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Abstract

Full Text

Physical Chemistry

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Electron-Donor Properties of the Hydroxyl Ion

(Presented by Academician M. I. Kabachnik on 15 IV 1964)

Usually, when considering most liquid-phase chemical processes, including biochemical processes (with the exception of some photochemical reactions), it is assumed that water can take part only in acid–base reactions. If, however, one takes into account that the ionization potential of hydroxyl ions is comparatively small (~2.6 eV in the gas phase (1)), the possibility is not excluded that it participates in oxidation–reduction processes of the type:

$$\mathrm{OH}^- + \mathrm{A} \rightarrow \mathrm{OH} + \mathrm{A}^-, \qquad (1)$$

where A is an electron acceptor. Even in the case where reaction (1) is thermodynamically unfavorable both in the gas phase and in the liquid phase when solvation effects are taken into account, the formation of very active OH radicals and their rapid disappearance can shift equilibrium (1) and ensure the occurrence of the process.

Fig. 1. EPR spectra of the TCNE ion-radical. Obtained in a solution of TCNE in a 1:1 mixture of water with ethyl alcohol.

Fig. 2. EPR spectrum of the TCNE ion-radical. Obtained in a solution of TCNE in alcoholic alkali.

The aim of the present work was an experimental verification of this assumption. For this purpose a series of organic compounds possessing pronounced electron-acceptor properties was selected: tetracyanoethylene (TCNE), chloranil, bro-

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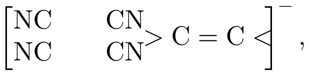
Fig. 3. EPR spectra of the ion-radicals of chloranil (a), p-benzoquinone (b), and duroquinone (c)

Figure 3: Fig. 3. EPR spectra of the ion-radicals of chloranil (a), p-benzoquinone (b), and duroquinone (c)

manil, *p*-benzoquinone, tetraquinoxalinedimethane, methylene blue, phthaloquinanine, methionine, vicasol, riboflavin, flavin mononucleotide, diphosphopyridine nucleotide, triphosphopyridine nucleotide, and some others. Since all the listed compounds are valence-saturated, transfer of one electron should lead to the appearance of ion-radicals, for the registration of which the method of electron paramagnetic resonance (EPR) can be used. In addition, the disappearance of OH^- ions can be registered potentiometrically, and the disappearance of active OH radicals—by the product of their recombination, hydrogen peroxide. We measured EPR spectra on a standard radio spectrometer of the EPR-2 IKhF type in aqueous and aqueous-alcoholic solutions. In studying aqueous solutions we used capillaries with an internal diameter of 0.5 mm.

Figure 1 shows the EPR spectrum of a saturated solution of TCNE in a 1:1 mixture of distilled water with ethyl alcohol; the pH of the solution at the initial mo—

the time point was 5.5 (then the pH slowly shifts into the acidic region). In the spectrum the hyperfine structure (h.f.s.), consisting of nine components, is clearly visible. Neither TCNE itself nor its alcoholic solution gives an EPR signal. Thus, apparently, the role of the alcohol consists only in increasing the solubility of TCNE. The intensity of the EPR signal observed at the beginning increases in parallel with increasing concentration of OH^- ions. Figure 2 shows the EPR spectrum from 0.1 ml of a 0.1 N TCNE solution in aqueous-alcoholic alkali (0.1 N KOH solution, 5% water). The parameters of the spectrum are identical with those of the spectrum in Fig. 1, but in this case it is possible to estimate the relative intensity of the principal components, which is found to be 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1, in exact agreement with the theoretical parameters of the spectrum of the TCNE ion-radical



$$\left[\begin{matrix}\mathrm{NC} \\ \mathrm{NC}\end{matrix} \quad \begin{matrix}\mathrm{CN} \\ \mathrm{CN}\end{matrix} > \mathrm{C} = \mathrm{C} < \right]^{-},$$

in which the unpaired electron interacts with four equivalent nitrogen nuclei of the CN groups. The distance between neighboring components of the spectrum is ~ 1.6 Oe. The spectrum obtained coincides with the spectrum of the TCNE ion-radical described in the literature (^{2}). We also observed additional outer components in the spectrum, due to the presence of radicals containing a $C^{13}N$ group.

Fig. 3. EPR spectra of the ion-radicals of chloranil *(a)*, *p*-benzoquinone *(b)*, and duroquinone *(c)*

When the alcoholic solution of TCNE and the aqueous-alcoholic alkali are mixed, the EPR signal appears practically instantaneously (the first recording was made 1 min after mixing the solutions). Subsequently, on storage in air, the signal intensity decreases, and it disappears completely after 5-10 min. Oxygen apparently takes part in the destruction of the radicals, since evacuation of the sample increases their stability. For equimolar 0.1 N solutions of TCNE and KOH it is possible to record a radical concentration amounting to approximately 10% of the amount of the initial TCNE. The appearance of the EPR signal upon mixing solutions of TCNE and alkali is accompanied by a sharp drop in the pH of the solution. In this case the number of added TCNE molecules is related to the number of disappearing OH^- ions approximately as 1:1.

As was already noted above, the OH radicals formed by reaction (1) should give hydrogen peroxide upon recombination. Indeed, hydrogen peroxide was detected by the ferricyanide color reaction method (^{3}) after mixing the alcoholic solution of TCNE with aqueous-alcoholic alkali. To avoid side processes, in this case all reactions were carried out in an argon atmosphere with solutions previously freed from gas.

The data presented indicate that the primary act in the interaction of TCNE with the OH^- ion is electron transfer with formation of a negative TCNE ion-radical.

Analogous effects were obtained with chloranil, *p*-benzoquinone, and duroquinone. The spectra of the radicals formed are shown in Fig. 3. In their parameters the signals coincide with known literature spectra of the corresponding semiquinones ($^{4-6}$). Under identical conditions the initial yield of ion-radicals decreases in the series chloranil, *p*-benzoquinone,

duroquinone, in qualitative agreement with the decrease in the electron affinity of these compounds. In chloranil the EPR signal appears already upon dissolving it in a water-alcohol (1:1) solvent. For equimolar 0.001 N solutions of chloranil and alkali, the concentration of radicals formed corresponds to several percent of the initial amount of acceptor. For *p*-benzoquinone it is possible to register up to 25% of the substance in radical form, but the process is complicated by secondary reactions, in particular polymerization, apparently due to the presence of mobile hydrogen atoms. However, the primary act, evidently, in this case too reduces to transfer of an electron from the OH^- ion to the acceptor molecule. Potentiometric measurements are also consistent with the proposed mechanism.

Investigation of all the acceptors listed at the beginning of the article gave qualitatively coincident results. Ion-radicals also arise upon mechanical grinding of dry alkali with an acceptor.

It is possible that the recently discovered formation of the ion-radical O_2^- when oxygen is passed through multiply distilled water (B. N. Raevskii—FPG, private communication) is connected with analogous electron-transfer effects.

It should be noted that, in the case of *p*-benzoquinone, the formation of ion-radicals in alkaline medium was found in works (7,8) and was explained by the course of rather complex chemical processes involving mobile hydrogen atoms. On the basis of the above it may be asserted that the formation of ion-radicals is not connected with the specific chemical structure of the compound, but is determined only by its electron-acceptor properties. In TCNE hydrogen atoms are absent altogether, and the formation of the radical is not connected with detachment of CN groups, as is proved by the presence of nine components of the hyperfine structure of the EPR signal. The interpretation given in works (7,8) is also contradicted by the hydrogen peroxide found by us, which indicates the formation of OH radicals.

It may be supposed that the participation of water in oxidation–reduction processes is not limited to hydroxyl ions and that, under suitable conditions and upon interaction with sufficiently strong electron donors, the H_3O^+ ion can play the role of an electron acceptor.

For biochemical processes proceeding with the participation of protein enzymes, transfer of an electron to acceptors, which include many coenzymes of biological oxidation, may occur also at physiological pH values. Let us recall that with the strongest of the acceptors investigated by us (TCNE, chloranil) we observed formation of ion-radicals at neutral or even weakly acidic pH. The shift of the process of ion-radical formation in biological systems toward neutral pH may be due either to an increased local concentration of hydroxyl ions on the protein surface, or to stabilization of ion-radicals by the protein, or to an increase in the electron affinity of acceptors when they are complexed by the protein. It may be supposed that water associated with biopolymer structures plays a considerably greater role in the course of the most important biological processes than was previously believed.

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