OPTICAL COMPOSITIONS OF SYNERGISTIC MIXTURES IN OXIDATION PROCESSES

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The effect of inhibitor mixtures (aromatic amines, phenols) in oxidation processes is frequently non-additive (synergism). The mechanism of inhibition in systems of this kind can be nicely described through a scheme of the following type \([1,2]\):

\[
\begin{align*}
\text{RH} & \xrightarrow{H^+} \text{RO}_2^- \\
\text{RO}_2^- + \text{RH} & \rightarrow \text{ROOH} + \text{R}^-(\text{RO}_2^-) \\
\text{ROOH} & \xrightarrow{\Delta} 2\text{RO}_2^- \\
\text{RO}_2^- + \text{RO}_2^- & \rightarrow \text{Products} \\
\text{AmH}(\text{Ph'O}) + \text{RO}_2^- & \rightarrow \text{Am}^-(\text{Ph'O}) + \text{ROOH} \\
\text{Ph'O} + \text{RO}_2^- & \rightarrow \text{Ph'O}^- + \text{ROOH} \\
\text{Am}^-(\text{Ph'O}) + \text{RO}_2^- & \rightarrow \text{Products} \\
\text{Ph'O}^- + \text{RO}_2^- & \rightarrow \text{Products} \\
\text{Am}^-(\text{Ph'O}) + \text{RH} & \rightarrow \text{AmH}(\text{Ph'O}) + \text{R}^-(\text{RO}_2^-) \\
\text{Am}^-(\text{Ph'O}) + \text{Ph'O}^- & \rightarrow \text{AmH}(\text{Ph'O}) + \text{Ph'O}^- \\
\end{align*}
\]

The regeneration of the effective inhibitor through reaction 9', and the suppression of free-radical formation through reaction (10), are the factors responsible for the synergistic effect (SE). It has been shown in [3] that the magnitude of such effect is determined by the effectiveness of each of the inhibitors and the kinetic parameters of the oxidizing substrate.

The present paper will describe the study of the SE of an inhibitor mixture acting through the mechanism of (1).

EXPERIMENTAL

Study has been made of the kinetics of hydroperoxide (ROOH) buildup in the oxidation of ethylbenzene at 120°C, the inhibitors being N-phenyl-\(\beta\)-naphthylamine (neozone-D) (n-D), 2,6-di-tert-butylphenol (DTBPh), and various mixtures of these two compounds with total inhibitor concentrations in the \((0.75-15) \cdot 10^5\) moles/liter range \((\text{inH})_{\text{tot}}\). The data obtained here were used to relate the length of the induction period \(r\) and the mixture composition at various values of \([\text{inH}]_{\text{tot}}\) (Fig. 1). The quantity \(r\) was defined as the time required for building up a 1 \(\cdot 10^{-2}\) mole/liter ROOH concentration in the system, ROOH being determined iodometrically.

Similar relations were developed theoretically. Following the methods of [4], the system of differential equations arising from mechanism (1) was solved on a BESM-6 computer. Here it was necessary to draw on
Fig. 1. Variation of the length of the induction period (r) with the composition of the neozone-D--DTBPh mixture, at various values of [InH]_{tot}, the total inhibitor concentration. a) Experimental values, obtained at the following values of [InH]_{tot} (mole/liter) \cdot 10^5: 1) 0.75; 2) 1.45; 3) 5.0; 4) 15.0 (oxidation of ethylbenzene, at 120°C). b) Values calculated for the same system, at the following values of [InH]_{tot} (mole/liter \cdot 10^5): 1) 1.0; 2) 5.0; 3) 15.0; 4) 50.0; 5) 500.0.

Fig. 2. Variation of SE (r_{mmx}/r_{ph}) with the total concentration of the neozone-D--DTBPh mixture, for ethylbenzene oxidation, using the data of Fig. 1: a) experimental; b) calculated.

measured values of the various rate constants for ethylbenzene oxidation inhibited n-D--DTBPh mixtures [2]:

\[
W_0 = 1.5 \cdot 10^{-5} \text{ mole/liter \cdot sec}, \quad k_0 = 25 \text{ mole/liter \cdot sec}, \quad k_3 = 0.64 \cdot 10^{-6} \text{ sec}^{-1}; \quad k_4 = 1.9 \cdot 10^7 \text{ liter/mole \cdot sec},
\]

\[
k_7 = 0.325 \cdot 10^4 \text{ liter/mole \cdot sec}, \quad k_9^0 = 0.25 \cdot 10^6 \text{ liter/mole \cdot sec}, \quad k_9^0/k_9^1 = 5 \cdot 10^{-3}; \quad k_9^0/k_9^1 = 1.5 \cdot 10^{-4}, \quad \text{and} \quad k_4/k_3 = 3 \cdot 10^{-3}.
\]

The value of [InH]_{tot} was varied from 1 \cdot 10^5 to 500 \cdot 10^5 moles/liter.

Fig. 3. Variation of SE (r_{mmx}/r_{ph}) with the neozone-D--DTBPh mixture composition, at various values of [InH]_{tot}, from the data of Fig. 1: a) experimental; b) calculated.