COMPLEX COMPOUNDS OF COPPER WITH o-PHENANTHROLINE AS CATALYSTS OF THE OXIDATION OF ETHYL BENZENE

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The use of complex compounds of metals of variable valence as catalysts of the oxidation of organic substances in a number of cases permits a substantial increase in the rate of these processes. The nature of the ligand bonded to the metal ion has a significant influence on the properties of the catalysts. A quantitative characterization of the influence of the structure of the ligand on the catalytic properties of metals was established in our investigation of the rate of decomposition of isopropylbenzene hydroperoxide to free radicals in the presence of substituted N-aryl-O-vanilaliminates of Co(II) (chain branching during oxidation) [1].

The use of complex compounds of metals opens up ways not only to increase the rate of the processes, but also to increase their selectivity. Thus, catalysis by complex compounds of molybdenum substantially increases the yield of oxides in the oxidation of unsaturated compounds [2]. The directed oxidation of ethylbenzene to acetophenone was achieved using tris-(triphenylphosphines) of metals of the platinum group as catalysts [3]. Although the list of such examples could be continued, we must state that the catalysis by complex compounds in oxidation reactions has practically not yet been investigated.

It is known that complexes of copper with o-phenanthroline in aqueous solutions are good catalysts of the oxidation of such difficultly oxidized compounds as methanol [4]. In this work we studied the catalytic action of mixtures of copper stearate with o-phenanthroline in the oxidation of ethylbenzene. The reaction was studied both at low temperature (50-80°) according to the absorption of oxygen on a manometric apparatus [5] and at a higher temperature (120°) according to the rate of consumption of ethylbenzene and the accumulation of hydroperoxides, alcohols, ketones, and acids.

EXPERIMENTAL METHOD

The initial hydrocarbon was analyzed on a Chrom-3 gas–liquid chromatograph. Polyethylene glycol-1500, applied in an amount of 5% of the weight of the carrier on adsorbent-G (40-60 mesh), was used as the packing, column length 2 m, diameter 3 mm; column temperature 120°; carrier gas argon; rate of delivery of the carrier gas 1.5 liters/h. The samples collected during the reaction were analyzed for their content of oxidation products of ethylbenzene: hydroperoxides, alcohols, ketones, and acids. The content of impurities was determined iodometrically. The alcohols were analyzed on a UR-20 IR spectrometer in the region of 3580 cm^{-1}, cuvette thickness 0.41 mm. The acids were titrated with alcoholic alkali. The ketone concentration was established by back titration (at −70°) of the hydrochloric acid liberated in the interaction of ketones with hydroxylamine hydrochloride. Thoroughly purified ethylbenzene, containing no oxidation products, was subjected to oxidation.

DISCUSSION OF RESULTS

Copper stearate in a mixture with o-phenanthroline manifests a substantial catalytic effect in the oxidation of ethylbenzene by molecular oxygen at 120°. The rate of oxidation of ethylbenzene at certain ratios of the components of the catalyst is almost two orders of magnitude greater than the rate of the uncatalyzed reaction (Fig. 1, curves 1, 4). The effect is apparently due to the formation of a complex compound of copper with o-phenanthroline (o-Ph), since $CuSt_2$ and o-phenanthroline in themselves are weak oxidation

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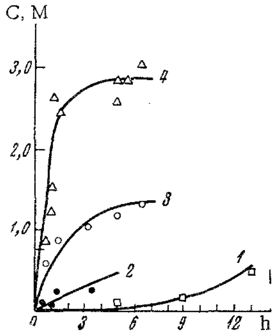

Fig. 1

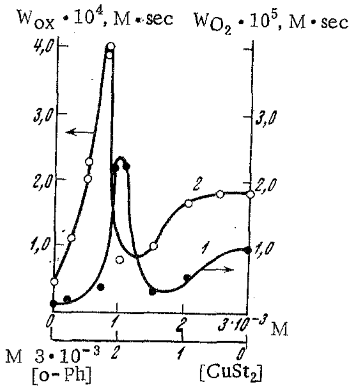

Fig. 2

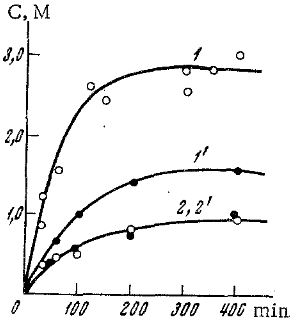

Fig. 3

Fig. 1. Kinetic curves of the consumption of ethylbenzene: 1) pure ethylbenzene: 2) [o-Ph] $= 3 \cdot 10^{-3}$ M; 3) [CuSt$_2$] $= 3 \cdot 10^{-3}$ M; 4) [CuSt$_2$] $= 0.75 \cdot 10^{-3}$ M, [o-Ph] $= 2.25 \cdot 10^{-3}$ M.

Fig. 2. Dependence of the rate of oxidation of ethylbenzene on the concentration of [o-Ph] and [CuSt$_2$] at 60 (1) and 120° (2); [CuSt$_2$] + [o-Ph] $= 3 \cdot 10^{-3}$ M.

Fig. 3. Kinetic curves of the consumption of ethylbenzene (1, 2) and accumulation of the sum of hydroperoxides, alcohols, ketones, and acids (1', 2') in the oxidation of ethylbenzene in the presence of o-Ph and [CuSt$_2$]: 1, 1') [o-Ph]/[CuSt$_2$] = 3 : 1; 2,2') [o-Ph]/[CuSt$_2$] = 1 : 1; [CuSt$_2$] + [o-Ph] $= 3.0 \cdot 10^{-3}$ M, 120°.

catalysts (curves 2 and 3). Extremely interesting patterns were obtained in an investigation of the dependence of the rate of oxidation of ethylbenzene on the composition of the catalyzing mixture at a constant total concentration of the components of the catalyst (Fig. 2, curve 2). With increasing CuSt$_2$ content in the mixture, at first, an increase in the reaction rate is observed, then at a ratio [o-Ph]/[CuSt$_2$] = 3 : 1, a maximum rate of oxidation is reached. When the ratio [o-Ph]/[CuSt$_2$] is further reduced, the rate of oxidation of ethylbenzene passes through a minimum (the ratio [o-Ph]/[CuSt$_2$] at the point of the minimum is close to 1 : 1). The maximum value of the reaction rate is more than twice as great as the rate of oxidation in the presence of CuSt$_2$ alone; the minimum value proves to be less than the rate of oxidation in experiments with CuSt$_2$ without additions of o-phenanthroline.

The dependence of the rate of oxidation of ethylbenzene on the composition of the CuSt$_2$–o-Ph mixture in the low-temperature oxidation of ethylbenzene is of an analogous nature. In this case the rate of absorption of oxygen was measured at 60° (see Fig. 2, curve 1). It was preliminarily demonstrated that the consumption of oxygen is due virtually only to oxidation of ethylbenzene, since the oxidation of o-phenanthroline in an inert solvent (anisole) proceeds at negligible rates. From a comparison of curves 1 and 2, it is evident that the positions of the maximum and minimum depend little on the temperature of the reaction. The ratio of the o-phenanthroline and copper stearate concentrations also substantially influences the composition of the oxidation products of ethylbenzene. Table 1 presents the composition of the basic oxidation products of ethylbenzene at ratios [o-Ph]/[CuSt$_2$] corresponding to maximum and minimum rates of oxidation of ethylbenzene after 6 h of oxidation.

From a consideration of the table it is evident that a mixture of [CuSt$_2$] with o-Ph promotes predominant formation of acetophenone in comparison with the uncatalyzed reaction, which is characterized by the formation of approximately equal amounts of acetophenone and methylphenylcarbinol. At the minimum reaction rate (ratio [o-Ph]/ [CuSt$_2$] = 1 : 1), the only oxidation product is acetophenone (the amount of acetophenone formed practically coincides with the amount of the hydrocarbon consumed).

At a composition of the mixture [o-Ph]/[CuSt$_2$] = 3 : 1 (at the maximum oxidation rate), acetophenone will also be the basic oxidation product. However, in this case a new reaction pathway appears, according to which up to 50% of the total amount of the reacted ethylbenzene is consumed. Possibly ethers or oxygen-containing polymer products are formed under these conditions together with alcohols, ketones, and acids.

In a consideration of the kinetics of the oxidation of ethylbenzene in the presence of CuSt$_2$ and o-Ph, it is necessary to take note of still another interesting peculiarity of this reaction. From the kinetic curves of the consumption of the hydrocarbon at ratios [o-Ph]/[CuSt$_2$] = 3 : 1 (curve 1) and 1 : 1 (curve 2, light

TABLE 1

Product	Concentration (M) at $[o\text{-}P]/[CuSt_2]$	
	3 : 1	1 : 1
Hydroperoxides.	0,0134	0,008
Methylphenylcarbinol . .	0,25	—
Acetophenone	1,3	1,02
Acids.	0,06	0,004
Hydrocarbon consumed .	2,9	1,03

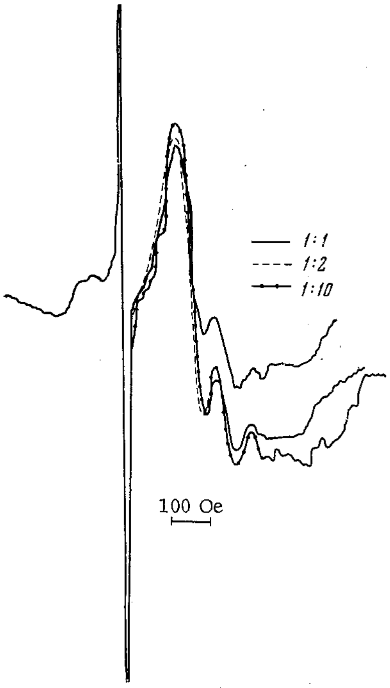

Fig. 4. EPR spectra of complexes of copper with o-Ph at various ratios of the concentrations of o-Ph and $CuSt_2$; $[CuSt_2]_0 = 5 \cdot 10^{-3}$ M, 50°.

points), cited in Fig. 3, it is evident that the rate of consumption of the hydrocarbon gradually drops with increasing depth of the processes, and oxidation practically ceases long before the complete consumption of ethylbenzene. Possibly the observed effect is associated with the formation of products that deactivate the catalyst.

One of the causes of the complex variation of the catalytic activity of a mixture of o-Ph and $CuSt_2$ as a function of the ratio of these substances may be the formation of several complexes with different compositions, differing in their catalyzing properties, in such a system. In an investigation of the oxidation of methanol in aqueous solutions of KOH in the presence of $CuCl_2$ and o-Ph [4], it was hypothesized that the catalytically active particle responsible for the strong acceleration of oxidation is a complex of o-phenanthroline with univalent copper. In our case, in all probability, catalysis is accomplished by complexes of divalent copper with o-Ph, since the appearance of the red color characteristic of complexes of Cu(I) with o-Ph was not observed.

It is known that copper salts can form complex compounds with o-Ph, with the composition $CuSt_2 \cdot n(o\text{-}Ph)$ (where $n = 1, 2, 3$), giving EPR spectra with various values of the splittings and the characteristic values of the g-factors. In view of this, we attempted to detect the formation of complexes of $CuSt_2$ with o-Ph in our system by the EPR method. Copper stearate does not give an EPR signal. The addition of o-Ph leads to the appearance of a signal due to the formation of complexes of copper with o-phenanthroline. It was found in this case that the shape of the EPR lines is unchanged when the ratio $[o\text{-}Ph]/[CuSt_2]$ is varied from 1 : 1 to 10 : 1 (Fig. 4). The values of the g-factor and ΔH_p do not depend on the composition of the mixture and are equal to $g = 2.1371$ and $\Delta H_p = 58$ Oe. The signal intensity is also practically independent of the amount of added o-Ph and is determined only by the $CuSt_2$ concentration. Consequently, only one complex is formed in appreciable amounts in hydrocarbon solutions at 60-80°. Possibly catalytic and inhibiting properties of the complexes of $CuSt_2$ with o-Ph of another composition, formed in our system but not detected according to the EPR spectra, are manifested during the reaction.

One of the possible explanations for the complex dependence of the rate of oxidation on the ratio $[o\text{-}Ph]/[CuSt_2]$ is the hypothesis that the effect obtained is associated with a change not in the composition of the complex, but in the absolute concentration of the complex $CuSt_2 \cdot o\text{-}Ph$. It is known that a change in the concentration of a compound of a metal of variable valence frequently leads not only to a change in the catalytic activity, but also to a transition from catalysis to inhibition of the oxidation process [5] as a result of a complex influence of the catalyst on various elementary steps of the oxidation process.

CONCLUSIONS

1. The effectiveness of the catalytic action of a mixture of copper stearate and o-phenanthroline in the oxidation of ethylbenzene is determined by the ratio of the components of the catalyzing system.

2. In the presence of phenanthroline complexes of copper, ethylbenzene is oxidized primarily to acetophenone. At a ratio of copper stearate and o-phenanthroline ensuring a maximum rate of the process, a new reaction pathway appears, according to which ~50% of the initial ethylbenzene is consumed.

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