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Abstract

Full Text

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On the Question of the Influence of Internal Hydrogen Bonds on the Color of Organic Compounds

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Solutions of dihalogen derivatives of 2,5-dihydroxy-*p*-benzoquinone or of halogenanilic acids possess an interesting peculiarity: while being violet in color, upon the addition of alkalis they sharply decrease the intensity of their color without changing their hue. Such behavior of these solutions is somewhat unusual, since analogous colored soluble organic substances capable of splitting off a hydrogen ion, if they do change in the presence of alkalis, acquire a deeper and more intense color. It is no accident that we have almost no one-color indicators with a colorless alkaline form.

Modern chemical theories of color explain in a definite way the bathochromic and hyperchromic effects that usually accompany a change in the pH of a solution of colored organic substances of acidic character. Thus, for example, according to the theory of Dilthey and Wizinger, the transition of a colored substance into the ionoid state results in an increase in absorptive capacity, so that the color intensity of ionoid compounds often exceeds the color intensity of the corresponding non-ionoid compounds by more than 100 times (1).

It is true that in those cases where the action of alkali ultimately leads to the filling of coordination vacancies, hypsochromic and hypochromic effects and even complete decolorization of the substance are observed. This is precisely the case, for example, in the transition of colored carbonium salts into colorless carbinol compounds.

However, halogenanilic acids are structurally simple substances:

[structural formula of halogenanilic acid]
where $X = \mathrm{Cl},\ \mathrm{Br}$ or J.

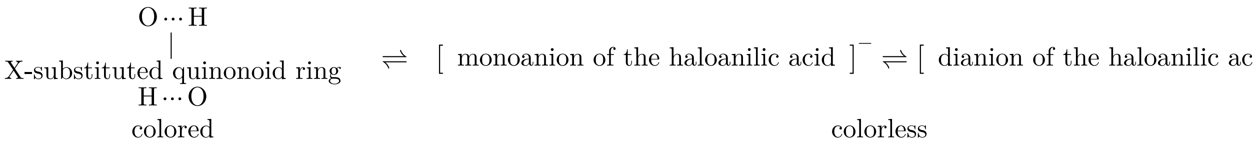
The halogen in these compounds is firmly bound, as follows both from the peculiarities of their synthesis (the action of alkali on tetrahalogen-*p*-benzoquinones) and from the fact that they interact with silver ions, even under relatively severe conditions, with the formation of the corresponding silver halogenanilates, and not silver halide.

In identifying the halogenanilic acids synthesized by us according to existing procedures and purified accordingly ($^{2-5}$), it turned out that they correspond to those reported in the literature*. They are strong acids. The hydrogen-ion exponents of their $5 \cdot 10^{-3}$ M solutions, calculated from electrical conductivity, were found to be, respectively: for chloranilic acid, 2.31; for bromanilic acid, 2.32; for iodanilic acid, 2.21. These data indicate that, in iodanilic acid, the hydrogen of the second hydroxyl is appreciably ionized.

When these substances are dissolved and when they interact with alkalis, it is unlikely that any serious disturbances of the structure of their molecules occur—so that the observed optical effect cannot be explained by this. Guided by the usual notions, it is rather more plausible to suppose that dissolution in the present case is accompanied by more or less extensive ionization, and interaction with alkalis by ordinary salt formation, followed by complete dissociation into ions.

It should be noted that the study and explanation of the optical properties of haloanilic acids is not only of known theoretical interest; the problem indicated also has a definite practical significance, since one of the substances considered—chloranilic acid—is used as a colorimetric reagent for calcium (6–9).

As a result of comparing and analyzing all the facts at our disposal, we have come to the conclusion that the dissociation of haloanilic acids should be described by the scheme:



$$\underset{\text{colored}}{\overset{\begin{array}{c}\mathrm{O}\cdots\mathrm{H}\\ |\end{array}}{\underset{\mathrm{H}\cdots\mathrm{O}}{\text{X-substituted quinonoid ring}}}} \rightleftharpoons \left[\ \text{monoanion of the haloanilic acid}\ \right]^{-} \rightleftharpoons \underset{\text{colorless}}{\left[\ \text{dianion of the haloanilic ac}\right.}$$

Thus, we believe that the concept of intramolecular hydrogen bonds provides the guiding thread for understanding the optical properties of solutions of haloanilic acids.

The representation given above of the structure of the acids and of their stepwise dissociation can hardly raise objections; the assumption of the reversibility of the process of destruction and formation of internal hydrogen bonds can be substantiated not only by references to analogies, but also by energetic considerations. As for the action of internal hydrogen bonds on the absorption spectrum of organic compounds, this question has been considered in the literature in the most varied aspects (10–12).

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* E. G. Kazakova and R. I. Storozheva took part in carrying out the experiments.

Fig. 1. Spectral curves of 0.002 M solutions of haloanilic acids (1) and their sodium salts (2): I –chloranilic, II –bromanilic, III –iodanilic

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From the scheme given above a number of consequences follow. First, upon dilution of solutions of haloanilic acids, the optical density of these solutions should decrease more rapidly than follows from calculation on the basis of the concentration of the dissolved substance.

Second, addition to these solutions of strong mineral acids should be accompanied by a noticeable increase in the intensity of the color, whereas addition of alkalis should be accompanied by its sharp decrease.

Third, soluble salts of these acids should color solutions the same color as the acids.

Fourth, the molar extinction coefficients of the acids at the absorption maximum should be considerably greater than those of the soluble salts.

Fifth, addition to solutions of the acids of water-miscible substances with a low dielectric constant should lead to an increase in the intensity of the color of the solutions.

All these consequences are in full agreement with the experimental facts, to the consideration of which we now turn.

Haloanilic acids and their salts are, in their optical properties, correspondingly similar, as is shown by the spectral curves recorded on the Pulfrich photometer (Fig. 1).

Accordingly, the molar extinction coefficients of the acids ($\varepsilon_{\mathrm{mol\,a}}$) and salts ($\varepsilon_{\mathrm{mol\,s}}$) are also similar for the spectral region around 550 mμ.

Acid	$\varepsilon_{\mathrm{mol\,a}} \cdot 10^{-3}$	$\varepsilon_{\mathrm{mol\,s}} \cdot 10^{-3}$
Chloranilic	0.77	0.18
Bromanilic	0.81	0.2
Iodanilic	0.84	0.25

The data presented indicate that the molar coefficient of a haloanilic acid is 3-4 times greater than that of its salt.

Fig. 1. Spectral curves of 0.002 M solutions of haloanilic acids (1) and their sodium salts (2): I –chloranilic, II –bromanilic, III –iodanilic

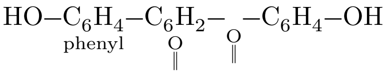
Upon dilution of the solutions, the molar extinction coefficients of the haloanilic acids decrease, owing to the increase in the degree of dissociation, as is evident from the data on the change in ε_{mol} of chloranilic and iodanilic acids at $\lambda_{\max}$ as a function of the solution concentration:

Concentration, mol/l	ε_{mol} of chloranilic acid ($\times 10^{-3}$)	ε_{mol} of iodanilic acid ($\times 10^{-3}$)
0.0020	0.77	0.84
0.0013	0.69	0.77
0.0006	0.66	0.74

Indeed, upon dilution of solutions of haloanilic acids, their light absorption decreases to a greater extent than can be calculated on the basis of the decrease in concentration. As for ε_{mol}, upon threefold dilution of the solution the latter decreases by 15-20%, i.e., by an amount exceeding the limits of experimental error.

When dilute mineral acids are added to the nearly colorless solutions of the substances under study, an increase in color intensity is observed quite clearly. The introduction into the acid solutions of substances that suppress dissociation (acetone) is also accompanied by a hyperchromic effect. The addition of alkalis to the brightly colored solutions, as already mentioned above, is accompanied by a sharp decrease in the intensity of the color.

For comparison with the compounds considered, we synthesized n, n'-dioxy-2,5-diphenylbenzoquinone-1,4 (13):



$$\mathrm{HO{-}\underset{phenyl}{C_6H_4}{-}\underset{\underset{\|}{O}}{C_6H_2}{-}\underset{\underset{\|}{O}}{}{-}C_6H_4{-}OH}$$

and became convinced that the transition of this substance into the ionoid state is accompanied by the usual bathochromic and hyperchromic effects: the substance itself at $\lambda = 430$ has ε_{mol} of the order of $7.5 \cdot 10^3$, whereas the product of its interaction with alkali at $\lambda = 550$ has ε_{mol} $1.1 \cdot 10^4$. This was to be expected, since in this case there are no internal hydrogen bonds in the molecule.

Thus, the facts considered in the present work should be taken into account when using halogenanilic acids in colorimetry.

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