ELECTRON TRANSFER IN THE REACTION OF SULFHYDRYL REAGENTS WITH BENZOQUINONES

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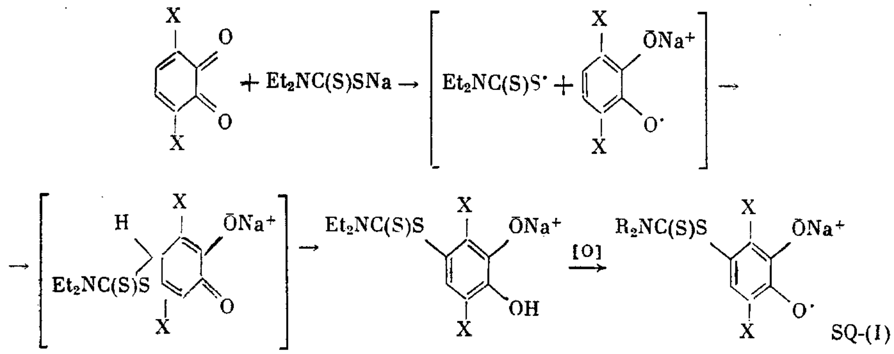
Sulfhydryl reagents (dithiocarbamates, xanthates, and dithiophosphates of alkali metals) and the corresponding disulfides are used in the flotation process of sulfide minerals [1]. In this process the reactivity of dithio anions $-C(S)S^-$ and dithio radicals $-C(S)S^\cdot$, formed by electron transfer from the anion to an acceptor, is significant. The use of sterically hindered benzoquinones with detection of the corresponding semiquinone anion-radicals is highly effective for studying the mechanism of electron (or hydrogen atom) transfer in oxidation—reduction reactions [2].

In this work we studied the EPR spectra of free radicals formed upon reaction of substituted benzoquinones with sulfhydryl reagents and upon reactions of semiquinone anion-radicals with disulfides of sulhydryl reagents.

The following sulfhydryl reagents were chosen for investigation: sodium diethyldithiocarbamate (I), ethyl potassium xanthate (II), potassium diethyldithiophosphate (III), and also disulfides of the sulfhydryl reagents tetraethylthiouram disulfide (TETDS) and ethyl dixanthogenide. 3,6-Di-tert-butyl-o-benzoquinone (Q_1) and 3,5-di-tert-butyl-o-benzoquinone (Q_2) were used as acceptors. In order to study the reaction of disulfides with semiquinone anion-radicals $Q^{\cdot-}$ they were reduced by sodium amalgam.

The EPR spectrum from the reaction of (I) with Q_1 in acetone consists of two groups of lines which belong to two types of free radicals. The EPR spectrum of one type of radical is a triplet of quadruplets caused by hyperfine interaction of the unpaired electron with two equivalent aromatic ring protons (a_H = 3.3 Oe) and the ^{23}Na nucleus (I = 3/2) with a hyperfine interaction constant, a_{Na}, of 0.24 Oe. According to [3] this spectrum corresponds to the semiquinone anion-radical $Q_1^{\cdot-}$ which is stabilized in solution as an ion pair $Q_1^{\cdot-}$ Na^+ (Fig. 1).

Formation of a semiquinone anion-radical is associated with electron transfer from the sulfhydryl reagent to the o-quinone. Short-lived thiyl radicals formed by electron transfer were not detected, apparently because of their extremely low stability. However, their formation is suggested by the second type of semiquinone radicals detected by us, the EPR spectrum of which is a doublet of quadruplets caused by hyperfine interaction of the unpaired electron with one proton of the aromatic ring (a_H = 3.0 Oe) and with the ^{23}Na nucleus (a_{Na} = 0.24 Oe). This spectrum indicates formation of a semiquinone anion-radical in which one aro-



X = *t*-Bu.

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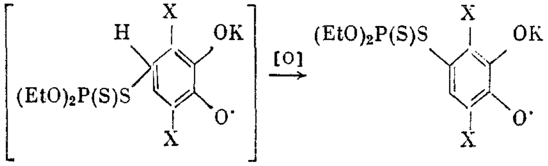
matic proton is substituted by a nonmagnetic nucleus. Apparently the thiyl radical formed by one-electron transfer in the solvent cage attacks $Q_1^{\cdot-}$ on the aromatic ring with formation of the diamagnetic anion. Oxidation of the latter by atmospheric oxygen under aerobic conditions leads to formation of the dithio substituted semiquinone anion-radical SQ-(I). Analogous substitution of the hydrogen atoms in the aromatic ring by active radicals was observed in studying the reaction of Q_1 with alcoholic alkali solution [4].

Upon reaction of potassium xanthate (EtOC(S)SK) with Q_1 the above two types of radicals are also formed. However, in the EPR spectra the hyperfine interaction with the potassium cation is not observed. With compound (III) as reagent the formation of $Q_1^{\cdot-}$ under dark conditions does not occur. Under UV exposure in the spectrometer resonator the EPR spectra of $Q_1^{\cdot-}$ and radical SQ-(II) are recorded. In the latter a hydrogen atom of the aromatic ring is replaced by $(EtO)_2P(S)S^{\cdot}$

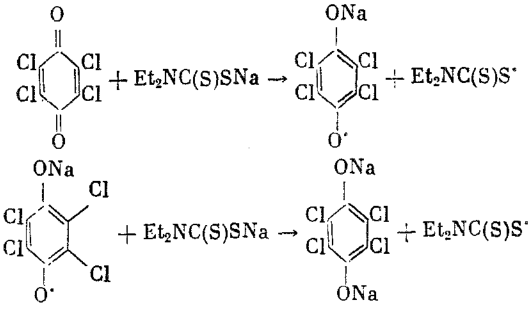
$$(EtO)_2P(S)SK + Q_1 \xrightarrow{h\nu} [(EtO)_2P(S)S^{\cdot} + Q^{\cdot-}K^{+}] \rightarrow$$



SQ-(II).

The EPR spectrum of the SQ-(II) radical is a doublet of doublets caused by hyperfine interaction with the ^{31}P nucleus (a_P = 18.0 Oe) and with one proton of the aromatic ring (a_H = 3.0). It should be noted that the yield of the SQ-(II) radical is insignificant in comparison with the starting $Q^{\cdot-}$, which is apparently associated with the high probability of the primary (thiyl and semiquinone) radicals escaping from the solvent cage (Fig. 2).

The thiyl radical formed by one-electron transfer can recombine with formation of disulfides. For example, by recombination of dithiocarbamate radicals thiouram sulfides are formed [5]. Therefore, one can assume that in our system disulfides of the sulfhydryl compounds can also be formed. In order to prove this assumption we have studied the reaction of (I) and (II) with p-chloranil in acetone-d_6. Upon reaction of p-chloranil with (I) the EPR spectrum of p-chloranil $Q^{\cdot-}Na^{+}$ was registered showing a singlet line of Δ = 2.7 Oe width. With excess sulfhydryl reagent a dark-green precipitate (disodium salt QNa_2) is formed and an EPR spectrum is not observed. After filtration the PMR spectrum of the solution, consisting of two line groups, was recorded. One of them corresponds to excessive sodium dithiocarbamate: δ CH_3, 1.13, δ CH_2, 4.00 ppm. Therefore, with excess sulfhydryl reagent two-electron reduction of p-chloranil occurs with formation of the disodium salt and disulfide.



$$2Et_2NC(S)S^{\cdot} \rightarrow Et_2NC(S)SS(S)CNEt_2$$

Analogously, upon reaction of excess (II) with p-chloranil a PMR spectrum is recorded of the excess xanthate (δ CH_3 1.14 ppm and δ CH_2 4.32 ppm) and of the dixanthogenide EtOC(S)SS(S)COEt (δ CH_3 1.35 and δ CH_2 4.64 ppm). The yield of anion-radicals depends on the structures of reagents (I), (II), and (III). In order to compare the efficiency of electron transfer, EPR spectra of $Q_2^{\cdot-}$ in equimolar solutions of Q_2 and reagents (I), (II), and (III) in acetone ($2\cdot10^{-2}$ M) were recorded. It turned out that the yield of $Q_2^{\cdot-}$ decreases in the series dithiocarbamate – xanthate – dithiophosphate. This agrees with the increase of oxidation–reduction (OR) potential in the same series [6]: (I) (−0.33 V), (II) (−0.03 V), (III) (+0.255 V) and the yield of $Q_2^{\cdot-}$ ($\varkappa$) is 300, 28, and 7 respectively. The quantity $\varkappa$ was calculated by the formula $\varkappa = I\cdot\Delta^2$, where I is the amplitude of the $Q_2^{\cdot-}$ EPR signal, and Δ is the line width (relative measurement error $\delta\varkappa$ = 15%).

We have also investigated the possibility of reaction of semiquinone anion-radicals with disulfides of sulfhydryl reagents. It turned out that upon reaction of $Q_1^{\cdot-}$ Na^{+} with TETDS,

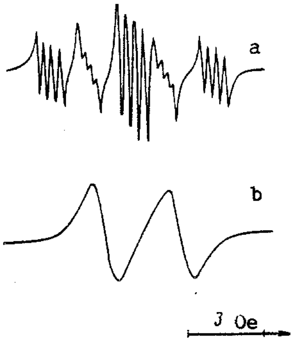


Fig. 1

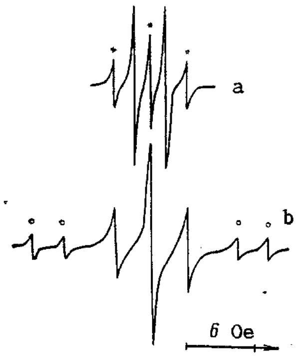


Fig. 2

Fig. 1. EPR spectra of sodium diethyldithiocarbamate solution with 3,6-di-tert-butyl-o-quinone (a) and 3,5-di-tert-butyl-o-quinone (b) in acetone.

Fig. 2. EPR spectra of free radicals forming upon reaction of 3,6-di-tert-butyl-o-quinone with potassium ethyl xanthate (a) and with potassium diethyldithiophosphate in THP under UV irradiation (b). The EPR spectrum of 3,6-di-tert-butyl-o-semiquinone anion-radical is marked by stars. The EPR spectrum of 4-substituted 3,6-di-tert-butyl-o-semiquinone anion-radical in the case of potassium diethyldithiophosphate is marked by circles.

the $Q_1^{\cdot-}$ EPR signal decreases and a doublet spectrum appears. These changes are observed upon reaction of $Q_1^{\cdot-}$ with ethyl dixanthogenide. Thus, upon reaction of semiquinone anion-radicals with disulfides active thiyl radicals are also formed, which react with the starting anion-radicals forming the above-described 4-substituted 3,6-di-tert-butyl-o-semiquinones. It is known [7, 8] that disulfides under the action of strong reducing agents decompose to thiyl radicals and the corresponding anions. Apparently, disulfides of sulhydryl reagents decompose by the same mechanism.

$$Q^{\cdot-} + Et_2NC(S)SS(S)CNEt_2 \rightarrow Q + Et_2NC(S)S^- + Et_2NC(S)S^{\cdot}$$

Subsequent formation of 4-substituted semiquinones proceeds analogously to the process described above.

EXPERIMENTAL

EPR spectra were recorded on a PÉ-1306 spectrometer at 20°C in solutions of acetone and THF. For irradiation of the solutions a DRSh-150 lamp was used. PMR spectra were recorded on a Tesla B-487 C spectrometer.

CONCLUSIONS

1. Electron transfer from sulfhydryl reagents to an acceptor (o-quinone) with formation of a semiquinone anion-radical and the corresponding thiyl radical was proved. The resultant radicals react between themselves with formation of 4-substituted 3,6-di-tert-butyl-o-semiquinone radical.

2. Disulfides of sulfhydryl reagents upon reaction with semiquinone anion-radicals decompose to dithio anions and dithio radicals.

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FLUOROINDENES.

10.* CYCLIZATION OF DIFLUOROCARBENE TO PERFLUORO-3-METHYLINDENE AND PERFLUORO-1-METHYLENEINDANE. THERMOLYSIS AND BROMINATION OF THE RESULTANT CYCLOPROPANE DERIVATIVES

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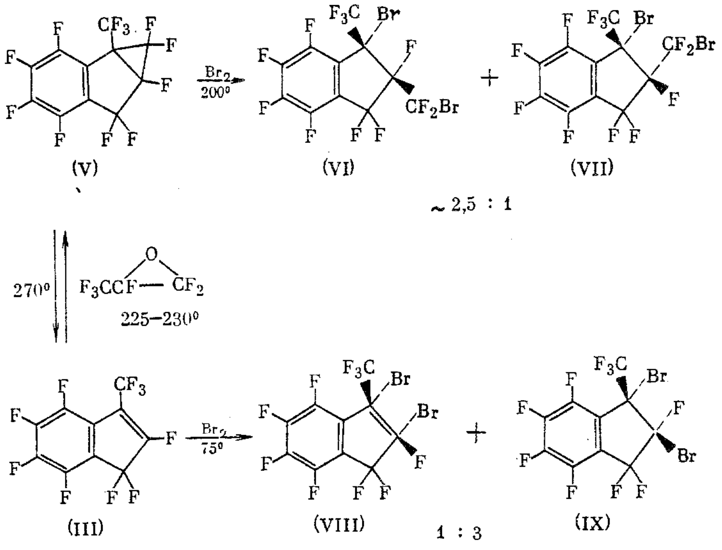
The cycloaddition product of $:CF_2$ to octafluoroindene (I), perfluoro-1,1a,6,6a-tetrahydrocycloprop[a]indene (II), isomerizes upon thermolysis mainly to perfluoro-2-methylindene or splits off $:CF_2$ [2]. These transformations of (II) differ essentially from those of the product of $:CCl_2$ cycloaddition to compound (I), which isomerizes to 1,2-dichloroperfluoro-1,4-dihydronaphthalene [3], and from those of the cycloaddition products of dihalocarbenes to indene, which form 2-halonaphthalenes [4]. In connection with this it was worthwhile to study the thermal transformations of $:CF_2$ cycloaddition products to other polyfluoroindenes. In this work we studied the reactions of perfluoro-3-methylindene (III) and perfluoro-1-methyleneindane (IV) with hexafluoropropylene oxide (HFPO) as a source of $:CF_2$ [5], and the thermolysis and bromination of the resultant products.

It was shown that from indene (III) and HFPO at 225°C perfluoro-1a-methyl-1,1a,6,6a-tetrahydrocycloprop[a]indene (V) is obtained. Under more rigid conditions compound (V) splits off $:CF_2$, giving indene (III). Perfluoro-2,3-dimethylindene, a possible isomerization product of cyclopropanone derivative (V), was not found {compare with the behavior of (II) [2]}. It should be noted that thermolysis of (V) proceeds under more rigid conditions than for (II) [2]. This agrees with the increased stability of perfluorocyclopropane after replacement of the F atoms by $CF_2{=}CF{-}CF_2$ [6, 7] or CF_3 groups [6, 8].



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*For previous report, see [1].
†Deceased.

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