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LETTERS
TO THE EDITOR

CIDNP-Effects in Photoreaction of Substituted Benzoquinone with Tetraphenylporphyrin

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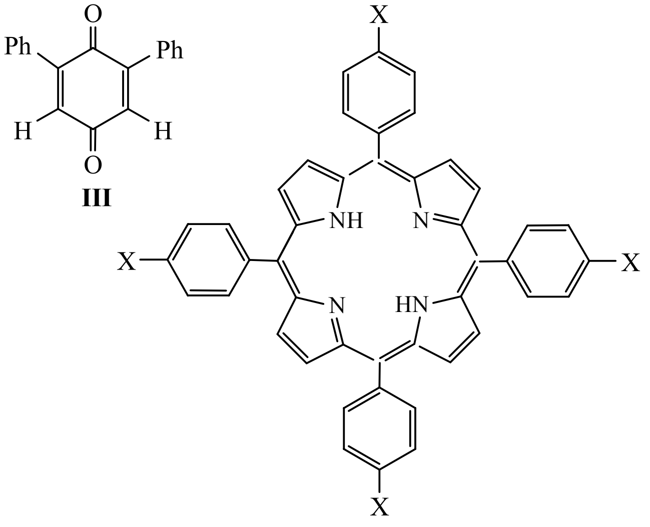
The photoreactions of quinones with the electron donors and hydrogen atoms have been previously described in details [1]. In this report we considered the photolysis of 2,6-dimethyl- (**I**), 2,6-di-*tert*-butyl- (**II**) and 2,6-diphenyl-*para*-benzoquinones (**III**) with tetraphenylporphyrin **IV** in deuterochloroform directly in the NMR spectrometer probe with simultaneous recording of the ^{1}H NMR spectra. The ^{1}H NMR spectra of the reaction mixture of tetraphenylporphyrin **IV** with quinones **I** and **II** under irradiation did not differ from the spectra recorded in the dark except for some signal broadening. The CIDNP (Chemically Induced Dynamic Nuclear Polarization) effects were not observed. In the case of quinone **III** the CIDNP effect was observed as a positive polarization of the *meta*-protons (δ 7.11 ppm) of the initial quinone. In the C^{13} NMR experiments we detected a significant increase of the signal. In the initial quinone we observed the positive polarization on the carbonyl carbon atom (δ_C 190 ppm) and the negative polarization on the *meta*-carbon atoms (δ_C 139 ppm). The carbon nuclei in the *meso*-positions of the porphyrin ring (δ_C 122 ppm) were negatively polarized. The polarization of the carbon nuclei in the substituted pyrrole ring was not detected. Thus, the delocalization of the electron density is likely to occur on the inner pyrrole ring.



III

IV, V

X = H (**IV**), Br (**V**).

Analyzing the CIDNP experiment results, we can conclude that the reaction of the triplet-activated quinone with porphyrin occurs via the electron transfer to the quinone to give the ion-radical pair. Both the products regenerated in the cage and the F-pairs, inducing the polarization of the same sign, contribute to the polarization. The strong negative polarization of the *meta*-carbon atoms indicates a negative sign of the hyperfine interaction constant on these atoms.

At the photolysis of quinone **III** with porphyrin **V** bromo-substituted in the aromatic ring the *g*-factor of the latter is 2.0060, that is more than the *g*-factor of quinone (2.0047). The signs of the signals in the experiment were inverted according to the theory of the CIDNP effects formation in a radical pair. The absence of the nuclear polarization and charge transfer in the case of quinones **I** and **II** is due to the presence of the electron-donor substituents in these compounds.

Apparently, the considered photoreaction with the electron transfer requires the presence of a charge-transfer complex between the reactants even in the dark conditions.

REFERENCES

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