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REACTIONS OF ONE-ELECTRON REDUCTION OF FREE INDOPHENOXY RADICALS

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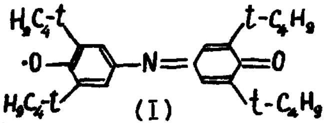
It has been previously shown /1/ that substituted indophenoxy radical (I), generated in more than 95 % yield by the oxidation, in vacuum, of the corresponding indophenol (II), by means of lead dioxide, is very stable, and its concentration does not change over long periods in nonpolar solvents up to 60°C. We have selected the radical(I) as a suitable one for the investigation of the electron transfer reactions in which free radicals act as an oxidant - electron acceptor.



(I)

It has been recently found /2/ that the hydroxylic ion able to give one electron to strong acceptor molecules with formation of corresponding anion-radicals. We have observed an analogous reaction between OH^- ion and the radical (I). The e.s.r. spectra show that the addition of an alcoholic solution of KOH to the radical (I), in vacuum, leads to a decrease in the concentration of the latter proportional to the ammount of alkali added. The solution of radical (I) in n-heptane was found by us, in accordance with /3/, to have characteristic absorption maxima at 312, 328 and 454mμ while the solution of the initial indophenol (II) absorbs at 270, 315 and 480mμ . When pouring together a yellow alcoholic solution of (I) with an alcoholic solution of KOH a characteristic blue colour appears with maximum at 670mμ . The addition of acetic acid changes the blue colour to pink one with absorption maxima which corresponds to indophenol (II). The dependence of radical concentration on the ammount of alkali added, determined from changing of the absorption maximum intensity of (I) at 454mμ , is linear with a slope corresponding to 1 mole of radicals reacting with 1 mole of alkali.The appearance of the blue colour with absorption maximum at 670mμ when a pink indophenol solution is treated by alcoholic alkali confirms the formation of PhO^- ions by interaction of (I) with KOH. The pink colour with absorption maximum corresponding to nondissociated (II) was renewed when acetic acid was added.

Alkalie metals are able to transfer an electron to molecules of organic acceptor with the formation of anion-radicals. We have studied this reaction using the free radical (I) as acceptor. Shaking its yellow dymethoxyethane solution over a potassium mirror on the reaction vessel surface in vacuum changes the colour to green and then to blue. The green solution shows absorption maxima of (I) which has not reacted as well as of the ion PhO^-, and the blue solution shows only the absorption maximum of the ion. Addition of acetic acid to the blue solution changes its colour to pink which is characteristic for the phenol (II).

We have also found that PhO^- ions are formed by interaction of radical (I) with para-nitrotoluene anion-radical (III) /4/. When the solutions of two radicals are poured together the colour of the mixture becomes blue with maximum at 670mμ and both (III) and (I) in the solution do not give rise to e.s.r. signals. Thus, transfer of an electron from (III) to (I) occurs with PhO^- and para-nitrotoluene formation in the experiments described above.

Polarographic reduction of radical (I) in 10^{-3} mol/l solution in 95 % ethyl alcohol or acetonitrile in the presence of 0,1 mol/l $NaClO_4$ gives rise to a wave with $E_{1/2}$ near 0,7 v relative to the anodic mercury pool. The characteristic colour of PhO^- ion appears in vicinity of the cathode at this potential. The potential difference $E_{3/4} - E_{1/4}$ indicates a reversible one-electron reduction.

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