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THE REACTION OF DIPHENYLAMINYL AND NITROXYL RADICALS

AND THEIR ROLE IN THE MECHANISM OF THE ANTIOXIDANT

EFFECT OF MIXTURES OF AN AROMATIC AMINE WITH NITROXYL

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It was found in [1, 2] that mixtures of alkyl radical acceptors (stable nitroxyl radicals, quinones) with phenols or aromatic amines exhibit a synergistic effect in inhibition of oxidation or hydrocarbons. The mechanism of action of such mixtures is not described by the set of reactions known for each of the inhibitors separately. It is thus necessary to study the reactions of the inhibitors and the corresponding radicals to elucidate the mechanism of the synergism.

The reaction of alkyl radical acceptors with the radicals formed from inhibitors reacting with $RO_2^{\cdot}$ radicals was studied in the present article on the example of the reaction of the nitroxyl radical with the diphenylaminyl radical. The effect of this reaction on the efficiency of action of a mixture of antioxidants was evaluated.

EXPERIMENTAL

The reaction of 2,2,6,6-tetramethyl-1-oxyl-piperidine ($>NO^{\cdot}$) with the diphenylaminyl radical $Ph_2N^{\cdot}$ was studied in chlorobenzene (pure brand) held over Al_2O_3 and distilled twice. Tetraphenylhydrazine (TPH), synthesized according to [3], was the source of the $Ph_2N^{\cdot}$ radicals. The experiments were conducted in a cell of the bubbling type in argon at 90°C. The concentration of diphenylamine (DPA) was determined spectrophotometrically at 20° based on the color which arose in the azo coupling reaction with diazotized p-nitroaniline at $\lambda = 484$ nm. According to [4], the error in determination of DPA due to the possible simultaneous presence of semidines is less than 10%.

DISCUSSION OF RESULTS

It is known that TPH decomposes with formation of diphenylaminyl radicals [5] which can recombine in the absence of an acceptor reagent (for example, nitric oxide [6] or screened phenols [7]) with formation of TPH or can undergo disproportionation [6, 8]. In decomposition of TPH in an inert solvent, the following reactions can thus take place:
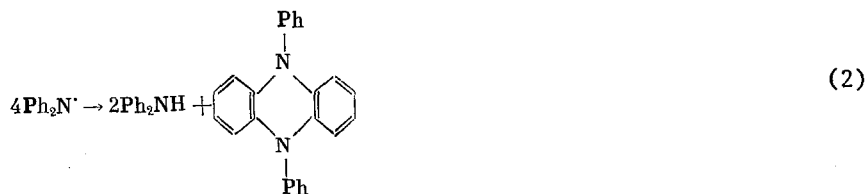
$$Ph_2N\!-\!NPh_2 \underset{k_r}{\overset{k_i}{\rightleftharpoons}} 2Ph_2N^{\cdot} \tag{1}$$

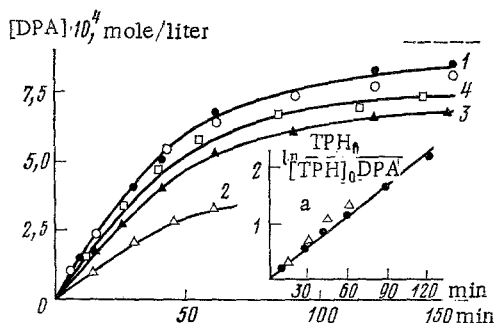$$4Ph_2N^{\cdot} \rightarrow 2Ph_2NH + \tag{2}$$

Fig. 1. Kinetic curves of accumulation of diphenylamine during decomposition of tetraphenylhydrazine. $[TPH]_0 \cdot 10^4$, mole/liter: 1) 9; 2) 4.5. The same in the presence of $1 \cdot 10^{-3}$ mole/liter of alkyl radical acceptors: 3) 2,2,6,6-tetramethyl-1-oxylpiperidine; 4) p-benzoquinone, $[TPH]_0 = 9 \cdot 10^{-4}$ mole/liter. Ar, 90°C.

In addition to diphenyldihydrophenazine, semidines are also formed [4, 8], in the amount of ~10% at 110°C according to the data in [8].

It was experimentally observed (Fig. 1, curves 1, 2) that DPH accumulates during decomposition of TPH in the absence of >NO˙, identified by TLC and spectrophotometrically. It was not possible to obtain the limit concentration of in the time interval being measured, but it is possible to assume from the shape of the curves that $[DPA]_\infty \to [TPH]_0$, corresponding to (1) and (2) in the literature. The process of formation of DPA is formally simplest to represent in the form of the following elementary stages:

$$Ph_2N˙ + Ph_2N˙ \xrightarrow{k_d} Ph_2NH + In˙˙ \qquad (3)$$

$$2In˙˙ \to Products \qquad (4)$$

From the differential equations corresponding to stages (1), (3), and (4), on the assumption of a quasistationary state with respect to the $Ph_2N˙$ radicals,

$$[Ph_2N˙]^2 = \frac{k_i[TPH]}{k_r + k_d} \qquad (5)$$

expressions for the change in [TPH] and [DPA] during the experiment were obtained:

$$-\frac{d[TPH]}{dt} = \alpha[TPH] = \frac{d[DPA]}{dt} \qquad (6)$$

where $\alpha = k_i k_d/(k_r + k_d)$. After integration of (6), the current concentration of TPH is equal to:

$$[TPH] = [TPH]_0 e^{-\alpha t} \qquad (7)$$

Substitution of (7) in (6) and subsequent integration results in an equation which describes the kinetics of accumulation of DPA:

$$[DPA] = [TPH]_0(1 - e^{-\alpha t}) \qquad (8)$$

When $t \to \infty$, it follows from (8) that $[DPA]_\infty = [TPH]_0$. The result of taking the logarithm of (8) is an equation for a straight line:

$$\ln \frac{[TPH]_0}{[TPH]_0 - [DPA]} = \alpha t$$

The tangent of the slope of the line is equal to the value of parameter α. Figure 1a shows that curves 1 and 2 straighten out at semilogarithmic coordinates, an hence, $\alpha = 3 \cdot 10^{-4}$ sec^{-1}.
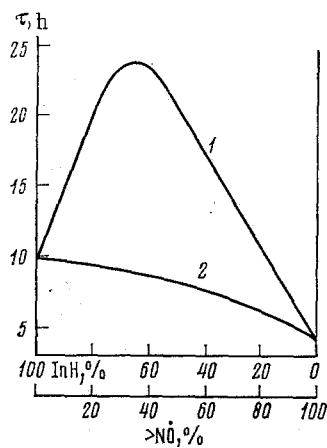
Fig. 2. Calculated induction period—composition dependence for a mixture of InH with >NO˙ with k_{ac}, liter/mole·sec: 1) $1 \cdot 10^6$; 2) 0 and $5 \cdot 10^2$.

The good correspondence of the experimental data with the proposed scheme indicates that the process of formation of DPA can be described by a set of stages of decomposition of TPH, recombination, and disproportionation of diphenylaminyl radicals. Accumulation of DPA actually takes place as a result of disproportionation of (2), and is not due to detachment of an H atom from the chlorobenzene. Special experiments showed that the rates of accumulation of DPA are similar in chlorobenzene and CCl_4.

The ratio of the recombination and disproportionation rate constants can be found by using the value k_i (90°C) = $2.2 \cdot 10^{-3}$ sec^{-1}, calculated based on k_i (70°C) = $2 \cdot 10^{-4}$ sec^{-1} [7] and E_a of the decomposition of TPH equal to 125.6 kJ/mole [6]. It was found that k_r/k_d = 6.3. The value of k_r/k_d, determined in [9] based on consumption of TPH, is equal to 5.3 (75°C) on conversion to k_i = $3.8 \cdot 10^{-4}$ sec^{-1}. Based on the data in [10], it is possible to assume k_r = 10^8 liter/mole·sec (90°C), while the disproportionation rate constant is k_d = $1.6 \cdot 10^7$ liter/mole·sec.

The results obtained show that formation of an inhibitor takes place during recombination of its radicals in the case of aromatic amines, as for phenols (in which the o or p position is either not substituted or contains alkyl groups with α-H atoms [11]:

$$In˙ + In˙ \rightarrow InH$$
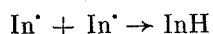
This reaction should be taken into consideration in the mechanism of action of inhibitors together with the known stages involving inhibitor radicals:

$$In˙ + RO_2˙ \rightarrow \text{Products} \qquad In˙ + In˙ \rightarrow \text{Products}$$

On introduction of >NO˙, a slight decrease in the initial rate of accumulation of DPA and the values of $[DPA]_\infty$ were observed. One of the causes of the decrease in $[DPA]_\infty$ could be the reaction of >NO˙ with DPA. According to [12], k = $1.5 \cdot 10^{-2}$ liter/mole·sec (128°C) for the reaction of >NO˙ with an aromatic amine. Assuming E_a = 35.6 kJ/mole [13], k = $5 \cdot 10^{-3}$ liter/mole·sec (90°C) was obtained. Let us evaluate the contribution of the reaction of DPA with >NO˙ to the experimentally observed decrease in the concentration of DPA in the presence of >NO˙ (Δ [DPA]). The maximum rate of this reaction is $4.5 \cdot 10^{-9}$ mole/liter·sec when [NO˙] = $1 \cdot 10^{-3}$ mole/liter and the limit concentration of [DPA] = $9 \cdot 10^{-4}$ mole/liter. Less than $2.4 \cdot 10^{-5}$ mole/liter of DPA is consumed in this reaction after 1.5 h, which is not more than 10% of the experimentally observed Δ[DPA] = $1.5 \cdot 10^{-4}$ mole/liter.

The decrease in the concentration of DPA in the presence of >NO˙ apparently occurs due to acceptance of $Ph_2N˙$ by this radical:

$$Ph_2N˙ + >NO˙ \xrightarrow{k_{ac}} \text{Products} \qquad (9)$$

It follows from (3) and (9) that $\Delta[\text{DPA}]$ after time τ in experiments without >NO· and with addition of >NO· is equal to:

$$\Delta[\text{DPA}] = \frac{1}{2} \int_0^\tau k_{ac} [\text{Ph}_2\text{N}\cdot]_{\text{NO}\cdot} [>\text{NO}\cdot] \, dt$$

where the index indicates the presence of >NO·.

Estimation of k_{ac} was performed as follows. Since $\Delta[\text{DPA}]$ is small ($\Delta[\text{DPA}]/[\text{DPA}]_\infty \approx$ 15%), it was assumed that the current concentration of >NO· is small and differed from the starting $[>\text{NO}\cdot]_0$, while $[\text{Ph}_2\text{N}\cdot]_{\text{NO}\cdot}$ could be calculated from Eq. (5). Then

hence,

$$\Delta[\text{DPA}] = k_{ac}(\alpha k_d)^{-1/2} [\text{TPH}]_0^{1/2} [>\text{NO}\cdot] (1 - e^{-\frac{\alpha}{2}\tau})$$

$$k_{ac} \simeq \frac{\Delta[\text{DPA}] \sqrt{\alpha k_d}}{[>\text{NO}\cdot]_0 \sqrt{[\text{TPH}]_0} (1 - e^{-\frac{\alpha}{2}\tau})}$$

For $[>\text{NO}\cdot]_0 = 1\cdot10^{-3}$ mole/liter, it was found that $k_{ac} = 5\cdot10^2$ liter/mole·sec. A slightly different value of k_{ac} (within an order of magnitude) was obtained with other concentrations of >NO·, which should apparently be attributed to the assumptions used and the errors in measuring the small $\Delta[\text{DPA}]$.

When the value of the rate constant is similar, Ph_2N radicals react with other alkyl radical acceptors: quinones (see Fig. 1, curve 4). The value of k_{ac} for p-benzoquinone is $3.5\cdot10^2$ liter/mole·sec (90°C).
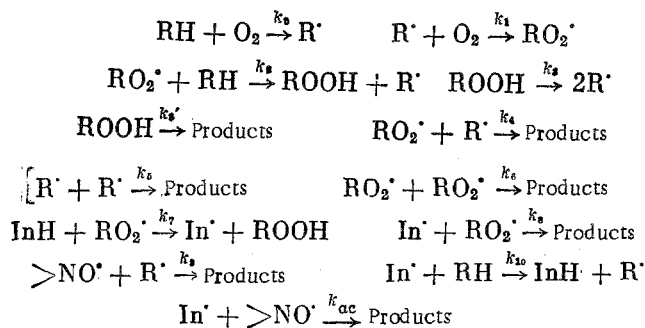
Let us analyze the role which the reaction of In· with Q plays in the mechanism of the antioxidant effect of mixtures of InH inhibitors with peroxide radicals and the Q acceptor of alkyl radicals. This reaction could result in an increase in the inhibiting effect if InH has a high value of the rate constant for the reaction with $\text{RO}\cdot_2$– radicals, but the In· formed participates in side reactions which result in an increase in the rate of formation of active radicals, for example, in the chain propagation reaction:

$$\text{In}\cdot + \text{RH} \rightarrow \text{InH} + \text{R}\cdot \qquad (10)$$

or a similar reaction with hydroperoxide. These undesirable processes are inhibited if $k_{ac}[\text{In}\cdot][Q] > k_{10}[\text{In}\cdot][\text{RH}]$, i.e., with values of k_{ac} where

$$k_{ac} > k_{10}[\text{RH}]/[Q] \qquad (11)$$

A synergistic effect was experimentally observed in mixtures of InH with Q during autooxidation of hydrocarbons with total concentrations of the components of $1.5\cdot10^{-4}$ mole/liter. $[\text{RH}] = 5-8$ mole/liter, and k_{10} (120°C) $\simeq 0.1-1$ liter/mole·sec. According to (11), synergism caused by inhibition of reaction (10) could take place in such conditions when $k_{ac} > 10^4$ liter/mole·sec. The validity of this estimation was verified on a computer. The antioxidant effect of a mixture of inhibitors, an aromatic amine with a nitroxyl radical, was modeled in autooxidation of ethylbenzene (120°C):

$$\text{RH} + \text{O}_2 \xrightarrow{k_0} \text{R}\cdot \qquad \text{R}\cdot + \text{O}_2 \xrightarrow{k_1} \text{RO}_2\cdot$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{k_2} \text{ROOH} + \text{R}\cdot \qquad \text{ROOH} \xrightarrow{k_3} 2\text{R}\cdot$$

$$\text{ROOH} \xrightarrow{k_3'} \text{Products} \qquad \text{RO}_2\cdot + \text{R}\cdot \xrightarrow{k_4} \text{Products}$$

$$\text{R}\cdot + \text{R}\cdot \xrightarrow{k_5} \text{Products} \qquad \text{RO}_2\cdot + \text{RO}_2\cdot \xrightarrow{k_6} \text{Products}$$

$$\text{InH} + \text{RO}_2\cdot \xrightarrow{k_7} \text{In}\cdot + \text{ROOH} \qquad \text{In}\cdot + \text{RO}_2\cdot \xrightarrow{k_8} \text{Products}$$

$$>\text{NO}\cdot + \text{R}\cdot \xrightarrow{k_9} \text{Products} \qquad \text{In}\cdot + \text{RH} \xrightarrow{k_{10}} \text{InH} + \text{R}\cdot$$

$$\text{In}\cdot + >\text{NO}\cdot \xrightarrow{k_{ac}} \text{Products}$$

The following values of the rate constants of the reaction [1] were used in the calculation: $k_0[\text{O}_2] = 6.2\cdot10^{-11}$ sec^{-1}, $k_1[\text{O}_2] = 2\cdot10^4$ sec^{-1}, $k_2 = 25$ liter/mole·sec, $k_3 = 6\cdot10^{-7}$ sec^{-1}, $k_3' = 6\cdot10^{-6}$ sec^{-1}, $k_4 = 1\cdot10^8$ liter/mole·sec, $k_5 = 5\cdot10^8$, $k_6 = 2\cdot10^7$, $k_7 = 1.3\cdot10^5$, $k_8 = 1\cdot10^8$, $k_9 = 4\cdot10^5$, and $k_{10} = 0.3$ liter/mole·sec. The values of k_{ac} varied. The dependences

of the induction period on the composition of the mixture were calculated; the time when $1 \cdot 10^{-2}$ mole/liter of hydroperoxide was formed in the system was used as the end of the induction period. The total concentration of inhibitors was set at $1.5 \cdot 10^{-4}$ mole/liter. When $k_{ac} = 1 \cdot 10^6$ liter/mole·sec (Fig. 2, curve 1), a significant synergistic effect is observed. Synergism did not take place with the experimentally observed value of $k_{ac} = 5 \cdot 10^2$ liter/mole·sec (see Fig. 2, curve 2). With this value of k_{ac}, according to (11), reaction (9) has no effect on the process, indicated by the almost total coincidence of the values of τ with the data obtained when $k_{ac} = 0$.

The reaction of In· with Q is thus not the cause of the synergistic effect of mixtures of inhibitors reacting with R· and RO_2.

CONCLUSIONS

1. Diphenylamine is formed during thermal decomposition of tetraphenylhydrazine (TPH) in chlorobenzene in an amount close to the starting concentration of TPH.

2. The kinetics of accumulation of diphenylamine is described by a set of stages of the decomposition of tetraphenylhydrazine, recombination and disproportionation of the diphenylaminyl radicals formed.

3. The rate constant of the reaction of diphenylaminyl radicals with 2,2,6,6-tetramethyl-1-oxyl-piperidine was estimated; it was shown that this reaction does not affect the antioxidant effect of a mixture of an aromatic amine and the nitroxyl radical.

4. The synergistic effect of a mixture of inhibitors InH with alkyl radical acceptors (Q) could be due to the reaction In· + Q → Products, if the rate of this reaction is greater than the rate of chain propagation In· + RH → InH + R·.

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