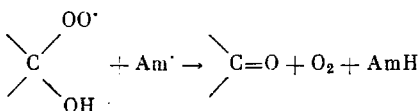


MECHANISM OF REPEATED CHAIN BREAKING AND THE INTERMEDIATE PRODUCTS  
OF TRANSFORMATION OF AROMATIC AMINES IN OXIDIZED ISOPROPANOL  
AND ETHYLBENZENE

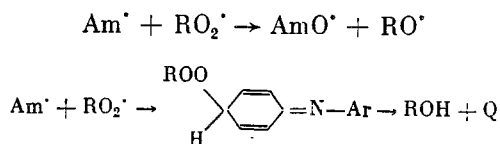
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Aromatic amines inhibit oxidation of alcohols [1, 2] and aliphatic amines [3] by repeatedly participating in chain breaking, which is caused by regeneration of the inhibitor in chain breaking events with the participation of its intermediate products. A mechanism of regeneration with the participation of the aminyl radical has been proposed for aromatic amines AmH [1]



In addition to Am<sup>•</sup>, nitroxyl radicals AmO<sup>•</sup> and quinone imines Q are formed from aromatic amines during inhibited oxidation according to the reactions [4]



Nitroxyl radicals cause repeated chain breaking, demonstrated on the example of oxidation of aliphatic amines in [3], polypropylene in [5], and paraffins in [6]. Quinone imine with a structure similar to quinone and quinones also repeatedly break chains in oxidized alcohols [7] and polypropylene [8]. In developed oxidation of a paraffin hydrocarbon, quinone imine has a prolonged inhibiting effect [9]. All of these findings suggest that not only aminyl radicals, but also other intermediate products of transformation of amines, primarily nitroxyl radicals and quinone imines, participate in repeated chain breaking caused by aromatic amines. This paper is devoted to the study of this subject.

#### EXPERIMENTAL

Inhibited oxidation of isopropanol and ethylbenzene was studied. Ethylbenzene was repeatedly shaken with H<sub>2</sub>SO<sub>4</sub>, washed with water, then with an alkaline aqueous solution of KMnO<sub>4</sub>, and again with water, dried over Na, and distilled in an atmosphere of N<sub>2</sub>. The isopropanol, acetonitrile, and chlorobenzene (Merck, for chromatography) were distilled before the experiment began. Azobisisobutyronitrile (AIBN), recrystallized twice from ethanol and then from benzene and twice from acetone, vacuum dried, and stored in the refrigerator, was used as the initiator. The following amines were used as inhibitors: diphenylamine (DPA), 4-hydroxydiphenylamine (ODPA), 4,4'-dimethoxydiphenylamine (MDPA), 4,4'-di-tert-butylphenylamine (BDPA), and dimethylbis(4-phenylaminophenoxy)silane (MPSI), purified by vacuum sublimation. Quinone monoanilide (QMA) was prepared by oxidation of ODPA in a solution of benzene by γ-activated MnO<sub>2</sub> with heating with a molar ratio of ODPA:MnO<sub>2</sub> = 1:4, and recrystallized from benzene. 4,4'-Dimethoxydiphenylnitroxyl (MDPNO<sup>•</sup>) was prepared according to [10].

Oxidation of isopropanol and ethylbenzene was conducted in the thermostated reactor of a manometric setup at 343 K. Intense stirring of the liquid caused the reaction to occur in kinetic conditions. The inhibitor was added in the form of a solution in acetonitrile in the amount of 0.1 ml per 2.9 ml of isopropanol or ethylbenzene. Samples (0.1 ml) were

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TABLE 1. Kinetic Characteristics of Aromatic Amines as Inhibitors of Oxidation of Ethylbenzene [343 K,  $p_{O_2} = 10^5$  Pa, AIBN initiator,  $v_i = 1.1 \cdot 10^{-6}$  mole/(liter·sec)]

Inhibitor	$[AmH] \cdot 10^4$ , mole/liter	$t_c$	$v_{AmO} \cdot 10^7$ , mole/(liter·sec)	$[AmO']_{max}$ , mole/liter	$v_Q \cdot 10^7$ , mole/ (liter·sec)	$[Q]_{max}$ , mole/liter
DPA	0.5	2,8	1,5	$2.2 \cdot 10^{-4}$	<1.6	$<5.4 \cdot 10^{-4}$
MDPA	1.0	3,4	1.0	$1.4 \cdot 10^{-4}$	<1.2	$<3.2 \cdot 10^{-4}$
MDPNO*	0.5	1,5	—	—	None	None
MPSI	1.0	5,7	1,4	$3.4 \cdot 10^{-4}$	<1.6	$<1.3 \cdot 10^{-3}$
ODPA	1.0	1,5	None	None	—	$1,4 \cdot 10^{-4}$
ODPA	2.0	1,5	None	None	—	—

\* $v_i = 8.1 \cdot 10^{-7}$  mole/(liter·sec).

TABLE 2. Kinetic Characteristics of Aromatic Amines and the Intermediate Products Formed from Them as Inhibitors of Oxidation of Isopropanol [343 K,  $p_{O_2} = 10^5$  Pa, AIBN initiator,  $v_i = 1.1 \cdot 10^{-6}$  mole/(liter·sec),  $v_2 = 8.22 \cdot 10^{-6}$  mole/(liter·sec)]

Inhibitor	$[AmH] \cdot 10^4$ , mole/liter	$\frac{v_i}{v_{AmH}}$	$t_c$	$t_v$	$v_{AmO} \cdot 10^7$ , mole/ (liter·sec)	$[AmO']_{max}$ , mole/liter	$v_Q \cdot 10^7$ , mole/ (liter·sec)	$[Q]_{max}$ , mole/liter
DPA	5.0	>500	—	>23	—	10	None	None
BDPA	5.0	>150	—	>19	—	—	»	»
MDPA	5.0	—	22	—	—	—	—	—
	10.0	2,4	—	>11	0,26	500	1,3	<2,3
MDPNO*	5.0	13	50	—	—	—	None	None
MPSI	2.0	—	18	—	None	None	—	—
	5.0	4.0	—	>15	»	»	2,4	4,9
ODPA	5.0	2.1	—	>14	»	»	3,3	3,3
QMA	0.5*	—	15	—	»	»	—	—
	1.0	—	9	—	»	»	—	—
	5.0	12	13	>27	»	»	—	—

\* $v_i = 2.75 \cdot 10^{-7}$  mole/(liter·sec).

taken during the experiment and after dilution with ethanol (to 2 ml), the spectrum was recorded in the visible and UV region on a Hitachi spectrophotometer. The extinction coefficient of QMA in ethanol solution containing 5% benzene was equal to  $(3.70 \pm 15) \cdot 10^3$  liters/(mole·cm) ( $\lambda$  450 nm). The concentration of amines and the change in the concentration in time were measured spectrophotometrically with the absorption in the region of 280 nm in consideration of the fact that the products formed are stable and also absorb in this region. The change in the concentration of AmH was calculated with the equation:  $[AmH]/[AmH]_0 = (D - D_\infty)/(D_0 - D_\infty)$ , where D,  $D_0$ , and  $D_\infty$  are the current, beginning, and final optical density, respectively. In many cases, the concentration of amines was determined from the data on the total absorption of the amine and products of the reaction at 380 or 460 nm and was calculated with the equation:  $[AmH]/[AmH]_0 = (D_\infty^p - D^p)/(D_\infty^p - D_0^p)$ , where  $D_0^p$  and  $D_\infty^p$  are the optical density of the solution at the beginning and end of the experiment. Both methods give similar results. The concentration of nitroxyl radicals formed from the amines was determined on an EPR-2 spectrophotometer using a sample of  $MnCl_2$  as the standard. The concentration of  $AmO'$  formed from MDPA (MDPNO\*) was determined with the absorption of light at 330 nm; the results of the spectrophotometric analysis coincided with the data from the EPR analysis.

The rate of initiation was calculated with the equation  $v_i = 2ek_d \cdot [AIBN]$ , setting the probability of exit of radicals into the bulk at  $e = 0.6$ , and the rate constant of decomposition of the initiator at  $k_d = 4.57 \cdot 10^{-5} \text{ sec}^{-1}$  (343 K) [11], and AIBN was added in the concentration of  $2 \cdot 10^{-2}$  mole/liter so that  $v_i = 1.10 \cdot 10^{-6}$  mole/(liter·sec). In calculating the rate of chain oxidation, corrections were made for separation of  $N_2$  from the AIBN and absorption of  $O_2$  in initiation:  $v = v_{gas} - (1.5 \cdot 0.5e^{-1})v_i = v_{gas} - 0.67v_i$  for initiated oxidation without any inhibitor [12] and  $v_{O_2} = v_{gas} - (1 - 0.5e^{-1})v_i = v_{gas} - 0.17v_i$  for initiated oxidation with an inhibitor, the acceptor  $RO_2'$ .

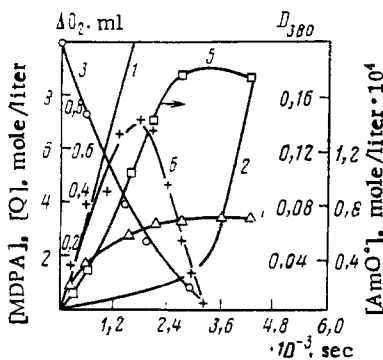


Fig. 1

Fig. 1. Initiated oxidation of ethylbenzene (343 K,  $p_{O_2}$   $10^5$  Pa, initiator [AIBN] =  $2 \cdot 10^{-2}$  mole/liter with addition of  $1 \cdot 10^{-3}$  mole/liter MDPA): 1, 2) absorption of  $O_2$  (1: without inhibitor); 3) change in the concentration of MDPA; 4) accumulation of quinone imine Q; 5) change in  $D_{380}$ ; 6) accumulation of nitroxyl  $AmO^\bullet$ .

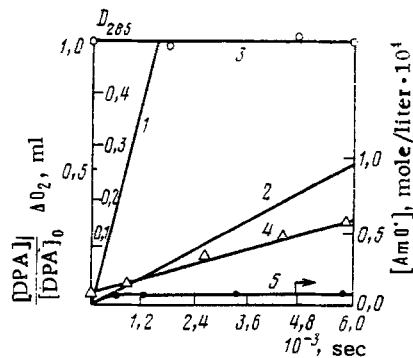


Fig. 2

Fig. 2. Initiated oxidation of isopropanol (343 K,  $p_{O_2}$   $10^5$  Pa, with addition of  $5 \cdot 10^{-4}$  mole/liter DPA): 1, 2) absorption of  $O_2$  (1: without addition of DPA); 3) change in the concentration of DPA; 4) change in the optical density  $D_{380}$ ; 5) accumulation of nitroxyl  $[AmO^\bullet]$ .

Inhibition coefficient  $f$  was determined by three different methods: with the ratio of the rates of initiation and consumption of the inhibitor  $AmH$  ( $f = v_i v_{AmH}^{-1}$ ), the induction period ( $f_\tau = v_1/[AmH]_0$ ,  $[AmH]_0$  is the initial concentration of inhibitor), the change in the rate of inhibited oxidation after time  $t$  ( $f_v = v_i v_t / (v_t - v_0)[AmH]_0$ ,  $v_0$  and  $v_t$  are the rates of inhibited oxidation with  $t = 0$  and  $t$ , respectively) [7].

The rate constant of the reaction of the peroxide radical with the  $AmH$  inhibitor was calculated with the initial rate of oxidation of isopropanol  $v$  using the ratio [7]

$$\frac{v_i}{v} \left(1 - \frac{v^2}{v_0^2}\right) = \frac{2k_{AmH} [AmH]_0}{k_p [(CH_3)_2CHOH]}$$

where  $v_0$  is the rate of inhibited oxidation;  $k_p$  is the chain propagation rate constant in isopropanol ( $k_p = 3.5$  liters/(mole·sec) [13]), and  $[(CH_3)_2CHOH] = 12.5$  moles/liter.

## DISCUSSION

The comparative study of the inhibiting effect of amines on oxidation of ethylbenzene and isopropanol revealed a difference in the products and method of inhibition of the amines when alkyl- and hydroxyperoxide radicals react with them. Addition of an amine to oxidized ethylbenzene causes the appearance of an induction period  $\tau$  which ends on consumption of the amine (Fig. 1). The nitroxyl radical is formed as an intermediate product, and the concentration passes through a maximum at time  $t = 0.5\tau$ . Quinone imine is the final product of transformation of the amine in these conditions (Fig. 1).

The quantitative characteristics of the inhibiting effect of amines in oxidized ethylbenzene are reported in Table 1. The stoichiometric chain-breaking coefficient varies in the range of 1.5-3 on conversion per amino group (there are two such groups in the molecule of MPSI). In all cases, the amine is converted into the corresponding iminoquinone, less of which is obtained at the end of the induction period than the amount of the starting amine added. As a consequence, other products of transformation of the amine accumulate in addition to the quinone imine. The nitroxyl radical is also formed from the amine as an intermediate product (in addition to ODPA). It accumulates in parallel with the quinone imine.

This is due to the parallel reactions of the aminyl radical  $Am^\bullet$  with  $RO_2^\bullet$  (see above). The sum of the initial rates of formation of Q and  $AmO^\bullet$  is always less than  $0.5v_i$ . As a consequence, both of these products do not deplete all of the primary products of transformation of the aminyl radicals. The kinetics of consumption were spectrophotometrically studied for MDPA (Fig. 1). The inhibition coefficient calculated with the ratio of  $v_i$  and  $v_{AmH}$  is

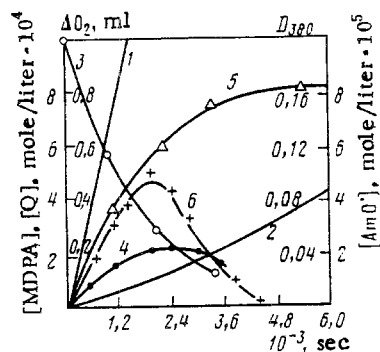


Fig. 3

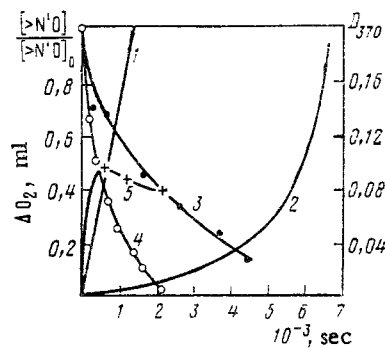


Fig. 4

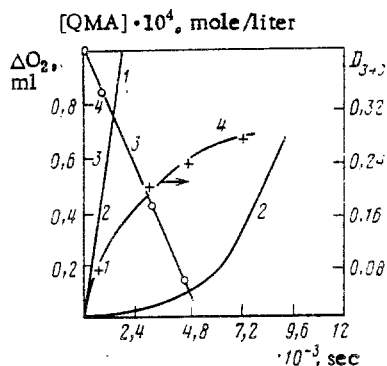


Fig. 5

Fig. 3. Initiated oxidation of isopropanol (343 K,  $p_{O_2}$   $10^5$  Pa, with addition of  $1 \cdot 10^{-3}$  mole/liter MDPA); 1, 2) absorption of  $O_2$  (1: without addition of MDPA); 3) change in the concentration of MDPA; 4) accumulation of quinone imine Q; 5) change in  $D_{320}$ ; 6) accumulation of nitroxyl  $[AmO^*]$ .

Fig. 4. Initiated oxidation of isopropanol (343 K,  $p_{O_2}$   $10^5$  Pa,  $[AIBN] = 2 \cdot 10^{-2}$  mole/liter with addition of  $1 \cdot 10^{-4}$  mole/liter MDPNO $^*$ ): 1, 2) absorption of  $O_2$  (1: without inhibitor); 3) change in the concentration of MDPNO $^*$  nitroxyl. Initiated oxidation of ethylbenzene (343 K,  $p_{O_2}$   $10^5$  Pa,  $[AIBN] = 2 \cdot 10^{-2}$ , MDPNO $^*$  added =  $5 \cdot 10^{-4}$ ); 4) change in the concentration of nitroxyl; 5) change in the optical density  $D_{370}$ .

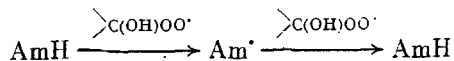
Fig. 5. Initiated oxidation of isopropanol (343 K,  $p_{O_2}$   $10^5$  Pa,  $[AIBN] = 2 \cdot 10^{-2}$  mole/liter with addition of  $5 \cdot 10^{-4}$  mole/liter QMA); 1, 2) absorption of  $O_2$  (1: with no additive); 3) change in the concentration of QMA; 4) increase in  $D_{340}$ .

$f_{AmH} = 2.4$ , while the coefficient calculated with the duration of inhibition is  $f_{\tau} = 3.4$ , i.e., the intermediate products have an inhibiting effect, particularly the nitroxyl radical. A separate experiment with the nitroxyl radical formed with MDPA (MDPNO $^*$ ) showed that it actually inhibits oxidation of ethylbenzene with an inhibition coefficient of  $f_{\tau} = 1.5$  (Table 1). The data obtained are in agreement with the data in the literature on products of transformation of DPA in oxidized cumene [4].

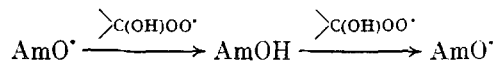
When amines are added to oxidized isopropanol, very prolonged inhibition is observed. It was only possible to estimate the inhibition coefficient with the induction period in a few cases,  $f > 10$  (Table 2). The estimation of  $f$  based on the change in the oxidation rate during the experiment  $t(fv)$  is also in agreement with these values. The values of  $f$  obtained are in agreement with the data in [1].

The composition of the products of transformation of the amines in isopropanol is significantly different from in ethylbenzene. In oxidized isopropanol, DPA is virtually not consumed during the experiment (Fig. 2), quinone imine Q is not formed from it, and a quasistationary concentration of the nitroxyl radical is rapidly established during the experiment.

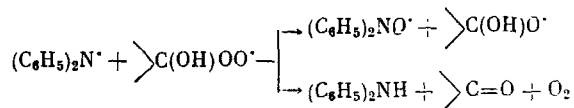
Since DPA inhibits oxidation (Table 2) but is not consumed, this indicates chain breaking with regeneration of AmH from Am<sup>•</sup> according to the cycle



In addition, cyclic chain breaking on the nitroxyl radical apparently also takes place



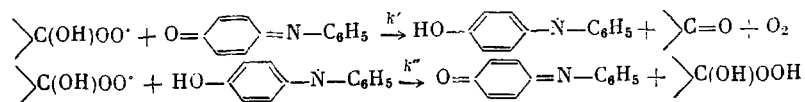
The absence of iminoquinone among the products indicates that the hydroxyperoxide radical does not attack the benzene ring of the diphenylaminyl radical but only reacts with the free valence carried by the N atom



Repeated chain breaking takes place in oxidized isopropanol on addition of MDPA, but a totally different composition of the products is obtained (Fig. 3). The starting amine is consumed relatively rapidly, and in the initial period,  $f = v_i/v_{\text{AmH}} = 2.4$ . As a consequence, the MDPA aminyl radicals are not reduced to an amine by the hydroperoxide radicals. Both iminoquinones and the nitroxyl radical were found among the products of oxidation: both products are intermediate and repeatedly break chains. It is totally possible that other products which also participate in chain breaking are formed. A similar picture is observed for MPSI, but the nitroxyl radical is not formed (Table 2). The same is also observed for ODP. The picture for BDPA is similar to DPA. From the very beginning of the experiment,  $v_{\text{AmH}} \ll v_i$  and  $f > 150$ .

To verify whether the nitroxyl radical formed from MDPA causes repeated chain breaking, experiments were conducted on oxidation of isopropanol and ethylbenzene with addition of  $(\text{CH}_3\text{OC}_6\text{H}_4)_2\text{NO}^\bullet$  (Fig. 4). The nitroxyl inhibits oxidation of both ethylbenzene and propanol, but with different inhibition coefficients:  $f_\tau = 1.5$  in ethylbenzene and 50 in isopropanol. The rate of uninhibited oxidation of isopropanol decreases as the nitroxyl is consumed, i.e., the products of transformation of the nitroxyl do not have an inhibiting effect. This experiment shows that aromatic nitroxyls repeatedly break chains in oxidized alcohols, effective intermediate inhibitors of the repeated effect.

The results of the experiments with ODP (Table 2) suggest that the quinone imine QMA causes repeated chain breaking. An experiment was conducted on oxidation of isopropanol with addition of QMA to verify this possibility (Fig. 5). Actually, QMA is an efficient inhibitor, causes repeated chain breaking ( $f = v_i/v_Q = 12$ ), and its products also inhibit oxidation ( $f_v > 27$ ). The following cycle of transformations, where each stage results in chain breaking, is most probable:



Since quinone imine can be reduced by both hydroxyperoxide and by hydroxyalkyl radicals, the experiments were conducted on oxidation of isopropanol in the presence of QMA ( $5 \cdot 10^{-5}$  and  $1 \cdot 10^{-4}$  mole/liter) at  $p_{\text{O}_2}$  of  $10^5$  and  $2 \cdot 10^4$  Pa (343 K). The experiments showed that the  $\text{O}_2$  absorption curves coincide in the induction period. In these experiments, ratio  $[\text{R}^\bullet]/[\text{RO}_2^\bullet]$  changed by five times, but this was not reflected in the kinetics of oxidation. As a consequence, the hydroxyalkyl radicals virtually do not participate in the reaction, but hydroperoxide radicals reduce the quinone imine. It is interesting that in going out of the induction period, the kinetic curves separate in these experiments: the higher  $[\text{RO}_2^\bullet]$ , the more rapidly oxidation takes place. The products of transformation of QMA apparently react with the hydroxyalkyl radicals, which results in more intense chain breaking with a decrease in  $[\text{RO}_2^\bullet]$ . As Table 2 shows, QMA is similar to aromatic amines with respect to

its activity. Since  $f = 9$  for QMA, the rate constant of the reaction of the peroxide radical with the radical form of QMA can be estimated. As shown,  $k' \geq 2 \cdot 10^5$  liters/(mole·sec), and since  $f = 2(1 + k''/k') = 11$ , then  $k'' \geq 7.4 \cdot 10^5$  liters/(mole·sec). The question of which radical is formed in reduction of QMA, phenoxyl or aminyl, remains open.

A comparison of the experiments on inhibition of oxidation of ethylbenzene and isopropanol first shows that all of the amines studied form chains stoichiometrically in oxidized ethylbenzene and repeatedly in isopropanol. Second, the composition of the products is different: qualitative similarity in ethylbenzene and isopropanol is only observed for MDPA. Third, it was clearly shown that aryl nitroxyl radicals and iminoquinones (QMA) inhibit oxidation of isopropanol by repeated chain breaking. Fourth, each aromatic amine in the oxidized alcohol causes a characteristic set of different reaction cycles of catalytic chain breaking. In inhibition of oxidation of DPA,  $Am^{\cdot}$  and  $AmO^{\cdot}$  participate in repeated chain breaking, MDPA:  $AmO^{\cdot}$  and Q; MPSI: Q; BDPA:  $Am^{\cdot}$ . Each aromatic amine thus has its own specific mechanism of repeated chain breakage in oxidized alcohols.

### CONCLUSIONS

1. Aminyl and nitroxyl radicals and quinone imines and the products of their transformation participate in repeated chain breaking in inhibition of oxidation of isopropanol by aromatic amines. One set of intermediate products takes place in cyclic chain-breaking reactions as a function of the structure of the amine.

2. The composition of the products of transformation of aromatic amines in oxidized ethylbenzene and isopropanol are different. The quinone imine and nitroxyl radical are formed from diphenylamine in ethylbenzene, while there is no quinone imine in isopropanol; quinone imine and the nitroxyl radical are formed from dimethylbis(4-diphenylaminophenoxy)silane in ethylbenzene, while quinone imine alone is formed in isopropanol.

3. Quinone monoanilide is reduced in the reaction with the isopropanol peroxide radical, and the radical formed in this reaction reacts with the peroxide radical.

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