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INTERACTION OF N-SUBSTITUTED PHENOTHIAZINES WITH HALOGEN-CONTAINING SOLVENTS

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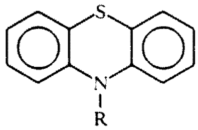
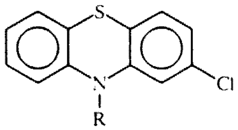
ESR spectroscopy was used to study the interaction of several N-substituted phenothiazines with halogen-containing solvents (CCl_4, $CHCl_3$, CH_2Br_2). The dissolution of phenothiazines in these solvents was found to be associated with an ESR signal indicating the presence of an oxidation-reduction reaction in which the halogen-containing compounds act as acceptors, and the phenothiazines act as electron donors. The HFS of the ESR spectra of the cation radicals obtained was studied.

We have previously [1, 2] carried out the synthesis of a series of phenothiazine derivatives of the type



I



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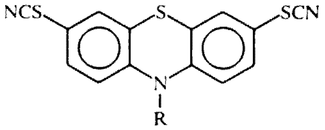

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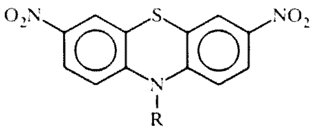
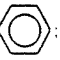


IVa-f

I–IV a R = H; I–IV b R = Me; I–IV c R = CH_2Me; I–IV d R = $CH(Me)_2$;

I–IV e R = CH_2–  ; I–IV f $CH_2C{\equiv}CH$

and studied their capacity for one-electron oxidation under action of concentrated H_2SO_4 concentrated HNO_3 in $HClO_4$ medium, and o-chloranil. The nature of the cation radicals thus obtained was confirmed by the ESR method and by measuring the magnetic susceptibility. A characteristic feature of the ESR spectra of cation radicals containing the CH_2R group at the nitrogen atom was found to be the presence of a quartet with a line strength ratio of 1:2:2:1 (Fig. 1); this differs from the expected spectral hyperfine structure pattern due to the interaction of the unpaired electron with the nitrogen nucleus and two equivalent protons. One of the possible reasons for this could be protonation of the radical center in acid media. However, when o-chloranil in a benzene medium acts on compounds I-IVc, e, f, which contain the fragment N-CH_2R, the ESR spectra also show the presence of a quartet (1:2:2:1) analogous to the one described above. Obviously, the hypothesis of protonation of the radical center is inapplicable in this case.

It was therefore of interest to study the effect of nonacidic oxidants on the nature of the ESR spectra of the cation radicals, including those with the CH_2R group at the nitrogen atom.

It was found that certain halogen-containing compounds (CCl_4, $CHCl_3$, CH_2Br_2) had the ability to oxidize the synthesized phenothiazines at room temperature both in the presence and in the absence of oxygen with the formation of radical products. It was found that the dissolution of all the investigated phenothiazine derivatives (I-IVa-f) in the indicated solvents

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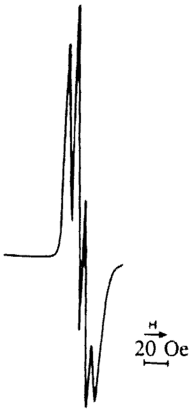


Fig. 1. ESR spectrum obtained during oxidation of compound IV in conc. H_2SO_4.

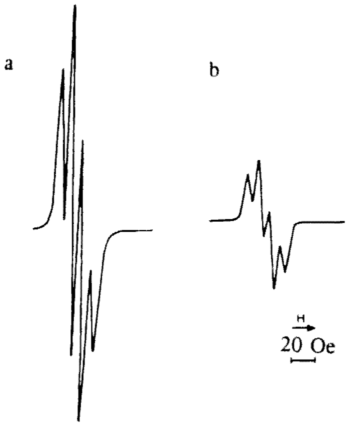


Fig. 2. ESR spectra of: a) compound Ie in CCl_4 ($2 \cdot 10^{-3}$ mole/liter); b) Ic in $CHCl_3$ ($2 \cdot 10^{-3}$ mole/liter).

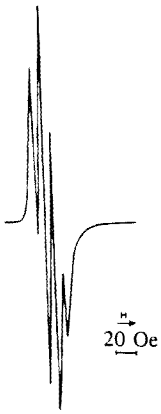
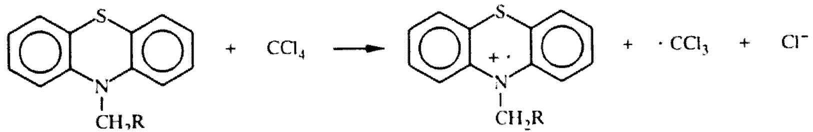


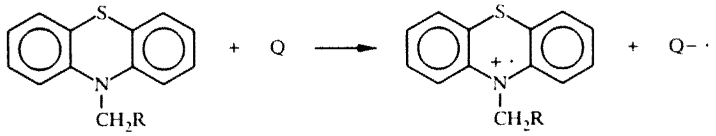
Fig. 3. ESP spectrum obtained during oxidation of compound Ie with o-chloranil in benzene ($2 \cdot 10^{-3}$ mole/liter).

at room temperature was accompanied by a color change and the appearance of an ESR signal increasing with time, the maximum strength being reached in 1 h. The ESR spectra obtained in the oxidation of derivatives I-IVc, e, f under these conditions, and also during the action of acids (conc. H_2SO_4, mixture of conc. HNO_3 and $HClO_4$) or o-chloranil, consisted of a quartet (1:2:2:1) (Figs. 2a and b, 3). Obviously, in this case also, an oxidation-reduction reaction takes place, for example in accordance with Scheme 1:



(1)

We found that the reaction of phenothiazine derivatives (I-IVa-d) with CCl_4, $CHCl_3$, and CH_2Br_2 is sharply accelerated when catalytic amounts of o-chloranil are added to the system (o-chloranil by itself reacts much more slowly with phenothiazines). A similar catalytic effect was observed earlier by Sosonkin et al. [3] in the oxidation of N,N,N',N'-tetramethyl-p-phenylenediamine with tetrachloromethane in the presence of 1,4-benzoquinone. They explained this by redox catalysis of electron transfer, which can be used as a satisfactory hypothesis in our case as well (Scheme 2a-2d):



(2a)

$$2\,Q^{-\cdot} \rightleftharpoons Q + Q^{2-} \tag{2b}$$

$$Q^{2-} + CCl_4 \longrightarrow Q^{-\cdot} + {\cdot}CCl_3 + Cl^- \tag{2c}$$

$$\cdot CCl_3 + Q^{-\cdot} \longrightarrow Q + {}^{-}CCl_3 \tag{2d}$$

o-Chloranil (Q) here acts as an electron carrier from the donor (phenothiazine) to the acceptor (CCl_4).

The halogen-containing solvents CCl_4, $CHCl_3$, CH_2Br_2 were tested for the absence of peroxides and phosgene.

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