Physical Chemistry

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structural formulas

Figure 1: structural formulas

spectrum

Figure 2: spectrum

Abstract

Full Text

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STUDY OF THE RADICALIZATION OF BENZOQUINHYDRONE AND PHENAZHYDRINE ON SOLID SURFACES BY THE E.P.R. METHOD

(Presented by Academician M. I. Kabachnik, 7 VII 1962)

In a previous work by one of us (^1) it was shown by the isotopic method that, in the formation of phenazhydrine (a) from phenazine and dihydrophenazine, the nuclei of these components become decolorized.

This observation was explained by the fact that, in the process of preparation or separation of phenazhydrine in solution, semiquinone radicals (b) are formed with equal probability from both nuclei.

In the present work we found by the e.p.r. method (an instrument of the RE-1301 type was used, with a sensitivity of 10^{13}–10^{12} particles of diphenylpicrylhydrazyl in the sample) that almost saturated solutions of phenazhydrine in anhydrous ether or dioxane do not possess paramagnetism. Consequently, dissociation into radicals is not detectable in them (the sensitivity of the instrument made it possible to detect dissociation of 0.001% of the phenazhydrine molecules in the sample).

In contrast, crystalline phenazhydrine is paramagnetic*: it gives a single absorption line 15 gauss wide, with a g-factor equal to 2.003. The intensity of this line increases by a factor of 2–3 upon heating for 30 min to 120°, and at this temperature no longer increases further.

Fig. 1. E.p.r. spectrum of phenazhydrine radical ions in a medium of 50% aqueous acetic acid

It is natural to suppose that the above-mentioned decolorization of the nuclei of the components in phenazhydrine is caused by the fact that formation of

Fig. 2. EPR spectrum of phenazhydrine adsorbed on acidic ion-exchange resin KU-2–4

Figure 3: Fig. 2. EPR spectrum of phenazhydrine adsorbed on acidic ion-exchange resin KU-2–4

its crystal lattice proceeds through radicals (possibly of type (b)), and some of the radicals remain in the formed lattice. Another possible explanation of the paramagnetism of solid phenazhydrine is that neighboring molecules in its crystal lattice are in donor–acceptor interaction with charge transfer (cf. (⁀2)).

Acidified solutions of phenazhydrine, in contrast to neutral solutions, give e.p.r. spectra consisting of 7 lines**; with an intensity ratio– intensities 1 : 4 : 8 : 10 : 8 : 4 : 1, corresponding to stable radical ions (c) (3). Figure 1 gives such a spectrum, obtained by us for a solution of phenazhydrine in 50% aqueous acetic acid.

In contrast to phenazhydrine, when benzoquinhydrone is formed from quinone and hydroquinone and when it is separated into these components by sublimation in vacuum, the nuclei of the components do not become discolored (5). Accordingly, in solutions of benzoquinhydrone in ether and dioxane, and in crystalline quinhydrone, both cold and at 120°, there are no semiquinone radicals and no paramagnetism is detected.

Fig. 2. EPR spectrum of phenazhydrine adsorbed on acidic ion-exchange resin KU-2–4

Complete discoloration of the nuclei of the quinhydrone components does occur, however, when they are separated into components by chromatography on aluminum oxide (1), and partial discoloration occurs upon sublimation in a glass apparatus, especially when glass-wool tubes are used (5). The cause of the discoloration had previously remained unclear. There are data in the literature (6) that, upon adsorption of quinhydrone on the alkaline surface of barium hydroxide octahydrate, stable semiquinone radical ions (d) are formed, readily detected by the EPR method.

On this basis we assumed that the same radical ions are also formed on other surfaces possessing basic properties and, indeed, found that the system aluminum oxide–solution of benzoquinhydrone in ether (in air or after thorough evacuation of the adsorbent and solution at 10^{-4} mm Hg) gives in the EPR spectrum an intense single line of width 7 G, with a g-factor equal to 2.003. In dioxane

* Control experiments showed that phenazine, used for the preparation of phenazhydrine, is not paramagnetic, while dihydrophenazine gives an absorption line two orders of magnitude weaker than phenazhydrine, but with the same parameters, and is evidently an impurity of phenazhydrine.

** Each of them has an even finer structure (⁀4).

solution the same line is observed, but of lower intensity. Since no hyperfine structure was observed by us, the radical detected cannot be identified, but it is highly probable that it has structure (d).

The formation of radical ions explains the discoloration of the nuclei of the benzoquinhydrone components upon contact with aluminum oxide by the fact that they arise from both nuclei upon dissociation of the quinhydrone molecule (e) in the direction indicated by the arrow, and upon further elimination of protons from radicals (f) on the basic surface.

(d) (e) (f)

It may be thought that the action of glass is analogous to the action of aluminum oxide. We, however, did not detect an EPR spectrum in the system glass powder—ethereal solution of quinhydrone, probably because of the insufficiently developed glass surface (1.2 m^2/g) and the correspondingly too low radical concentration for detection. In the system aluminum oxide—ethereal or dioxane solution of phenazhydrine (the solution and adsorbent were degassed) —no EPR spectrum is observed. Bearing in mind that phenazhydrine radical ions are stable in an acidic medium, these data are also consistent with the fact that acidic centers are absent on the surface of Al_2O_3 (cf. (^{7})).

In contrast to this, in the case of aluminosilica gel (an industrial spherical aluminosilicate cracking catalyst, calcined in air at 500°* and dehydrated), EPR spectra are observed upon adsorption from ether or dioxane solutions of both quinhydrone and phenazhydrine. It follows from this that centers of both acidic and basic nature are present on the surface of this adsorbent, as had previously been assumed from indirect data(ˆ7). The correctness of the interpretations given is confirmed by the fact that adsorbents with a surface of purely acidic nature give EPR spectra only with phenazhydrine, whereas adsorbents with a purely basic surface give them only with quinhydrone.

We demonstrated this using as examples the strongly acidic cation exchanger KU-2-4 and the strongly basic anion exchanger IRA-400**: phenazhydrine solutions give EPR spectra only with the former, and quinhydrone solutions only with the latter. In the system with phenazhydrine, the spectrum shows a distinctly incomplete resolution into 7 lines (the same as upon adsorption on aluminosilica gel) (Fig. 2).

This character of the spectrum apparently confirms the formation, upon adsorption on an acidic surface, of radical ions (c), whose spectrum, as noted above, consists of 7 lines.

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* When working with an uncalcined and non-dehydrated adsorbent, the signal intensity decreased and the splitting disappeared in experiments with phenazhydrine.

** The ion exchangers were repeatedly washed with pure water for several days to remove mineral acid or alkali completely and were used in the wet state after pressing on filter paper. Upon dehydration by evacuation, EPR spectra were not observed, probably because of a narrowing of the "pores," which made them inaccessible to the adsorbed particles.

Note: Figure translations are in progress. See original paper for figures.

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