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THE INFLUENCE OF RADICAL ACCEPTORS AND THE NATURE OF SOLVENTS ON THE CIDNP SIGN AND INTENSITY IN THE DIAZONIUM SALTS - KNO_2 AND PHENYLHYDRAZINE - QUINONES INTERACTIONS

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The interaction of diazonium salts, $p\text{-X-}C_6H_4N_2^{+}BF_4^{-}$, (where X = H, NO_2, Cl, Br) with an excess of KNO_2 in the 1:1 dimethylsulphoxide - acetonitrile mixture at 40° has shown enhanced absorption for C_6H_5X products. On addition of the radical acceptor, 4-methyl-2,6-di-tert.-butylphenol (ionol - HI), the polarization changes its intensity and sign(Fig. 1).*

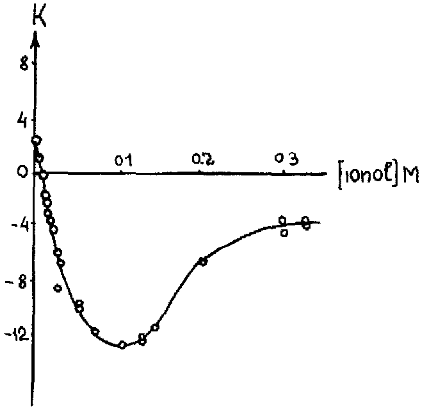

Fig. 1. The effect of ionol addition upon the $K = \frac{I_{max} - I_{o\infty}}{I_{o\infty}}$ values, where I_{max} is the maximum signal intensity of polarized benzene protons, $I_{o\infty}$ is the signal intensity for benzene after the reaction has completed; $[C_6H_5N_2^{+}BF_4^{-}] = 0.25$ M, $[KNO_2] = 0.5$ M, t° = 40°.

The phenomena observed are attributed to the fact that in the absence of an acceptor the benzene enhanced absorption contribution to polarization is dominant; enhanced absorption is built up in the uncorrelated radical pairs (I) $\overline{\underline{\text{Ar}}^{\bullet}\ {}^{\bullet}\text{ONO}}^{u}$ ($\Delta g < 0$, $a > 0$) which are formed due to the relative stability and

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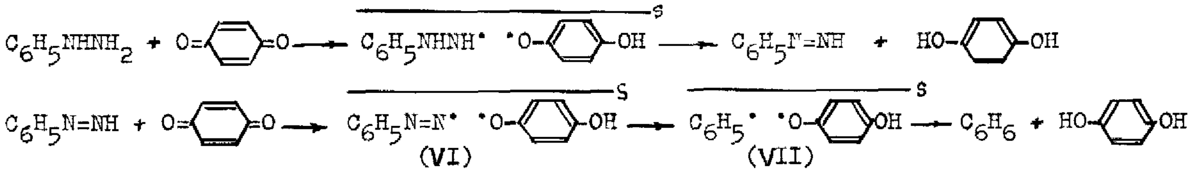
* The effect of free radical traps on CIDNP was reported in a number of communications /1/.

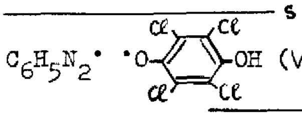
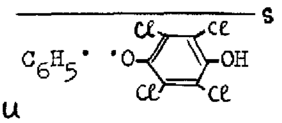
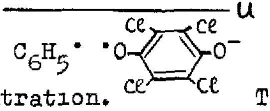
the high concentration of $NO_2^\bullet$ radicals. The contribution of the U-pairs to the polarization is reduced as the concentration of $C_6H_5^\bullet$ and $NO_2^\bullet$ radical-trapping ionol increases. At [HI] = 0.0033 M it equilibrates the contribution of singlet pairs $\overline{ArN{=}N^\bullet\ {}^\bullet ONO}^S$ (II) and $\overline{Ar^\bullet\ {}^\bullet ONO}^S$ (III) producing emission for benzene. EVer increasing ionol concentration leads to a rise in benzene emission due to a greater predominance of II and III pairs. Emission reaches the maximum at [HI] = 0.11 M. The subsequent benzene emission intensity drops are accounted for by the fact that more and more radical pairs (II and III) are substituted by $\overline{ArN{=}N^\bullet\ {}^\bullet I}^S$ (IV) and $\overline{Ar^\bullet\ {}^\bullet I}^S$ (V) pairs involving ionol radicals as [HI] increases. The IV-V pairs seem to have a smaller absolute Δg value than that for II and III pairs because $g_{I^\bullet}$ = 2.0044 /2/ is likely to be smaller than $g_{ONO^\bullet}$ /2/. At an ionol concentration higher than 0.25 M the polarization intensity is decreased slowly. One can assume that the IV and V pairs mainly exist in the system and an increase in the ionol concentration merely reduces their life time.

A scheme of reaction mechanism has recently been reported for the phenylhydrazine oxidation by 1,4-benzoquinone /3/:



According to the scheme, reaction product, benzene, is resulted from $C_6H_5^\bullet$ radicals having escaped the geminate pairs (VI and VII) where $\Delta g < 0$ and $a > 0$.

We have studied the influence of the nature of solvent and acid or alkali additions upon the polarization effects in this reaction and in the oxidation of phenylhydrazine by tetrachloro-1,4-benzoquinone (chloranil). The oxidation of phenylhydrazine by chloranil in tetrahydrofuran proved to give emission signals for benzene protons. However, the sign and the intensity of polarization vary on addition of water to solvent (Fig. 2).

This phenomenon is attributed to the fact that the ratio of contributions of correlated pairs  (VIII) and  (IX) and the diffusive pairs  (X) to polarization varies depending upon the water concentration. The correlated VIII-IX pairs are responsible for benzene emission ($\Delta g < 0$, $a > 0$)* and uncorrelated pairs

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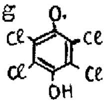
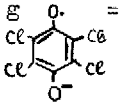
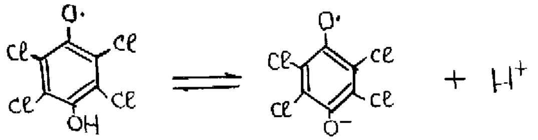
* g  = 2.005+0.00I; g  = 2.0058 /2/. The addition of water to solvent changes the g-factor weakly /4/.

X induced by stable chloranil radical anions and the $C_6H_5^{\bullet}$ radicals - for benzene enhanced absorption. The contribution of X pairs increases as fast as the water concentration in solution rises because, in this case, the equilibrium (I) shifts to the right and the concentration of chloranil anion-radicals increases.


(1)

In the oxidation of phenylhydrazine by benzoquinone the addition of water to tetrahydrofuran leaves the sign of polarization unaffected but makes the emission signal intensity more prominent (Fig. 2, b).

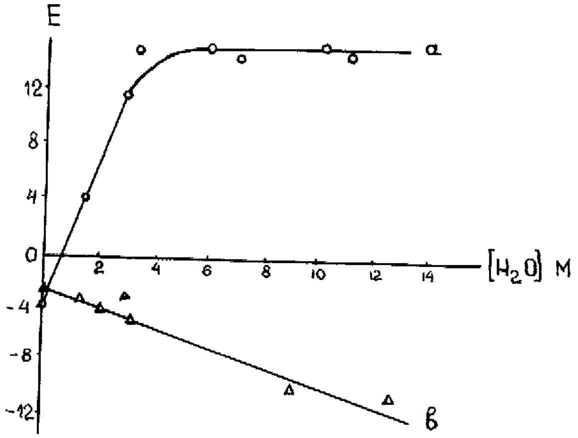
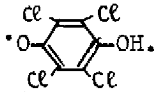
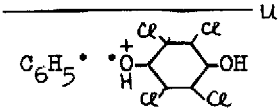


Fig.2. The dependence of the enhancement coefficient of nuclear polarization on the water concentration in tetrahydrofuran in the oxidation of phenylhydrazine by benzoquinone (b) and chloranil (a)

This reaction differs from that involving chloranil because  radical is a weaker acid compared to . The equilibrium of the type (1), for this case, is shifted to the left at any water concentration. An increase in enhancement coefficient (E) is probably due to the longer life time of the VI-VII pairs because of the water solvation of the radical pairs.

The effect of alkali additions on the sign and magnitude of the enhancement coefficient confirms our concepts. The presence of alkali shifts the equilibrium of type (1) to the right. Accordingly, alkali additions lead to the change in the phase of the benzene proton polarization from E to A in tests with chloranil at low water concentrations. In the absence of alkali, in this case, equilibrium (1) shifts to the left. With benzoquinone, the change in the phase occurs both at low and high water concentrations.

The addition of hydrochloric acid has the same effect though it shifts equilibrium (1) to the left. It can be accounted for by the fact that in the acid solutions, some relatively stable chloranil radical-cations are formed to give U-pairs XI ($\Delta g < 0$ and $a > 0$)



(XI)

The $C_6H_5^\bullet$ radicals escaping these pairs gives enhanced absorption for benzene protons. The radical-cations corresponding to benzoquinone seem to be less stable as compared with radical-cations from chloranil. Therefore, with benzoquinone, the addition of acid leaves both CIDNP sign and intensity unaffected.

We think that CIDNP effects in systems involving relatively stable radicals are especially sensitive to the factors affecting the concentration and the stability of these radicals. The phenomena deserve a more thorough investigation as they open the way for a detailed study of the mechanism of free radical conversions.

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