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CHEMICAL NUCLEAR POLARIZATION IN THE OXIDATION OF PHENYLHYDRAZINE BY 1,4-BENZOQUINONE OR TETRACHLORO-1,4-BENZOQUINONE

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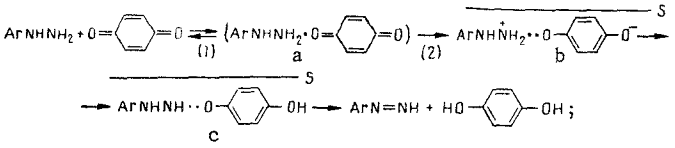
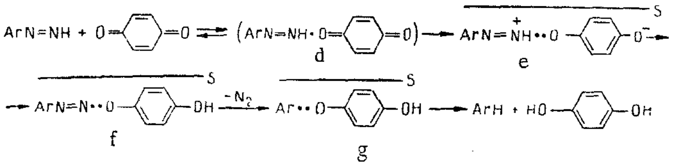
Negatively polarized products C_6H_5X are formed when phenylhydrazine or its derivatives n-$XC_6H_4NHNH_2$ are oxidized by 1,4-benzoquinone in solution in acetic acid with ether [1], in acetonitrile, or in a mixture of CCl_4 with ethanol [2]. By the method of chemical nuclear polarization (CNP) we have investigated the kinetics of accumulation of these products [2] and have studied the polarization effects in other reagents involved in the process; we suggest the following scheme for the reaction mechanism:





with stage 2 as the limiting one. The sign of the polarization E in components C_6H_5X is explained by their formation from aryl radicals coming from singlet (s) pairs for g for which $\Delta g < 0$ and $a > 0$.

It seemed of interest to study the reaction of phenylhydrazine with tetrachloro-1,4-benzoquinone (chloranil), which gives semiquinone radical-anions which are more stable than quinone [3]. In this case the probability of formation of radical pairs with uncorrelated spins (u pairs) in the reaction mixture is higher, and we can expect that the sign of the CNP of benzene will be opposite to that observed in experiments with benzoquinone and will depend on the experimental conditions. The reaction with chloranil is also interesting because chloranil is a much stronger oxidizing agent than benzoquinone (their respective electron affinities are 1.14-1.5 V and 0.4-0.77 V [4]), and it was important to elucidate how this fact affects the oxidation rate.

L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Teoreticheskaya i Éksperimental'naya Khimiya, Vol. 12, No. 3, pp. 406-410, May-June, 1976. Original article submitted July 14, 1975.

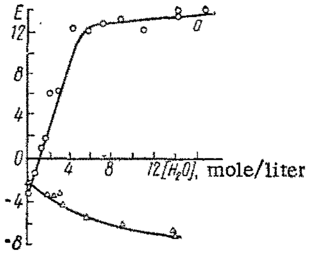


Fig. 1

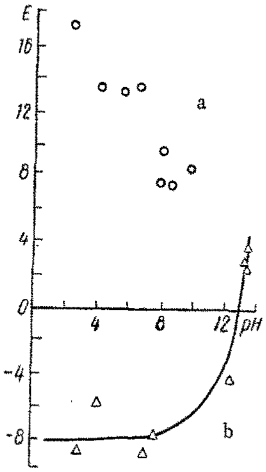
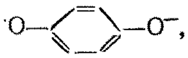
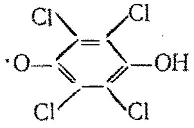
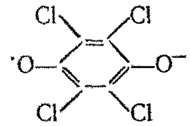
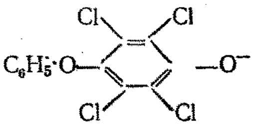


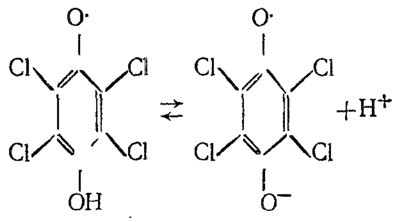
Fig. 2

Fig. 1. Amplification factor of CNP, E, in benzene, formed by reaction of phenylhydrazine with chloranil (a) or with benzoquinone (b), vs concentration of water in tetrahydrofuran. Concentrations of reagents: a) [phenylhydrazine] = 0.25 mole/liter, [chloranil] = 0.08 mole/liter; b) [phenylhydrazine] = 0.25 mole/liter, [benzoquinone] = 0.08 mole/liter. Temperature 40°C.

Fig. 2. Amplification factor of CNP, E, in benzene formed by reacting phenylhydrazine with chloranil (○) or with benzoquinone (Δ) vs pH at ends of experiments. [Phenylhydrazine] = 0.25 mole/liter; [benzoquinone] = [chloranil] = 0.08 mole/liter. Temperature 40°C.

We found that the reaction of phenylhydrazine with chloranil goes much faster (in comparable conditions) than that with benzoquinone. If we assume that same mechanism as above for both reactions, then this observation confirms that the process is limited by stage 2, because the rate of this stage should increase with the electron affinity of the quinones. In anhydrous tetrahydrofuran the reaction of phenylhydrazine with chloranil gives negatively polarized benzene, but in the oxidation of phenylhydrazine by chloranil in a solution of aqueous tetrahydrofuran (10 moles/liter water) positively polarized benzene is formed, whereas in experiments with benzoquinone in the same conditions the benzene is negatively polarized.

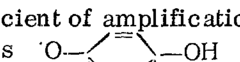
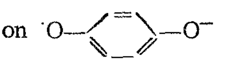
If we assume that the g factors of the radicals , ,  and  are equal or nearly equal [5], then to explain the appearance of positive polarization in benzene we must assume that in experiments with chloranil benzene is formed not only from $C_6H_5^{\cdot}$ radicals coming from S pairs of form f or g but also from $C_6H_5^{\cdot}$ radicals coming from u pairs of the type  (h). The ratio of the contributions made by s and u pairs to the CNP, and correspondingly the value and sign of the amplification factor of the CNP, E, depend on the concentration of water in the solvent (Fig. 1, curve a). We explained these effects by supposing that the equilibrium



(A) (B)

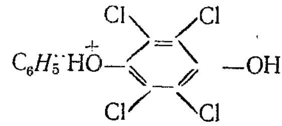
(I)

moves increasingly to the right as the concentration of water increases in the tetrahydrofuran. As a result there is an increase in the concentration of stable radical-anions B, and thus in the contribution made to the polarization by the u pair h, giving positively polarized benzene. The action of water is probably due to two factors – to increase in the dielectric constant of the solvent, and to specific solvation which increases the stability of the radical-anions B. At water concentrations above 5-6 moles/liter, equilibrium (I) is practically entirely shifted to the right, and further change in the water content of the solution has no influence on the value of E.*

In the reaction with benzoquinone, addition of water to tetrahydrofuran has the opposite effect (see Fig. 1, curve b): The coefficient of amplification of negatively polarized benzene increases. This must be due to the fact that the radicals  are more weakly acidic than the radicals A, and for any concentration of water an equilibrium of type (I) remains shifted to the left. Furthermore, the radical-anion  is less stable than B. As a result, the contribution of u-pairs to the total polarization of benzene is less than the contribution of s pairs f and g at any water concentrations. Increase in the water concentration increases the intensity of negative polarization, perhaps because hydration of the radicals increases the lifetimes of the s pairs f and g.

These considerations are confirmed by the influence of additions of acid or alkali on the sign and magnitude of the amplification factor of CNP. Addition of alkali shifts an equilibrium of type (I) to the right. In conformity with this, in experiments with chloranil the presence of small amounts of NaOH in the reaction mixture leads to disappearance of negative polarization of benzene, while the presence of large quantities of alkali leads to the appearance of positive polarization. This effect is appreciable only for low concentrations of water in the solution, because for water concentrations of over 5-6 moles/liter, equilibrium (I) is completely shifted to the right even without alkali, and we observe positive polarization (see above).

Hydrochloric acid has the same action as alkali, although it shifts equilibrium (I) to the left and suppresses formation of u pairs h. To explain the action of acid we postulated that in acid solutions relatively stable radical-cations are formed, and are also capable of giving u pairs



in which $\Delta g < 0$ and $a > 0$. On coming from these pairs the $C_6H_5^{\cdot}$ radicals should be converted to positively polarized benzene. Radical-cations corresponding to chloranil are evidently more stable than those from benzoquinone. For this reason, in experiments with benzoquinone addition of acid changes neither the sign nor the intensity of the polarization. Conversely, addition of alkali alters the signs of the polarization from E to A in this case also.

The influence of additions of acid or alkali was studied in more detail in solutions containing 9-14 moles/liter of water in tetrahydrofuran. In this series of experiments we measured the pH at the end of the reaction. The results are plotted in Fig. 2, which plots the amplification factor E vs the pH at the ends of the experiments with chloranil and benzoquinone. The sign of the polarization of benzene from the reaction with benzoquinone changes from E to A at pH values above 13 (see Fig. 2b), while the intensity of polarization in experiments with chloranil decreases symbatically with rise of pH (Fig. 2a). This last observation can be explained by supposing that as the pH rises the ionic route for decomposition of the intermediate product of the reactions (phenyldiimide) becomes increasingly important [8]:

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*We calculated E as in [6] for the case in which $k \gg \beta$; in each case, β was determined by the method in [7].

$$C_6H_5N{=}NH \xrightarrow{-H^+} C_6H_5N{=}N^- \xrightarrow{-N_2} C_6H_5^- \xrightarrow{+H^+} C_6H_6. \tag{II}$$

This process competes with the reactions of formation of benzene by a radical route. Reaction (II) gives unpolarized benzene which is mixed with polarized benzene and reduces the amplification factor of CNP. In experiments with quinone this effect is negligible because the increase of the pH makes possible not only process (II) but also the formation of u pairs.

When excess phenylhydrazine reacts with chloranil in aqueous tetrahydrofuran we observe negative polarization of the protons of the phenylhydrazine ring. Against this, in the oxidation by quinone the original phenylhydrazine is polarized positively [2]. Negative polarization of phenylhydrazine can be explained by the hypothesis that in experiments with chloranil, radical-ions $ArNHNH_2^{+\cdot}$, coming from s pairs of type b and from analogous u pairs, undergo electron exchange with the original phenylhydrazine and are converted to polarized molecules. The contribution made by u pairs to the polarization is greater than that of s pairs.

In conclusion, we may note that CNP effects similar to those found by us in this work must be expected when relatively stable radicals are formed in a system under investigation, because their concentration can be appreciable and may essentially change with the experimental conditions. These effects have hitherto been little studied. They open up new possibilities for the study of fine details of the mechanisms of free-radical reactions.

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