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Abstract

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ON THE MECHANISM OF THE SYNERGISTIC EFFECT OF MIXTURES OF INHIBITORS IN LIQUID-PHASE OXIDATION REACTIONS

The essence of the phenomenon of synergism in the action of mixtures of inhibitors is that the inhibition period of oxidation processes in the presence of two inhibitors in some cases proves to be longer than the inhibition period that could be obtained on the assumption of additivity of the action of the inhibitors taken ([1,2]).

There are several points of view on the mechanism of the phenomenon of synergism. The most widespread assumption is that synergism appears when mixtures of inhibitors are used, one of which breaks the oxidation chains, while the other reacts with hydroperoxides and, in this way, decreases the concentration of free radicals in the system. However, this case is not general. Synergism is also observed under the action of mixtures of inhibitors, each of which interacts with the radicals that carry the chain process ([2]).

We proposed that in this case one of the causes of synergism is the interaction of the inhibitors with one another. The existence of such an interaction of inhibitors was established by us using several pairs of inhibitors as examples, one of which belonged to the class of amines and the other to hindered phenols (neozone D-2,6-di-*tert*-butylphenol, neozone D-2,6-di-*tert*-butyl-4-methylphenol, neozone D-tetraisopropylphenolphthalein, etc.) ([4]).

The kinetics of consumption of each of the inhibitors of a given pair was measured in the process of oxidation of ethylbenzene initiated by dinitrile of azoisobutyric acid, and it was shown that in such a system only the phenol is consumed, whereas the concentration of the amine changes very little. After the phenol has been consumed, the amine begins to be consumed at a rate corresponding to the rate of interaction of this inhibitor with free radicals.

The same result was obtained by the chemiluminescence method, from the change in the character of the curves of luminescence intensity in the coordinates $I/I_0 - t$ (where I_0 and I are the intensities of chemiluminescence without inhibitor and in the presence of inhibitor) ([5]). The observed phenomenon of inhibition of amine consumption was explained by the interaction of the amine and the phenol. The amine radical formed in the reaction of the amine with

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

peroxide radicals abstracts hydrogen from the phenol, and thus regeneration of the amine occurs in the system:

$$\mathrm{Am}\cdot + \mathrm{PhOH} \rightarrow \mathrm{AmH} + \mathrm{PhO}\cdot .$$

To establish the connection between the interaction of inhibitors and the phenomenon of synergism, in the present work the kinetics of oxygen absorption was studied during the oxidation of ethylbenzene in the presence of two mixtures of inhibitors (neozone D–2,6-di-*tert*-butylphenol and neozone D–4-oxy-3,5-di-*tert*-butyl-ω-nitrostyrene). Dinitrile of azoisobutyric acid was used as initiator I. The initiation rate (W_i) was equal to $2 \cdot 10^{-7}$ mole/l • sec. Under the experimental conditions, the oxidation reaction was an unbranched chain process, since the ethylbenzene hydroperoxide formed is sufficiently stable.

For these systems the kinetics of inhibitor consumption was also measured, and it was shown that here there occurs the same interaction of the amine radical with the phenol, accompanied by regeneration of the amine, as in the case of the inhibitors studied by us earlier (^{4}).

The amine is practically not consumed as long as phenol is present in the system (Fig. 1).

Figure 2 shows the dependence of the inhibition period (τ) of the ethylbenzene oxidation process on the ratio of inhibitor concentrations in their mixture at one and the same total inhibitor concentration.

Fig. 1. Consumption of inhibitors when they are present together in the oxidation reaction of ethylbenzene initiated by azobisisobutyric acid dinitrile. 1 —neozone D, 2—4-oxy-3,5-di-*tert*-butyl-ω-nitrostyrene. Temperature 70°, $W_i = 2 \cdot 10^{-7}$ mol/l • sec

Fig. 2. Dependence of the inhibition period τ on the composition of the mixture at a constant total concentration of inhibitors ($4 \cdot 10^{-4}$ mol/l) for the mixture neozone D–2,6-di-*tert*-butylphenol. Temperature 70°, $W_i = 2 \cdot 10^{-7}$ mol/l • sec

The dotted line in this figure shows what the inhibition periods would be under simple summation of the inhibiting action of both inhibitors. As is seen from Fig. 2, the values of τ in the presence of neozone D–2,6-di-*tert*-butylphenol mixtures deviate from the law of additivity in the direction of an increase in the inhibiting action of the inhibitor mixture. At low concentrations of neozone D in a mixture with 2,6-di-*tert*-butylphenol, the inhibition period of ethylbenzene oxidation corresponds to the value of τ obtained under the action of neozone D alone. An analogous picture is also observed for another pair of inhibitors, neozone D-4-oxy-3,5-di-*tert*-butyl-ω-nitrostyrene. The result obtained is in complete agreement with the supposition that reaction (5) (see scheme) is the cause of synergism in such systems.

The mechanism of action of an inhibitor mixture, under the condition that each of them reacts with two RO_2 radicals and taking into account the interaction between them, can be represented by the following scheme:

$$\mathrm{I} \xrightarrow[k_i,\ RH]{} RO_2 \tag{0}$$

$$\mathrm{AmH} + \mathrm{RO_2} \xrightarrow{\mathrm{k_1}} \mathrm{Am\cdot} + \mathrm{RO_2H} \tag{1}$$

$$\mathrm{PhOH} + \mathrm{RO_2} \xrightarrow{\mathrm{k_2}} \mathrm{PhO\cdot} + \mathrm{RO_2H} \tag{2}$$

$$\mathrm{Am\cdot} + \mathrm{RO_2} \xrightarrow{\mathrm{k_3}} \tag{3}$$

$$\mathrm{PhO\cdot} + \mathrm{RO_2} \xrightarrow{\mathrm{k_4}} \tag{4}$$

$$\mathrm{Am\cdot} + \mathrm{PhOH} \xrightarrow{\mathrm{k_5}} \mathrm{AmH} + \mathrm{PhO\cdot} \tag{5}$$

$$\mathrm{PhO\cdot} + \mathrm{AmH} \xrightarrow{\mathrm{k_6}} \mathrm{PhOH} + \mathrm{Am\cdot} \tag{6}$$

The expressions for the change in the concentration of substances and radicals have the following form

$$\frac{d(\mathrm{RO_2})}{dt} = W_i - k_1(\mathrm{AmH})(\mathrm{RO_2}) - k_2(\mathrm{PhOH})(\mathrm{RO_2}) - k_3(\mathrm{Am\cdot})(\mathrm{RO_2}) - k_4(\mathrm{PhO\cdot})(\mathrm{RO_2}),$$

$$\frac{d(\mathrm{Am\cdot})}{dt} = k_1(\mathrm{AmH})(\mathrm{RO_2}) + k_6(\mathrm{PhO\cdot})(\mathrm{AmH}) - k_3(\mathrm{Am\cdot})(\mathrm{RO_2}) - k_5(\mathrm{Am\cdot})(\mathrm{PhOH}),$$

$$\frac{d(\mathrm{PhO\cdot})}{dt} = k_2(\mathrm{PhOH})(\mathrm{RO_2}) + k_5(\mathrm{Am\cdot})(\mathrm{PhOH}) - k_4(\mathrm{PhO\cdot})(\mathrm{RO_2})$$

$$- k_6(\mathrm{PhO\cdot})(\mathrm{AmH}),$$

$$-\frac{d(\mathrm{AmH})}{dt} = k_1(\mathrm{AmH})(\mathrm{RO_2}) + k_6(\mathrm{PhO\cdot})(\mathrm{AmH}) - k_5(\mathrm{Am\cdot})(\mathrm{PhOH}),$$

$$-\frac{d(\mathrm{PhOH})}{dt} = k_2(\mathrm{PhOH})(\mathrm{RO_2}) + k_5(\mathrm{Am\cdot})(\mathrm{PhOH}) - k_6(\mathrm{PhO\cdot})(\mathrm{AmH}).$$

Assuming

$$\frac{d(\mathrm{RO_2})}{dt} = 0, \qquad \frac{d(\mathrm{Am\cdot})}{dt} = 0, \qquad \frac{d(\mathrm{PhO\cdot})}{dt} = 0,$$

we arrive at the following expression for the ratio of the rates of consumption of the inhibitors:

$$\frac{d(\mathrm{AmH})/dt}{d(\mathrm{PhOH})/dt} = \frac{k_1(\mathrm{AmH})}{k_2(\mathrm{PhOH})}\,\frac{1 + 2\dfrac{k_6}{k_1k_4W_i}\,[k_1(\mathrm{AmH}) + k_2(\mathrm{PhOH})]^2}{1 + 2\dfrac{k_5}{k_2k_3W_i}\,[k_1(\mathrm{AmH}) + k_2(\mathrm{PhOH})]^2}.$$

After simple transformations this expression can be represented as the equation of a straight line

$$\frac{A-1}{2B^2} = \frac{k_6}{k_1k_4W_i} - A\,\frac{k_5}{k_2k_3W_i},$$

where

$$A = \frac{d(\mathrm{AmH})/dt}{d(\mathrm{PhOH})/dt}\,\frac{k_2(\mathrm{PhOH})}{k_1(\mathrm{AmH})}; \qquad B = k_1(\mathrm{AmH}) + k_2(\mathrm{PhOH}).$$

The quantities (AmH) and (PhOH), as well as the rates of consumption of the inhibitors, are determined experimentally from kinetic curves of the change in inhibitor concentration with time.

By plotting the dependence of $(A-1)/2B^2$ on A, one can obtain the ratios of the constants k_5/k_3 and k_6/k_4, provided that the values of the constants k_1 and k_2, and also W_i, are known.

Treating in this way the experimental consumption curves of neozone-D and tetraisopropylphenolphthalein when jointly present in the oxidation process of ethylbenzene (^{4}), we obtained a straight line in the coordinates $[(A-1)/2B^2]$

$-A$, and hence the ratios of the reaction-rate constants: $k_5/k_3 = 4 \cdot 10^{-4}$ and $k_6/k_4 = 9.5 \cdot 10^{-6}$ (Fig. 3).

The choice of precisely this pair of inhibitors is due to the fact that here a significant consumption of neozone-D is observed in the initial segment of the reaction, and the determination of the concentration and rate of consumption of the inhibitors can be carried out with a greater degree of accuracy.

The obtained values of the ratios of the constants make it possible to judge the probability of occurrence of the corresponding elementary stages of the process. The ratios of the rates of reactions 5 and 3, and 6 and 4, are respectively equal to

$$\frac{W_5}{W_3} = \frac{k_5}{k_3}\frac{(\mathrm{Am}\cdot)(\mathrm{PhOH})}{(\mathrm{Am}\cdot)(\mathrm{RO}_2)}; \tag{7}$$

$$\frac{W_6}{W_4} = \frac{k_6}{k_4}\frac{(\mathrm{PhO}\cdot)(\mathrm{AmH})}{(\mathrm{PhO}\cdot)(\mathrm{RO}_2)}. \tag{8}$$

The concentration of RO_2 radicals can be obtained by solving algebraic equations (1)–(3)

$$(\mathrm{RO}_2) = \frac{W_i}{2[k_1(\mathrm{AmH}) + k_2(\mathrm{PhOH})]}.$$

Under the conditions of our experiments, $(\mathrm{RO}_2) = 3.3 \cdot 10^{-9}$ mole/liter; the constants k_1 and k_2 were determined by the chemiluminescence method [6] and are respectively $1.3 \cdot 10^5$ and $1.1 \cdot 10^5$ liter/mole • sec [4]. It follows from equation (7) that the rates of reactions (5) and (3) become comparable at an inhibitor concentration $\sim 10^{-5}$ mole/liter, i.e., 10 times smaller than the initial $(\mathrm{PhOH}) = 1.2 \cdot 10^{-4}$ mole/liter used in our experiments. This indicates that reaction (5) is indeed the principal pathway by which the Am· radical reacts.

Analogous calculation for the rates of reactions (6) and (4) shows that reaction (6) plays a minor role in such systems, since its rate under the conditions of our experiments is ~ 3 times lower than the rate of reaction (4).

Fig. 3. Consumption of inhibitors in their joint presence in the oxidation reaction of ethylbenzene initiated by dinitrile of azoisobutyric acid. **1** –neozone-D; **2** –tetraisopropyldiaminodiphenylmethane; temperature 70°, $W_i = 2 \cdot 10^{-7}$ mole/l • sec; **3** –straight line in coordinates $\frac{A-1}{2B^2}$–A, obtained by treating these experimental dependences according to the scheme given.

Thus, the proposed scheme of hydrocarbon oxidation under the action of inhibitor mixtures, in which the interaction of the amine radical with phenol, accompanied by regeneration of the amine, is taken into account, describes well the experimentally observed features of the joint action of these inhibitors.

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Note: Figure translations are in progress. See original paper for figures.