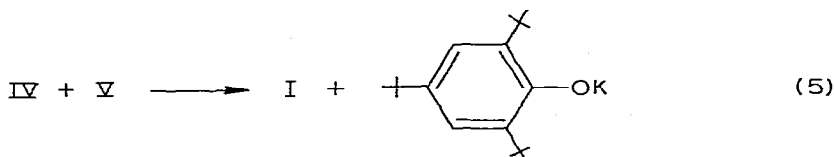
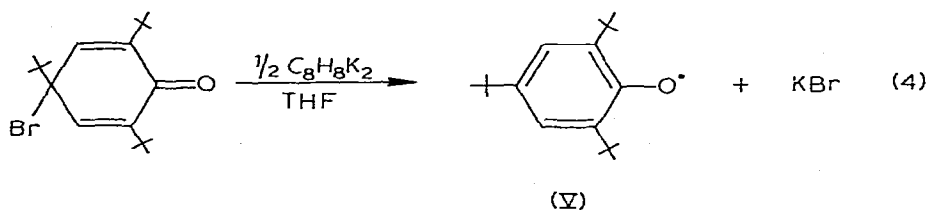
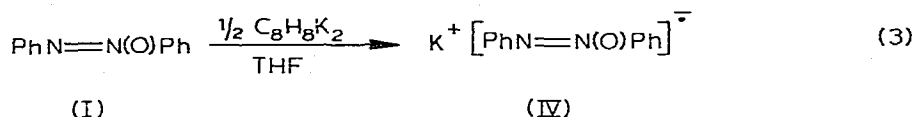


It seemed obvious that azoxybenzene (I) in a homogeneous medium (donor $C_8H_8K_2$) should also react according to eqn. 1, giving the dianion or, after the protonation and the rearrangement, benzidine. We carried out this reaction with a donor acceptor ratio equal to 1/2. However, it was found unexpectedly that benzidine did not form at all and the proton donor treatment gave a 96% yield of azobenzene (II), and cyclooctatetraene, C_8H_8 (100%).

Oxygen treatment of the reaction solution gave the initial azoxybenzene and tar-products. If 2,4,6-tri-*t*-butyl-phenoxy radical is used as an oxidizing agent up to 75% of azoxybenzene can be recovered with the aid of column chromatography. At the same time 2,4,6-tri-*t*-butylphenol is obtained (the yield being 90%, as determined by IR spectroscopy before the column separation*). Thus, it was ascertained that azoxybenzene reduction by means of $C_8H_8K_2$ in THF can proceed selectively, to anion-radical (IV) only, (eqns. 3-5).

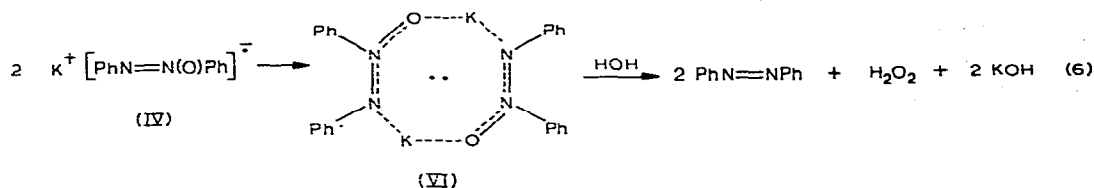


The data from our experiments show that potassium salts of anion radicals of azoxybenzene are stable in THF. These data are confirmed by the literature data concerning the stability of sodium salt of I in THF and its liability to form the diamagnetic dimer. Water treatment leads to the decomposition of the salt and to the formation of hydrogen peroxide (0.4 mole per mole of the initial azoxybenzene [3]).

The transformation of potassium salt IV to dimer VI under our experimental conditions is possible as well, eqn. 6. This explains both the inactivity

* In principle, this phenol can be formed also in the course of transfer either of electrons from azodianion (III) or hydrogen atoms from hydrazobenzene, cf. ref. 2. In our experiments the artefact of this kind is excluded: the preceding account demonstrates that azodianion or hydrazobenzene did not form at all. For this reason the yield of phenol may serve as a measure of the stability of anion radicals of azoxycompounds.

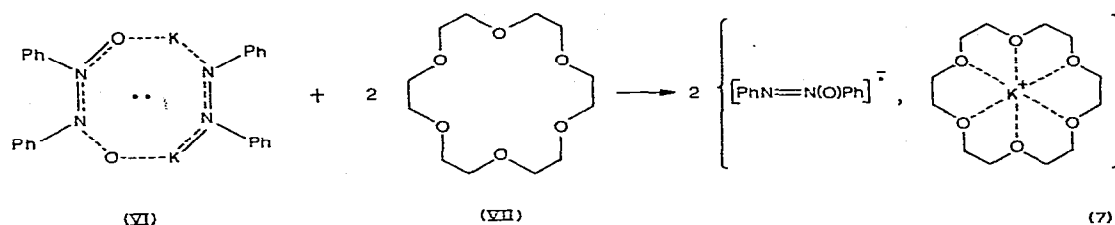
of the potassium salt of the azoxybenzene anion radical in further electron transfer reactions and its conversion to azobenzene (II) in the case of water treatment (eqn. 6).



The stability of coordination complex VI is ensured by delocalization of two superfluous electrons within the cycle which is formed during the interaction of potassium cations with azoxy groups of the anion radicals. Potassium cations are able to offer their low unfilled orbitals for such delocalization.

Azobenzene (a compound without any oxygen atoms) gives anion radicals which are unable to form a coordination complex with the potassium cation, and an electron transfer reaction continues further than in the case of azoxybenzene (see eqn. 2).

If the ion coordination is indeed the reason for the azobenzene formation according to eqn. 6, then bringing potassium cations out of the reaction sphere, in our opinion, must change the course of the process. Indeed, in the presence of a potassium acceptor, viz. 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6-ether", VII) other reaction products were formed. After column separation of the products we obtained not only azobenzene (62%), but also hydrazobenzene (the yield of benzidine being about 15%) and azoxybenzene (17%). The ring diameter in crown ether VII amounts to 2.6-3.2 Å [4]. This is well in agreement with the size of the potassium cation whose diameter is equal to 2.66 Å. It is possible that crown ether partially destroys the coordination complex VI, (eqn. 7).



For this reason the reaction in the presence of crown ether VII continues in part further, to azodianion. Under such conditions the quantity of the donor used is insufficient (eqn. 3) and a part of azoxybenzene (I) is recovered unchanged.

Complex formation through coordination of two potassium cations and two azoxybenzene anion radicals may be the main cause of differences between reduction of azoxybenzene at the electrode and under conditions of electron transfer in the homogeneous media.

Decomposition of coordination complexes of the type studied is due to removing the potassium cation out of the reaction sphere, it may be regarded as a way to change the reactivity of electron transfer products.

Experimental

All experiments were conducted in an argon atmosphere, the reagents were free from oxygen.

*Preparation of 2,4,6-tri-*t*-butylphenoxy radical*

A solution of 0.8513 g (0.0025 g-m) of 2,4,6-tri-*t*-butylbenzoquinobromide-1,4 [5] in 20 ml of THF was cooled to -60°C and a solution of $\text{C}_8\text{H}_8\text{K}_2$ in 20 ml of THF (from 0.1296 g, 0.00125 g-m of C_8H_8) was added. These blended solutions exhibited dark blue colour, absorption band in electronic spectrum at 625 nm ($\epsilon = 300 \text{ l mole}^{-1} \text{ cm}^{-1}$), compare with data in ref. 6. In the ESR spectrum of the solution sample was observed the characteristic structure of 2,4,6-tri-*t*-butylphenoxy radical [7]. The mixture was stirred for 30 min and the temperature was allowed to rise to -10°C and then 2 ml of 25% acetic acid was added. The colour of the solution did not change, but a white precipitate deposited. After the determination of the yield of C_8H_8 (100%) by the GLC method [8], the precipitate was filtered off and dried. This precipitate was soluble in water and in the presence of silver nitrate gave yellow silver bromide as a sediment. The precipitate was potassium bromide, the yield being 0.261 g (88%).

After evaporation of the filtrate a yellow residue (0.64 g) was obtained with m.p. 141°C . In acetic acid solution, in the presence of benzene, this substance reacted with potassium iodide and iodine was evolved. The PMR spectrum in carbon tetrachloride solution revealed peaks of methyl groups δ_1 0.85 and δ_2 1.27 ppm with the ratio of the intensities 1/2, a signal due to phenyl protons with δ 6.7 ppm was also observed. Bands of hydroxyl group were detected neither in the PMR nor IR spectra. Thus, 2,4,6-tri-*t*-butylphenoxy peroxide was obtained (lit. m.p. 147°C [9]) in 93% yield.

Electron transfer to azobenzene

A solution of 0.17 g of azobenzene (0.0009 g-m) in THF was mixed at -60°C with a solution of $\text{C}_8\text{H}_8\text{K}_2$ (from 0.098 g or 0.009 g-m of C_8H_8) in THF. After stirring for 30 min the temperature was allowed to rise to -5°C and 2 ml of 25% acetic acid or water was added. The yield of C_8H_8 was determined (100%); at -5°C 30 ml of 30% sulfuric acid and 25 ml of water were added. After washing with ether the obtained solution was made alkaline and extracted with ether. After solvent removal 0.11 g of benzidine was obtained with m.p. 127°C (65%).

Upon diazotizing and treating with an alkali solution of β -naphthol the product gave a violet dye. In the ethereal layer the initial azobenzene was not recovered.

Electron transfer to azoxybenzene

1. A solution of 0.9 g of azoxybenzene (0.005 g-m) in THF was mixed at -60°C with a THF solution of $\text{C}_8\text{H}_8\text{K}_2$, which was prepared from 0.26 g (0.0025 g-m) of C_8H_8 . After stirring for 30 min the temperature was allowed to rise to -5°C and 2 ml of 25% acetic acid were added. The yield of C_8H_8 was determined (100%); at -5°C 40 ml of 30% sulfuric acid was poured into

the mixture, allowed to stand for 10 h and diluted with 25 ml of water and extracted with ether.

From the ether extract 0.79 g of azobenzene was obtained (96%) with m.p. 66°C. The product was also identified by TLC with an authentic substance (alumina, eluents benzene/petroleum ether 4/1). The acidic solution was neutralized with alkali and extracted with ether. The ether extract was dried over sodium sulfate, filtered off and dry hydrogen chloride was passed through the resulting filtrate. No precipitate was obtained. Ether was evaporated and the residue was treated with nitrous acid. One drop of the obtained solution was applied to filter paper together with one drop of the alkaline solution of β -naphthol (so called "run out test"). There was no coloured streak at the place of contact between the two drops, i.e., benzidine was absent.

2. Azoxybenzene anion radical (0.5 g, 0.00254 g-m) and 2,4,6-tri-*t*-butylphenoxy radical (0.866 g, 0.00254 g-m) were prepared in THF solution in separate vessels.

The solution of the phenoxy radical was filtered from potassium bromide and then mixed with the solution of azoxybenzene at -30°C. After a period of 1.5 h 2 ml of 25% acetic acid or water was poured into the mixture at -5°C. The resulting solution was evaporated to dryness, the residue was dried in vacuo, weighed and one part of it dissolved in carbon tetrachloride. In this sample the intensity of the IR absorption band at 3630 cm^{-1} was measured to determine the yield of 2,4,6-tri-*t*-butylphenol (92%). Other bands in this spectrum coincided with the literature data [9]. The remaining part of the residue was dissolved in 20 ml of 10% sulfuric acid with cooling. The solution was extracted with ether, the extract was washed with 10% solution of sodium hydrocarbonate, then with water to remove base, and was dried over magnesium sulfate. Ether was further evaporated, the residue was dissolved in petroleum ether and was passed through an alumina column. The composition of fractions was checked by the TLC method. Upon distilling petroleum ether 0.37 g of azoxybenzene (75%) and 0.02 g of azobenzene (4%) were obtained.

3. Experiment 1 was repeated with introduction of an acceptor of potassium cations into the reaction mixture. For this purpose a THF solution of $\text{C}_8\text{H}_8\text{K}_2$ (from 0.065 g or 0.000625 g-m) of C_8H_8 was poured at -60°C into a THF solution which contained 0.25 g (0.00125 g-m) of azoxybenzene. After 25 min of stirring, a THF solution of 0.33 (0.00125 g-m) of 18-crown-6-ether [10] was added. The mixture was stirred for 30 min at -15°C, then at -5°C and 2 ml of 25% acetic acid or water were added. After that, at the same temperature, 40 ml of 30% sulfuric acid was poured into the mixture. The resulting solution was allowed to stay for 10 h and then was extracted with ether. The ethereal layer was dried over sodium sulfate, evaporated and the residue was dissolved in a 2/1 hexane/benzene mixture. After alumina column separation the following substances were obtained: azobenzene (0.13 g, 62%) with m.p. 66°C and 0.05 g of azoxybenzene (17.5%) with m.p. 34°C. These substances were identified by TLC on alumina with authentic compounds. The acidic aqueous layer was neutralized with alkali and extracted with ether. After washing and drying the ethereal extract was evaporated. White crystals of crude benzidine were obtained (0.03 g, ca. 15%). The latter product after treatment with nitrous acid gave with an alkaline solution of β -naphthol in the "run our test" a streak of an intense

violet colour. The m.p. of the *N,N*-diacetyl derivative was 315°C (lit. m.p. 317°C [11]).

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