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Abstract

Full Text

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INTERACTION OF TWO INHIBITORS IN THE REACTION OF HYDROCARBON OXIDATION

It is known that the retarding action of inhibitors on chain oxidation reactions is due to chain termination through the interaction of the free radicals that carry the chain process with inhibitor molecules. The rate of consumption of an inhibitor and, consequently, the duration of the induction period are determined by the concentration of radicals in the system (^{1}). In the presence of two inhibitors in the system, the rate of consumption of each of them should be determined by the value of the rate constant for its interaction with free radicals and by the concentration of the given inhibitor. Therefore one might have expected that, in this case, the induction period of the reaction would be additively composed of the induction periods caused by each inhibitor separately.

However, in a number of cases it turns out that a combination of two inhibitors produces an effect much stronger (or much weaker) than the sum of the actions of each of them separately (synergism or antagonism). It is known, for example, that the induction period for the oxidation of hydrocarbons at a temperature of 160° in the presence of phenyl-β-naphthylamine (neozone-D) and ionol (2,6-di-tert.-butyl-4-methylphenol) is greater than the sum of the induction periods obtained for each of these inhibitors (^{2}).

The phenomenon of synergism observed in the joint action of two inhibitors is widely used in practice, but the reasons for its occurrence have not yet been definitively established. To elucidate the mechanism of action of a pair of inhibitors, one of which belongs to the class of amines and the other to phenols, the present work studied the kinetics of consumption of 2,6-di-tert.-butylphenol and neozone-D during the oxidation of ethylbenzene.

The reaction was carried out at 70° in the presence of an initiator—azobisisobutyric acid dinitrile—at a constant initiation rate

$$W_i = 2 \cdot 10^{-7} \text{ mol/l} \cdot \text{sec.}$$

Under these conditions an unbranched reaction proceeds, since the ethylbenzene hydroperoxide formed is stable and practically does not decompose (^{3}). Thus,

Fig. 1. Consumption of inhibitors during oxidation of ethylbenzene initiated by dinitrile of azoisobutyric acid, under the joint action of two inhibitors (dark symbols) and upon introduction of each inhibitor separately (light symbols); circles—neozone-D, triangles—2,6-di-tert-butylphenol. Temperature 70°. $W_i = 2 \cdot 10^{-7}$ mol/l • sec

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the system under study is extremely simple. Before the start of the experiment, weighed portions of the initiator and of each inhibitor in ethylbenzene solution were introduced into the oxidation cell. The kinetics of inhibitor consumption were followed from the change in its concentration in samples taken at different time intervals after the start of oxidation.

The inhibitors were analyzed spectrophotometrically by the colors formed upon their azo coupling with diazotized *p*-nitroaniline: for neozone-D—in an acidic medium ($\lambda = 535$ mμ), and for 2,6-di-tert.-butylphenol—in a weakly alkaline medium ($\lambda = 590$ mμ).

If only one inhibitor is present in the system (neozone-D or 2,6-di-tert.-butylphenol), it is consumed at a rate equal to half the initiation rate, i.e., one inhibitor molecule reacts with two RO_2 radicals (Fig. 1, open symbols). In the joint presence of these inhibitors the picture changes sharply. The rate of consumption of 2,6-di-tert.-butylphenol remains practically the same as in experiments in which only this inhibitor was used (Fig. 1, filled triangles).

Neozone-D in the presence of 2,6-di-tert-butylphenol is practically not consumed at all, and its concentration remains constant almost until the moment of complete consumption of 2,6-di-tert-butylphenol. After this, neozone-D begins to be consumed at a rate close to $W_i/2$ (Fig. 1, dark circles). This phenomenon is reproduced at different ratios between the concentrations of amine and phenol ($1:1$ and $1:3$) and for different total concentrations of inhibitors.

A similar picture was obtained for other pairs of inhibitors: neozone-D—2,6-di-tert-butyl-4-methylphenol and neozone-D—tetraisopropylphenolphthalein (4) (Fig. 2, I). Replacement of neozone-D by another amine—diphenylamine—in the pair with 2,6-di-tert-butylphenol (Fig. 2, II) also led to a strong retardation of amine consumption in the presence of the substituted phenol. In Fig. 2, II the consumption curves of each of these inhibitors when introduced into the system separately are also presented.

Fig. 1. Consumption of inhibitors during oxidation of ethylbenzene, initiated by dinitrile of azoisobutyric acid, under the joint action of two inhibitors (dark symbols) and upon introduction of each inhibitor separately (light symbols);

Fig. 2. Consumption of inhibitors during oxidation of ethylbenzene initiated by dinitrile of azoisobutyric acid, under the joint action of two inhibitors (dark symbols) and upon introduction of each inhibitor separately (light symbols): I —a—neozone-D, b—tetraisopropylphenolphthalein; II—v—diphenylamine, g—2,6-di-tert-butylphenol. Temperature 70°. $W_i = 2 \cdot 10^{-7}$ mol/l • sec

Figure 2: Fig. 2. Consumption of inhibitors during oxidation of ethylbenzene initiated by dinitrile of azoisobutyric acid, under the joint action of two inhibitors (dark symbols) and upon introduction of each inhibitor separately (light symbols): I—a—neozone-D, b—tetraisopropylphenolphthalein; II—v—diphenylamine, g—2,6-di-tert-butylphenol. Temperature 70°. $W_i = 2 \cdot 10^{-7}$ mol/l • sec

circles—neozone-D, triangles—2,6-di-tert-butylphenol. Temperature 70°. $W_i = 2 \cdot 10^{-7}$ mol/l • sec

Fig. 2. Consumption of inhibitors during oxidation of ethylbenzene, initiated by dinitrile of azoisobutyric acid, under the joint action of two inhibitors (dark symbols) and upon introduction of each inhibitor separately (light symbols): I—*a*—neozone-D, *b*—tetraisopropylphenolphthalein; II—*v*—diphenylamine, *g*—2,6-di-tert-butylphenol. Temperature 70°. $W_i = 2 \cdot 10^{-7}$ mol/l • sec

When comparing the curves it is necessary to take into account that, unlike 2,6-di-tert-butylphenol, diphenylamine has an inhibition coefficient close to three. Diphenylamine was analyzed by the method described in (5).

To explain the causes of this phenomenon, it was first necessary to establish whether the observed rates of consumption of the inhibitors are in accordance with the values of the rate constants for their interaction with free radicals (K_i). We measured the values of K_i for all the inhibitors used in the present work by means of the recently proposed chemiluminescent method for determining the rate constants of interaction of inhibitors with radicals carrying the chain process (6). This method is based on quenching of chemiluminescence arising during recombination of RO_2 radicals upon introduction of an inhibitor into the reaction zone. The chemiluminescence quenching curve by various additions of neozone-D is shown in Fig. 3. The tangent of the angle of the anamorphosis of this curve in the coordinates

$$\sqrt{\frac{I_0}{I}}$$

(where I_0 is the emission intensity in the absence of inhibitor, I is the in-

the glow intensity after introduction of the inhibitor) on the inhibitor concentration gives the value $K_i/\sqrt{W_i K_6}$.

Knowing W_i and the rate constant for recombination of RO_2 radicals (K_6) (for ethylbenzene $K_6 = 1.9 \cdot 10^7$ l/mol • sec (7)), it is easy to find the value of K_i.

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

Inhibitors	2,6-di-tert.-butylphenol	Diphenylamine	Tetraisopropylphenol	Neozon-D
$K_i \cdot 10^{-4}$, l/mol • sec	0.95	4.4	11.4	13

Fig. 3. Curve of chemiluminescence quenching by various concentrations of 2,6-di-tert.-butylphenol and its anamorphosis in the coordinates $\sqrt{I_0/I}$, [InH]

The value of K_i for neozon-D is 13.5 times greater than for 2,6-di-tert.-butylphenol. Consequently, at equal concentrations, neozon-D should have been consumed at a rate 13.5 times greater than 2,6-di-tert.-butylphenol. In the experiment, however, we observe the opposite picture. The same conclusion is led to by comparison of the values of K_i for the other pairs of inhibitors as well. Thus, the phenomenon we have discovered—the inhibition of amine consumption in the presence of phenols—cannot be explained by differences in the effectiveness of these inhibitors.

We assumed that in this system the inhibitor radical formed in the interaction of an amine with RO_2 abstracts hydrogen from the phenol and is converted back into an amine. The amine concentration thus changes only insignificantly as long as phenol is present in the system.

This assumption is consistent with the literature data ([8],[9]), from which it follows that radicals of the type $R_1\dot{N}R_2$ are active and readily react with polymers and hydrocarbons, forming the corresponding compounds R_1NHR_2.

The results obtained point to one more interesting fact concerning the mechanism of the joint action of two inhibitors. It is known that the diphenylamine radical in an oxidizing hydrocarbon medium is readily converted into a radical of the type R_1NOR_2 ([10],[11]). We assumed that, in our case, the radical apparently reacts with phenol more rapidly than it is converted into a nitroxyl radical. Indeed, if this were not so, amine regeneration would not occur and inhibition of amine consumption in the presence of phenol would not be observed.

Fig. 4. Accumulation of diphenylamine (increase in the optical density of the color upon azo coupling of diphenylamine with diazotized *p*-nitroaniline) during the initiated oxidation of ethylbenzene with the addition of tetraphenylhydrazine ($5 \cdot 10^{-4}$ mol/l). 1 —in the presence of ionol ($1 \cdot 10^{-3}$ mol/l), 2 —without ionol. Temperature 70°. $W_i = 2 \cdot 10^{-7}$ mol/l • sec.

Direct experimental proof of such an interaction of the radical $R_1\dot{N}R_2$ with phenol was obtained by us in an experiment on the initiated oxidation of ethylbenzene in the presence of ionol and tetraphenylhydrazine, which is···

serves as a source of diphenylazotyl radicals $[(Ph)_2\dot{N}]$. In this system, appreciable amounts of diphenylamine $(Ph)_2NH$ accumulate (Fig. 4).

It is quite possible that the results of the present work will subsequently help to explain the causes of the synergism observed for such pairs of inhibitors at higher temperatures.

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