HYDROCARBON OXIDATION IN THE PRESENCE OF SULFUR-CONTAINING MONOVALENT COPPER COMPOUNDS

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Nitrogen- and sulfur-containing Cu(II) complexes are effective inhibitors of liquid-phase hydrocarbon oxidation at 75-125°C [1, 2]. Inhibition here is the result of deactivation of the RO₂⁻ peroxide radicals resulting from hydrocarbon oxidation through interaction with the complex chelate junctions. It seemed of interest to investigate the possibility of oxidation inhibition through sulfur-containing Cu(I) complexes.

With this end in view, study was made of the oxidation of ethylbenzene (EB) by O₂ in the presence of adducts of Cu(I) acetate with N,N'-derivatives of thiourea

\[ \text{R}^1\text{NH} - \text{C} = \text{S} \quad \text{S} = \text{C} \quad \text{NHR}^2 \]

whose Cu(I) atoms are directly surrounded by either S or O atoms [3].

EXPERIMENTAL

The ethylbenzene used here had been purified by standard methods. Hydrocarbon oxidation by O₂ was carried out at 75°C in the presence of azobisisobutyronitrile (AIBN), the inhibitor, at a concentration of 4.9 \times 10^{-3} \text{ mole/liter}. Complex (I) was obtained from NIikhIMPOLIMER; complexes (II) and (III) were obtained from the laboratories of the Moscow State University. Oxidation of EB was followed by observing the O₂ uptake in a manometric system equipped with an automatic pressure regulator.

Polarographic oxidation of (II) was carried out in a Radelkis OH-102 polarograph. A rotating Pt electrode served as the indicator electrode [4].

Analysis for Cu(I) was carried out spectrophotometrically, working at 545 nm and using the colored complex formed with biquinoline.

DISCUSSION OF RESULTS

Addition of (I)-(III) not only inhibited the oxidation of EB, but also led to the appearance of an induction period (τ) on the kinetic oxygen up-take curves (Fig. 1). Oxidation inhibition curves of this type are characteristic of cases in which inhibition results from RO₂⁻ destruction through interaction with a complex additive. The fact that the Ni analog of complex (I) did not inhibit oxidation is an indication of the importance of the presence of the Cu(I) for RO₂⁻ interaction with the complex. Derivatives of free thiourea (TU) complexes either did not inhibit the oxidation at all [ligands of (I) complexes], or inhibited it only weakly [ligands of (II) complexes].

For all three complexes, the length of the induction period increased linearly with increasing inhibitor concentration. Determined from τ, the respective values of the inhibition coefficient \( f = W_1 \cdot \tau / (\text{II}, \text{III}) \)\(_0\), for (I), (II), and (III) were 1.7, 1.4, and 1.2.


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These values are greater than the inhibition coefficient \( f = 0.8 \) of Cu(II) bis(\( \alpha \)-thiopicolineanilide) [Cu(tpa)\(_2\)] in EB oxidation under these same conditions. Compounds (I)-(III) were, however, less active than Cu(II) bis(N,N'-dialkyldithiocarbamate) [Cu(dtc)\(_2\)] with \( f = 4.5 \) [5]. From this it followed that the inhibiting action of sulfur-containing Cu complexes is not fixed by the oxidation state of the central metal atom alone, the ligand type being a fact of considerable importance here.

The inhibiting activity of Cu(II) dialkyldithiocarbamates in EB oxidation was correlated with the half-wave potential \( (E_{1/2}) \) for complex oxidation on the Pt electrode, the easier the oxidation the more effective the complex in inhibiting the oxidation. The existence of such correlation showed the degree of inhibition to be largely determined by electron transfer from the original complex to the free radical, despite the fact that complex reaction products may well have had some effect on the overall inhibition (i.e., on the value of \( f \)).

The TU adducts also underwent gentle polarographic oxidation on the Pt electrode. Comparison of the \( E_{1/2} \) values for (II) and Cu(tpa)\(_2\) taken from this work, and the \( E_{1/2} \) value for Cu(dtc)\(_2\) taken from [2], with the \( f \) values for these same complexes given in Table 1, showed the behavior of (II) to be entirely consistent with the activities of the Cu(II) compounds, and this despite the marked differences in chelate junctions and reaction mechanisms. The inhibiting action associated with Cu(tpa)\(_2\) and Cu(dtc)\(_2\) traces back to ligand oxidation, a process involving Cu(II) without alteration of the Cu oxidation state [2], whereas the inhibiting action resulting from the TU complexes studied here involves Cu(I) oxidation, as will be shown below.

It is seen from curve 1 of Fig. 2 that Cu(I) was consumed during the induction period \( \tau \) of a complex (II) - inhibited oxidation. The fact that the disappearance of Cu(I) was not the result of direct \( O_2 \) oxidation of the complex was indicated by noting that the disappearance rate was considerably lower in oxidations without addition of the complex (curve 2). The Cu(I) concentration varied with time, but in a complex manner, first passing through a minimum and then rising again to eventually reach a stationary value. The minimum on the concentration curve corresponded with the end of the induction period. Complex (I) behaved in a similar manner.

The disappearance of Cu(I) could have been the result of oxidation through the reaction: Cu(I) + RO\(_2^\cdot\) \rightleftharpoons Cu(II) + RO\(_2^\cdot\). The hydroperoxide (HP) of \( \alpha \)-phenylethyl should appear in the system as soon as EB oxidation begins (i.e., at the end of the induction period), and a new stationary Cu(I) concentration should be established, the hydroperoxide reducing the metal in the higher oxidation state and oxidizing the metal ions in the lower oxidation state [6]

\[
\text{ROOH} + \text{Cu(I)L} \rightarrow \text{RO}^\cdot + \text{Cu(II)(OH)L} \\
\text{ROOH} + \text{Cu(II)L}_2 \rightarrow \text{RO}_2^\cdot + \text{Cu(I)L} + \text{HL}
\]

Compounds (I)-(III) differed in their ability to increase the EB oxidation rate at the end of the induction period (comparison being with the oxidation rate observed in the presence of the initiator alone), an effect which comes into play once the complex concentration has reached a certain threshold value (Fig. 3). It could be assumed that this was a reflection of catalysis by the products from RO\(_2^\cdot\) interaction with the adducts (Cu-containing compounds and products from oxidation of the organic portion of the complex).

Since a similar increase in oxidation and destruction rates following complete inhibitor (metal complex) consumption has been reported in the oxidation of tetralin and other polymeric substances, the possibility suggests itself of using these complexes in preparing polymers with controlled decomposition rates [7, 8].