of TMPD is not accompanied by the formation of free radicals.

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