CORRELATION BETWEEN THE OXIDIZABILITY OF DITHIOCARBAMATES OF METALS AND THEIR INHIBITING ACTIVITY IN OXIDATION PROCESSES

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In a study of the inhibition of the liquid phase oxidation of hydrocarbons by complex compounds of copper, we detected an effective inhibition of the oxidation by sulfur-containing chelates, bis-(α-thiopicolinamidines) [1] and bis(hexamethyleniminedithiocarbamate) copper (II) [2] (HMIDTC-Cu) on account of the interaction of copper complexes with free radicals, carrying the oxidation chains. It was shown that the inhibiting properties of the investigated chelates are due chiefly to the chelate centers Cu(N, S)₂ and Cu(S, S)₂. The inhibiting properties of a number of metal N, N-dialkyldithiocarbamates (DTC) were also established in [3].

In this work we studied the influence of the ligand on the inhibiting activity of N, N-dialkyldithiocarbamates of copper (II):

\[
\begin{align*}
R' & \quad \text{S} \quad \text{S} \quad \text{Cu} \quad \text{S} \quad \text{S} \quad \text{N} \quad \text{R} \\
R & \quad \text{R}' \quad \text{CuH}_{2} (I); \quad R'=\text{t-C}_{6}H_{5}, \quad R'=\text{C}_{6}H_{4}(CH_{3})CH (II); \\
R & \quad \text{R}' \quad \text{CuH}_{2} (III); \quad R'=\text{t-C}_{6}H_{5}, \quad R'=\text{C}_{6}H_{4}(CH_{3})CH (IV) \\
R & \quad \text{R}' \quad \text{CuH}_{2}, \quad R'=\text{C}_{6}H_{4}(CH_{3})CH (IV)
\end{align*}
\]  

and the influence of the nature of the central metal atom in a comparison of the complex (II) with its Ni and Zn analogs. The complexes were synthesized from the corresponding dithiocarbamates of Na and acetates of Cu, Ni, and Zn, and were characterized by elementary analysis and the melting points [4, 5].

The absorption of O₂ under conditions of low-temperature (75°) oxidation of ethylbenzene, initiated by azobisisobutyronitrile ([AIBN] = 4.9 · 10⁻³ M, W₁ = 4.5 · 10⁻⁷ mole/liter · sec) was studied. As can be seen from Fig. 1, additions of the complexes (I), (III), and (IV), as well as (II) [2], induced an inhibition of oxidation (curves 3-6). The value of the induction period is 65-85 min and increases in the series (IV) < (I) < (II) < (III). The appearance of an induction period in the process of initiated oxidation of ethylbenzene after the introduction of DTC unambiguously indicates an interaction of the chelates with free radicals, leading to termination of the oxidation chains.

The mechanism of this interaction has not yet been established. In a study of the inhibition of processes of oxidation by zinc dithiophosphates [6], it was suggested that the site of attack by the radicals in the chelate is the sulfur atoms. In [1, 2] it was suggested that free radicals interact with the metal ion, resulting in a transfer of electrons from the ligand to the free radical, which in this case is an oxidizing agent. Such a transfer of electrons is promoted by the covalent nature of the Cu–S bond in the investigated DTC-Cu [7]. As a result of the interaction of RO₂⁺ with the chelate, the ligand will be oxidized without any change in the valence state of copper, as was also observed in [1, 8]. An analogous mechanism has been established for the oxidation of ascorbic acid by molecular oxygen, catalyzed by metal ions [9].

The conversion of the chelate (I) during the process of oxidation was studied. The compound behaves entirely analogously to the complex (II) [2]: it is consumed during the induction period of oxidation, with the formation of an intermediate paramagnetic product. The method of analysis of (I) and its conversion products by the ESR method was described in [2].
Fig. 1. Kinetics of the absorption of oxygen in the oxidation of ethylbenzene. 1) Without additives. In the presence of: 3) (IV); 4) (I); 5) (II); 6) (III); 7) HMIDPC-Ni; 8) HMIDPC-Zn. 2) Accumulation of Cu(I) during oxidation in the presence of (I), 75°, [AIBN] = 4.9·10^{-3} M, [chelate] = 5·10^{-4} M.

Fig. 2. Kinetics of the consumption of the complex (II) in the initiated oxidation of ethylbenzene, 75°, [AIBN] = 4.9·10^{-3} M. The arrow marks the moment of introduction of the sodium salt.

The consumption of (I) evidently is not accompanied by any change in the valence state of copper. In the case of the introduction of excess DTC-Na into the system at some time after the beginning of the reaction, a practically complete regeneration of the initial chelate (I) is observed (Fig. 2). This is evidence that during the breakdown of the complex, copper remains divalent, while the products of oxidation of the initial ligand (DTCOx) are weakly bound to the central metal ion. Therefore, in the presence of DTC-Na, the following reactions are possible:

\[
\begin{align*}
Cu(DTC)_2 & \rightarrow RO^- \rightarrow Cu(DTCOx) + \\
Cu(DTCOx) & \rightarrow Na DTC \rightarrow Cu(DTC)_2 + Na(DTCOx)
\end{align*}
\]

Moreover, during the induction period, Cu(I) cannot be detected in a system containing the chelate (I); it was analyzed spectrophotometrically at 545 nm in the form of a colored complex with biquinolyl [10]. It appears in small amounts after the oxidation process emerges from the induction period (see Fig. 1, curve 2), evidently as a result of redox conversions of copper with the participation of the hydroperoxide formed in the course of the oxidation.

A comparison of the data obtained for the chelates (I) and (II) [2] shows a complete analogy in their behavior in the case of inhibition of the oxidation of ethylbenzene. The complexes (III) and (IV) were investigated in less detail; however, the basic effects of inhibition also occurs for them, and the chelates (I)–(IV) differ by no more than 30% with respect to inhibiting effectiveness (with respect to the value of the induction period). Thus, the structure of the ligand influences only the magnitude of the effect of inhibition, and not its mechanism.

Since the DTC are subjected to oxidative conversions in the process of inhibition of the oxidation of ethylbenzene, we studied the reactivity of the complexes (I)–(IV) in the model reaction of polarographic oxidation on a rotating Pt-electrode in acetonitrile solution according to the method of [11] (ON-102 polarograph). In all cases a polarographic wave was observed, corresponding to the oxidation of the initial dithiocarbamate.

In a comparison of the half-wave potentials cited in Table 1 with the induction periods oxidation in the presence of the corresponding chelate (see Fig. 1), it can be seen that a correlation is observed between the inhibiting activity of the chelates and their tendency for oxidation. The more readily the chelate is oxidized, the more effective its inhibiting action. The pattern obtained confirms the fact that the inhibition by DTC-Cu is associated with the oxidation of the latter in the reaction with free radicals.

The increase in the effectiveness of the interaction of DTC with free radicals in ethylbenzene undergoing oxidation and the drop in the half-wave potentials in the case of polarographic oxidation in the series