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BRIEF COMMUNICATIONS

THE STABILITY OF THE FREE RADICALS OF HUMIC AND FULVIC ACIDS

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Humic acids (HAs) and fulvic acids (FAs) are of interest because of their capacity for decreasing the toxicity of metals [1], for inhibiting the activity of enzymes [2], etc. The reactivity of the free radicals (FRs) of these natural compounds has been studied inadequately [3]. In the present paper we consider the influence of hydrogen peroxide and sodium nitrite in aqueous solution on the free radicals of humic and fulvic acids.

Solutions of HAs and FAs with a concentration of 50 mg/liter were treated with H_2O_2 and $NaNO_2$ in amounts of 50-200 mg/liter at pH 2, and the mixtures were left for 48 h. The increase in concentration to 10^{12}-10^{14} spins/g necessary for spectrometry was achieved by sorbing the humic substances on ÉDÉ-10P anion-exchange resin in the OH form, the solution being passed through the column at the rate of 1-3 ml/min. Then ESR spectra of air-dry samples of the resin were recorded on a TSN-254 radiospectrometer in the three-centimeter range at 20°C. To determine the concentration of FRs in the sample, calibration of the intensities of the derivative ESR signals with g 2.0043 (for the HAs) and 2.0056 (for the FAs) was carried out with respect to the initial samples.

As can be seen from Fig. 1, an increase in the concentration of H_2O_2 led to a rise, and increase in that of $NaNO_2$ to a fall, in the intensities of the ESR signals of the HAs and FAs.

Assuming that the intensity of the signals depended only on the concentration of FRs (since all the other parameters were standardized), the influence of the additives can be explained in the following way. The g-factors of the signals lie in the region characteristic for cyclic π-radicals [4]. The most probable process is, therefore, the interaction of H_2O_2 with the phenolic groups of the humic substances with the intermediate formation of the cation radicals of the phenols and the deprotonation of their phenoxyls:

$$—PhOH+OH^{\bullet} \rightarrow PhOH^{+\bullet}+OH^{-} \rightarrow —PhO^{\bullet}+H_2O.$$

The action on the phenoxyls of the anion radicals $O_2^{-\cdot}$ and $O^{-\cdot}$ formed in the decomposition of H_2O_2, which is capable of decreasing the FR signal [5], did not appear in this case, apparently because of the sorption of the anion radicals at the ion-exchange centers of the HAs and FAs: $-NH-Cl + O^{-\cdot} \rightarrow -NH-O+Cl$. Then the unpaired electron passes to the heterocyclic fragment of the HA or FA, as was confirmed by the characteristic value of the g-factor. $NaNO_2$ decreases the concentration of HA and FA FRs as a consequence of oxidation by the NO_2 radical present in solutions of nitrites, for example, to phenyl cations:

$$—PhO^{\bullet}+2NO_2^{\bullet} \rightarrow —PhO^{+}+2NO_2^{-}+O_2.$$

In addition, as is known [6], amine groups of aromatic compounds form diazonium salts in solutions of nitrites, and this may also be assumed for humic substances:

$$4\,(—Ph—NH_3)+4NO_2^{-} \rightarrow 4\,(—PhN_2^{+})+6H_2O+O_2.$$

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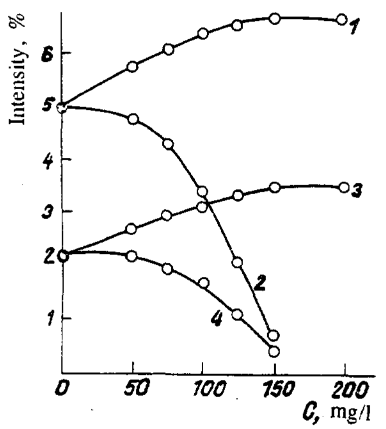

Fig. 1. Influence of the concentration of H_2O_2 (1, 2) and $NaNO_2$ (3,4) in solutions of humic (1, 3) and fluvic (2, 4) acids on the intensity of the ESR signals of the free radicals.

The subsequent spontaneous breakdown of the diazonium salts is accompanied by the formation of radicals, reactions with which are also capable of decreasing the concentration of HA and FA FRs. Thus, depending on the nature of the FRs of the oxidant an increase or a decrease in the number of FRs in HAs and FAs is observed.

REFERENCES

1. H. Shanmukara and J. Neelakantan, Bull. Environ. Contam. Toxicol., **44**, No. 6, 840-843 (1990).
2. Sh. Zhorobekov, S. O. Karabaev, and K. Kydyralieva, Coordination Compounds of Metals with Bioligands [in Russian], Frunze (1987), pp. 118-128.
3. Yu. Yu. Navosha, S. G. Prokhorov, V. P. Strigutskii, et al., Pochvovedenie, No. 1, 109-113 (1992).
4. E. J. Hamilton and H. Fischer, Magn. Reson. Rev., 1, 351-387 (1972).
5. É. G. Rozantsev and V. D. Sholle, The Organic Chemistry of Free Radicals [in Russian], Khimiya, Moscxow (1979).
6. A. S. Dneprovskii, and T. I. Temnikova, Theoretical Principles od Organic Chemistry [in Russian], Khimiya, Leningrad (1991).