- 8. V. I. Nefedov, Poverkhnost', No. 1, 4 (1982).
- 9. Handbook of Solubility [in Russian], Vol. 1, Book 1, Izd. Akad. Nauk SSSR, Moscow-Leningrad (1961), p. 542.
- 10. A. V. Mashkina, Kinet. Katal., 16, 925 (1975).
- V. I. Nefedov, N. P. Sergushin, and M. A. Ryashentseva, Dokl. Akad. Nauk SSSR, <u>213</u>, 600 (1973).
- 12. M. A. Ryashentseva and V. I. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 1642 (1973).
- 13. D. Lichtman, J. H. Craig Jr., V. Sailer, and M. Drinkwine, Appl. Surface Sci., 7, 325 (1981).
- 14. D. Brion, Appl. Surface Sci., 5, 133 (1980).
- 15. A. S. Manocha and R. L. Park, Appl. Surface Sci., <u>1</u>, 129 (1977).

# STRUCTURE AND CATALYTIC PROPERTIES OF COMPLEXES OF COPPER WITH ANKB-2 AMPHOLYTE IN THE REACTION OF OXIDATION OF CYCLOHEXENE

| A. I. Kokorin and V. V. Berentsveig | UDC 541.6:541.128:541.49:546.56: |
|-------------------------------------|----------------------------------|
|                                     | 542,943.7:547.592.2              |

Complexes of transition metal ions with ion-exchangers of different types exhibit catalytic activity in reactions of liquid-phase oxidation of organic compounds [1-4]. In the case of nitrogen-coordinating macroligands, the catalytic reaction is accompanied by partial oxidation of the polymer matrix itself, which results in a decrease in the activity of the starting catalyst [3, 4]. The structure and catalytic properties of complexes of Cu(II) with ANKB-2 ampholyte in the reaction of oxidation of cyclohexene (CH) are studied in this paper.

#### EXPERIMENTAL

ANKB-2 ampholyte was synthesized at the Scientific-Research Institute of Plastics. It is the oxidized copolymer of 2-methyl-5-vinylpyridine and divinylbenzene (DVB) containing  $\alpha$ -picolinic acid chelating groups. The proportion of DVB was ~8%. Complexes of Cu(II) with the ion-exchanger were prepared by treating the resin for 2 days with aqueous solutions of copper nitrate at 20°C in static conditions. The amount of applied copper was determined by trilonometric back titration. Freshly recrystallized  $\alpha$ -picolinic acid (PA) was used as the low-molecular-weight analog for determining the composition and structure of the Cu-(ANKB-2) complex.

The EPR spectra were recorded in quartz ampuls at 77 and 298 K on an EPR-V radiospectrometer from the Institute of Chemical Physics, Academy of Sciences of the USSR. The principal values of the g factor  $(g_{\parallel}, g_{\perp}, g_{0})$  and hyperfine interaction (HFI) constants of the unpaired electron with copper nuclei  $(A_{\parallel}, a_{0})$  and <sup>14</sup>N nitrogen  $(a_{\parallel}^{N}, a_{\perp}^{N}, a^{N})$  were determined from the spectra according to [5].

Liquid-phase oxidation of CH was conducted in a static thermostatted system at 75°C. A reactor of the long-necked flask type was filled with 2 ml of cyclohexene with an initial concentration of hydroperoxide of 0.02 mole/liter. The concentration of catalyst was 25 g/liter.

The products were analyzed on a Khrom-5 chromatograph with a 2-m column packed with Chromaton N-AW with 10% tricyanoethoxypropane; the column temperature was 120°C and the carrier gas (He) flow rate was 30 ml/min. The hydroperoxide was analyzed titrimetrically.

## RESULTS AND DISCUSSION

Figure 1 shows that addition of PA to a 50% water-methanol solution of Cu(II) of constant concentration at pH 5.5-5.9 results in the successive formation of three types of com-

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1727-1730, August, 1988. Original article submitted April 29, 1987.



Fig. 1. EPR spectra of complexes of Cu(II) with  $\alpha$ -picolinic acid at 77 K in a 50% mixture of D<sub>2</sub>O and CD<sub>3</sub>OD: components of the parallel (1-3, 6, 7) and perpendicular (4, 5) orientations of the complexes. [Cu]<sub>0</sub> = 0.005 mole/liter; [Pa]/[Cu] = 1 (1), 2 (2, 4, 6), 10 (3, 5, 7). hfs from  $\alpha \parallel N$  nitrogen nuclei.

plexes in the solution. Subsequent addition of a ligand does not result in a change in the EPR spectrum. The analysis of the hyperfine structure (hfs) of the N nuclei (Fig. 1) permits precisely identifying the complexes  $Cu(PA)_2$  and  $Cu(PA)_3$ . The presence of two N atoms in the coordination sphere of the Cu ion in the  $Cu(PA)_2$  complex is confirmed by the fact that five lines of an additional hfs are observed in the high-field component of the EPR spectrum of this complex in solution. The parameters of the EPR spectra of all complexes at 77 K are reported in Table 1. A comparison of these data with the parameters of the complexes in solution at 298 K (CU(PA):  $a_0 = 60.1$  G;  $g_0 = 2.158$ ;  $Cu(PA)_2$ :  $a_0 = 67.6$  G;  $g_0 = 2.124$ ;  $a^{N} = 11.5$  G) indicates that the composition and structure of the low-molecular-weight complexes do not change on freezing. It was not possible to measure the values of  $a_0$  and  $g_0$  for complex  $Cu(PA)_3$  due to the superposition of its EPR spectrum with the spectrum of  $Cu(PA)_2$  up to [PA]/[Cu] = 80, which indicates the low stability constant of this complex in water-methanol solution at room temperature.

A comparison of the EPR parameters of the Cu(ANKB-2) complexes (Fig. 2, Table 1) with the data for the low-molecular-weight analog PA showed that complexes of the composition Cu[2N, 2O] containing two N and O atoms from two units of the polymer chain are formed in the ampholyte. The slightly lower value of  $g_{\parallel}$  in comparison to Cu(PA)<sub>2</sub> indicates slight strain of the structure of the complex with the macroligand. The data are in good agreement with the results obtained in [6]. The structure of the Cu(ANKB-2) complexes remains unchanged up to maximum filling of the matrix of the ampholyte with copper ions. This is indicated by the coincidence of the experimentally measured value of  $g_0 = 2.128 \pm 0.004$  (the concentration of Cu(II) in ANKB-2 was 4.2 mg eq/g) with  $g_0' = (g_{\parallel} + 2g_{\perp})/3 = 2.124$  calculated from the data in Table 1.

The analysis of the EPR spectra of Cu(ANKB-2) complexes with a different concentration of copper showed (Fig. 2) that broadening of the EPR lines due to a dipole-dipole interaction between complexes is observed up to the value of ~0.3 mg eq/g; after measuring it in



Fig. 2. EPR spectra of Cu(ANKB-2) complexes at 77 K and with a concentration of copper in the ampholyte of: 1) 0.016; 2) 0.1; 3) 0.19; 4) 0.35; 5) 0.96 mg eq/g.

Fig. 3. Dependence of total  $W_{O_2}$  and specific  $W'_{O_2}$  of the rates of absorption of  $O_2$  in liquid-phase oxidation of cyclohexene (a), width of the down-field component of the EPR spectrum  $\Delta H_{1/2}$ , average local concentration of copper  $\langle C_M \rangle$ , and proportion of the singlet line in the EPR spectrum  $\beta$  (b) on the concentration of Cu(II) in the ANKB-2 ampholyte. a) 75°C;  $[C_6H_{10}]_0 = 9.66$  mole/liter, [Ct] = 25 g/liter;  $p_{O_2} = 0.1$  MPa.

TABLE 1. Parameters of the EPR Spectra of Complexes of Cu(II) with ANKB-2 and  $\alpha$ -Picolinic Acid at 77 K

| Complex   | A ∥ ± 2. Oe                      | g    ± 0,004                     | g <sub>1</sub> ± 0,004           | $a_{\perp}^{\mathbf{N}} \pm 0.3$ | $a_{\parallel}^{N} \pm 0.3$ |
|---|----------------------------------|----------------------------------|----------------------------------|----------------------------------|-----------------------------|
|   |                                  |                                  |                                  | Oe                               |                             |
| Cu (ANKB-2)<br>Cu (PA)<br>Cu (PA)<br>Cu (PA) <sub>2</sub><br>Cu (PA) <sub>3</sub> | 172,0<br>148,5<br>170,0<br>155,5 | 2,250<br>2,332<br>2,259<br>2,284 | 2,061<br>2,070<br>2,059<br>2,059 | -<br>14.3<br>12,6                | -<br>-<br>9,6<br>9,0        |

accordance with [7], it is possible to estimate their average local concentration  $\langle C_M \rangle$  (Fig. 3). An increase in the concentration of ions from 0.3 to 1.0 mg eq/g causes the spectrum to become a single line due to a spin-exchange interaction between paramagnets (Fig. 2). There is an increase in the contribution of the singlet component, evaluated in analysis of the EPR spectra on an ES-1050 computer (Fig. 3), similar to what was reported in [7] for the Cu(II)-linear polyethylenimine system, in addition to the further broadening of the components of the anisotropic signal in this region in the experimental spectrum.

Cu(ANKB-2) complexes are catalysts of liquid-phase oxidation of CH by molecular oxygen. Cyclohexene hydroperoxide (ROOH) is the basic product of the reaction. A small amount of cyclohexenol and cyclohexenone is also formed together with ROOH, and the amount of ketone present is ~1.2 times greater than the amount of alcohol. The dependence of the total  $W_{O_2}$  and specific  $W'_{O_2}$  rates of absorption of  $O_2$  in oxidation of CH on the concentration of copper in the ANKB-2 ion-exchanger is shown in Fig. 3. Figure 3 indicates that an increase in the concentration of Cu(II) by 10 times results in a decrease in  $W'_{O_2}$  by ~5 times. The selectivity of the reaction (for ROOH) simultaneously decreases from 95-100 to 67-70%. The decrease in  $W'_{O_2}$  with an increase in the concentration of copper is apparently due to the fact that as the granules of the ampholyte are filled with Cu(II) ions, diffusion of the reagents into the bulk of the ANKB-2 is hindered and only the complexes located on the surface of the granules remain catalytically active. Since no complexes with a composition other than Cu[2N, 20] were recorded within the limits of the precision of the experiment, it is possible to hypothesize that they are catalytically active in the reaction of oxidation of CH. However, the possibility of occurrence of the reaction due to impurity centers cannot yet be excluded.

Repeated (>3 times) or prolonged ( $\geq 6$  h) use of Cu(ANKB-2) complexes was not accompanied by a decrease in their activity in any case. The EPR spectra of the catalyst before and after the reaction also remained unchanged, i.e., there were no changes in the composition and structure. Cu(ANKB-2) complexes are thus not only active, but in contrast to the systems Cu(AN-251) and Cu(AN-521) [3-4], they are also very stable catalysts of liquid-phase oxidation of CH.

We would like to thank A. N. Druzhinina for assistance in conducting the experiments.

### CONCLUSIONS

1. The structure of complexes of Cu(II) with ANKB-2 ampholyte, the features of filling of the polymer matrix by copper ions, and the catalytic activity of the complexes in the reaction of liquid-phase oxidation of cyclohexene by oxygen were investigated. The complexes located on the surface of the granules of the ion-exchanger are catalytically active when the concentration of Cu(II) increases.

2. It was found that there are no changes in the composition and structure of the Cu(ANKB-2) complexes during catalytic oxidation of cyclohexene.

#### LITERATURE CITED

- V. V. Berentsveig, I. G. Syshchikova, O. E. Dotsenko, and A. M. Evseev, Zh. Fiz. Khim., 58, 2722 (1984).
- 2. V. D. Kopylova, A. P. Rudenko, E. L. Frumkina, et al., Zh. Fiz. Khim., <u>57</u>, 2325 (1983).
- 3. V. V. Berentsveig, O. E. Dotsenko, A. I. Kokorin, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2211 (1982).
- 4. A. I. Kokorin, V. V. Berentsveig, V. D. Kopylova, and E. L. Frumkina, Kinet. Katal., 24, 181 (1983).
- 5. G. M. Zhidomirov, Ya. S. Lebedev, S. N. Dobryakov, et al., Interpretation of Complex EPR Spectra [in Russian], Nauka, Moscow (1975).
- 6. L. S. Molochnikov, B. K. Radionov, and O. N. Babkin, Zh. Fiz. Khim., <u>59</u>, 703 (1985).
- 7. A. I. Kokorin and A. A. Shubin, Zh. Strukt. Khim., <u>29</u>, 1892 (1988).