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THE EFFECT OF STERIC HINDRANCE OF THE PHENOLIC HYDROXYL ON THE EQUILIBRIUM BETWEEN OXYPHENYL-DIAZONIUM SALTS AND QUINODIAZIDES

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The ease of transition of the aromatic system of a phenol molecule into the cyclohexadienone system in various reactions (phenol—dienone rearrangement) strongly depends on the degree of steric hindrance of the hydroxyl group in the initial phenol (^{1}). Using various 2,6-dialkylphenols as examples, it was shown ($^{1-3}$) that cyclohexadienones are most stable and are formed most readily from phenols having tertiary alkyl groups in the 2 and 6 positions. However, no quantitative evaluation has so far been carried out of the effect of the volume of the ortho-alkyl groups of phenols on the ease of their conversion into cyclohexadienones. In one of our previous papers (^{4}), in order to determine such a regularity, we attempted to use the reverse reaction of salt formation of certain 4-hydroxy-3,5-dialkylbenzaldehydes. In these compounds the presence, in the para position of the phenol, of a strongly electronegative carbonyl group causes rearrangement of the aromatic bond system with participation of this group

[structural formula: 3,5-dialkyl-4-hydroxybenzaldehyde] $\underset{H^+}{\overset{OH^-}{\rightleftarrows}}$ [structural formula: quinoid anion form]

We showed that the equilibrium constant of this reaction decreases as the steric hindrance of the phenolic hydroxyl decreases. However, we were unable to extend this reaction to the lower members of the series, since in the case of slight shielding of the phenolic hydroxyl in *p*-hydroxybenzaldehydes, salt formation occurs at the hydroxyl group without rearrangement of the aromatic bond system.

In the present work we studied the effect of ortho-alkyl groups on the shift of the equilibrium between the quinoid and aromatic bond systems, using as an example the reversible conversion of quinodiazides into diazonium salts under the action of acids, a reaction characteristic of the entire series of these compounds.

[structural formula of quinodiazide] $\overset{H^+}{\rightleftarrows}$ [structural formula of hydroxyphenyldiazonium salt]

$$\text{I},\ R = R' = H;\quad \text{II},\ R = R' = CH_3;\quad \text{III},\ R = CH_3,\ R' = C(CH_3)_3;$$

$$\text{IV},\ R = R' = CH(CH_3)_2;\quad \text{V},\ R = R' = C(CH_3)_3$$

All 2,6-dialkyl-*p*-quinodiazides, the synthesis of which we described earlier (^{5}), and the corresponding hydroxyphenyldiazonium chlorides have different absorption maxima in the ultraviolet region. Moreover, for the unsubstituted quinodiazide (I), L. A. Kazitsyna et al. (^{6}) showed that, in during the transition from a neutral solution medium to an acidic one, a reversible reaction of conversion of the quinodiazide into an oxyphenyldiazonium salt takes place. These circumstances allowed us to apply a spectrophotometric method to study the equilibrium conversion of 2,6-dialkyl-*p*-quinodiazides into diazonium salts as a function of the pH of the medium. Table 1 gives the UV-spectral data for the quinodiazides and oxyphenyldiazonium salts that we studied; the latter exist only in sufficiently acidic media. Weakly acidic solutions of these compounds are characterized by the presence of absorption maxima of both the quinodiazide and the oxyphenyldiazonium salt. With increasing acidity, the absorption maximum of the quinodiazide decreases and the yellow color of the solution disappears. Figure 1 shows the UV spectra of 2-methyl-6-*tert*-butyl-*p*-quinodiazide and its salt.

Table 1

No.	R	R_1	UV spectra: quinodiazide λ	UV spectra: quinodiazide lg E	UV spectra: diazonium salt λ	UV spectra: diazonium salt lg E	lg K
I	H	H	252347	3.604.55	313	4.50	3.19
II	CH_3	CH_3	255362	3.794.61	323	4.30	2.83
III	CH_3	$C(CH_3)_3$	258365	3.824.59	325	4.28	2.72
IV	$CH(CH_3)_2$	$CH(CH_3)_2$	260365	3.974.57	325	4.27	2.76
V	$C(CH_3)_3$	$C(CH_3)_3$	265364	3.814.46	323	4.37	1.65

Fig. 1. UV spectra of aqueous-alcoholic solutions of 2-methyl-6-*tert*-butyl-*p*-quinodiazide: 1 —pH 7.00; 2 —pH 3.15; 3 —pH 1.00

Fig. 1. UV spectra of aqueous-alcoholic solutions of
2-methyl-6-tert-butyl-p-quinodiazide: 1 –pH 7.00; 2 –pH 3.15; 3 –pH 1.00

Figure 1: Fig. 1. UV spectra of aqueous-alcoholic solutions of 2-methyl-6-tert-butyl-p-quinodiazide: 1 –pH 7.00; 2 –pH 3.15; 3 –pH 1.00

Fig. 2. Effect of the pH of the medium on the equilibrium constant of the reaction of conversion of quinodiazide into a diazonium salt.

Figure 2: Fig. 2. Effect of the pH of the medium on the equilibrium constant of the reaction of conversion of quinodiazide into a diazonium salt.

The concentration of the forms in the equilibrium reaction as a function of the pH of the medium was determined from the optical density of these forms on an SF-4 spectrophotometer in standard cuvettes with an absorbing-layer thickness of 1 cm at $22^\circ \pm 0.5$. A solution of the quinodiazide in methyl alcohol was diluted with hydrochloric acid of a definite concentration, calculated so that the concentration of the quinodiazide in the working solution was $2.5 \cdot 10^{-5}$ mol/liter. The quinodiazide sample was weighed before the start of the experiment; the solution was kept in a dark place and diluted to the required concentration before measurement.

The equilibrium constant of the reaction under consideration serves as a quantitative characteristic of the influence of the *ortho*-alkyl groups on the ease of transition of the aromatic system of bonds into the quinoid one. From what has been set forth, in general form the following equilibrium reaction takes place:

$$\mathrm{H}^+ + A = \mathrm{HA}^+,$$

whence

$$\mathrm{pH} = \lg K + \lg \frac{(A)}{(\mathrm{HA}^+)}.$$

$$\mathrm{pH} = \lg K - \lg \left(\frac{D_0}{D} - 1 \right),$$

where D_0 and D are the optical densities of the initial concentration of quinodiazide at a specified pH.

In the coordinates pH and $\lg \left(\frac{D_0}{D} - 1 \right)$, we should obtain a straight-line relationship; moreover, the intercept cut off by the straight line on the abscissa axis must be equal to $\lg K$ (Fig. 2). Table 1 gives the $\lg K$ values for the equilibrium reaction of conversion of quinodiazide into a diazonium salt.

Fig. 2. Effect of the pH of the medium on the equilibrium constant of the reaction of conversion of quinodiazide into a diazonium salt:

1 —2,6-di-tert-butyl-*p*-quinodiazide;
2 —2-methyl-6-tert-butyl-*p*-quinodiazide;
3 —2,6-diisopropyl-*p*-quinodiazide;
4 —2,6-dimethyl-*p*-quinodiazide;
5 —*p*-quinodiazide.

The results we obtained clearly show that, with increasing steric hindrance of the phenolic hydroxyl, the equilibrium shifts toward formation of the quinoid system of bonds. The tendency of the aromatic system to pass into the quinoid form is most sharply expressed (in contrast to other 2,6-dialkylphenols) in 2,6-di-tert-butyl-*p*-quinodiazide. Unsubstituted *p*-oxyphenyldiazonium chloride likewise differs sharply in the indicated properties from other oxyphenyldiazonium salts and rearranges into quinodiazide with considerably greater difficulty.

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