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Abstract

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INVESTIGATION OF THE STRUCTURE OF THE *p*-DIMETHYLAMINOPHENYLDIAZONIUM CATION

Earlier investigations ([1], [2]) showed that double diazonium salts with metal halides are constructed ionically, like diazonium chlorides, i.e., the cation is the aryldiazonium ion, while the anion consists of metal halide complexes or the halide ion $[ArN_2]^+An^-$.

The properties of such ionically constructed diazonium salts are determined by both the anion and the cation.

Diazonium salts with the anions $ZnCl_4^{2-}$, $CdCl_4^{2-}$, $HgCl_4^{2-}$, $SbCl_4^-$, $SbCl_6^-$ are more stable, whereas those with the anions $Cu_2Cl_3^-$ are less stable both in solutions and in the solid state, relative to the diazonium chlorides themselves. The stability of the salts also depends to some extent on the halide that is part of the anion: for example, $(p\text{-}NO_2C_6H_4N_2)_2^+CdCl_4^{2-}$ is a sufficiently stable salt, whereas the salt $(p\text{-}NO_2C_6H_4N_2)_2CdJ_4^{2-}$ cannot be obtained because of decomposition ([1]).

The structure of the diazocation also affects the stability and reactivity of diazonium salts. The structure of the diazocation depends on the substituent in the phenyl ring. This is clearly seen from the change in the position of the absorption band in the IR spectra corresponding to vibrations of the diazonium group, and, according to our experimental data ([3]), the frequency of the diazonium group of the diazocation ν_{CN_2} depends linearly on the substituent constant σ, i.e., this dependence is described by an equation analogous to the Hammett equation $\nu = \nu_0 + \rho\sigma$. The value of the frequency ν_{CN_2} for the cation of *p*-N,N-dimethylaminophenyldiazonium ($\nu = 2166$ cm^{-1}) does not fall on the previously derived linear dependence $\nu - \sigma$. This indicates that the structure of the *p*-N,N-dimethylaminophenyldiazonium cation differs substantially from the structure of other aryldiazonium cations, even those with such strong electron-donating substituents as the OH and OCH_3 groups ([3]).

This circumstance is also reflected in the special properties of *p*-N,N-dimethylaminophenyldiazonium chloride and its salts with metal halides: their greater thermal stability, specific coloration, and special sensitivity to light. The absorption corresponding to vibrations of the diazonium group for *p*-N,N-dimethylaminophenyldiazonium chloride lies in the region intermediate between the corresponding absorption region of aliphatic ([4])

Fig. 1. UV spectra of p-N,N-dimethylaminophenyldiazonium borofluoride in water, conc. HCl, 4 N H_2SO_4 (1), in 70% H_2SO_4 (2), in 75% H_2SO_4 (3), in 80% H_2SO_4 (4), in 85% H_2SO_4 (5)

Figure 1: Fig. 1. UV spectra of p-N,N-dimethylaminophenyldiazonium borofluoride in water, conc. HCl, 4 N H_2SO_4 (1), in 70% H_2SO_4 (2), in 75% H_2SO_4 (3), in 80% H_2SO_4 (4), in 85% H_2SO_4 (5)

and aromatic diazo compounds ([5], [6]). Utsetel ([6]) explains such a strong displacement of the absorption band corresponding to the diazonium group of *p*-N,N-dimethylaminophenyldiazonium chloride, relative to the corresponding frequencies of other diazocations, by the fact that the true structure of the compound is intermediate between two structures:

$$(CH_3)_2N - \quad - \overset{+}{N} \equiv N \leftrightarrow (CH_3)_2\overset{+}{N} = \quad = \overset{+}{N} + \overset{-}{N}$$

Andersen and Stidli ([7]), in order to explain the special properties of diazonium compounds whose phenyl ring contains an amino group, propose for them a completely quinoid structure:

$$\begin{matrix} R_1 \\ R_2 \end{matrix} N = \overset{+}{N} = \quad = \overset{+}{N} = \overset{-}{N}$$

As proof of the quinoid structure, they consider the similarity of the UV spectra of an aqueous solution of *p*-N,N-dimethylaminophenyldiazonium chloride and an ether solution of diphenylquinonemethane.

The formation of a quinoid (or similar) structure of the diazocation is a characteristic feature inherent only in amino-substituted diazonium compounds. *o*- and *p*-oxyphenyldiazonium chlorides, which have strong electron-donor substituents, can give compounds with a quinoid structure only as a result of elimination of HCl, forming the so-called quinonediazides. This transformation is easily followed with the aid of UV spectra ([8]):

$$HO{-}C_6H_4{-}\overset{+}{N} \equiv NCl \underset{+HCl}{\overset{-HCl}{\rightleftharpoons}} O{=}C_6H_4{=}\overset{+}{N}{=}N^-$$

We set ourselves the goal of determining the conditions under which the structure of the cation of *p*-N,N-dimethylaminophenyldiazonium will be benzenoid (or close to it). The object of investigation we chose was *p*-N,N-dimethylaminophenyldiazonium borofluoride, since it is readily obtained in an analytically pure state; the method of investigation was spectroscopy in the UV and IR regions.

Fig. 1. UV spectra of *p*-N,N-dimethylaminophenyldiazonium borofluoride in water, conc. HCl, 4 N H_2SO_4 (1), in 70% H_2SO_4 (2), in 75% H_2SO_4 (3), in 80% H_2SO_4 (4), in 85% H_2SO_4 (5)

The UV spectra of *p*-N,N-dimethylaminophenyldiazonium borofluoride in water, dilute HCl and H_2SO_4, and in concentrated HCl are identical (Fig. 1): they have two absorption bands with maxima at 245 mμ ($\lg\varepsilon = 3.63$) and 380 mμ ($\lg\varepsilon = 4.77$). These data agree with the results obtained by Anderson and Stidley ([7]) for a solution of *p*-N,N-dimethylaminophenyldiazonium chloride in dilute HCl. Changes in the spectrum of the compound under study begin only when 60% H_2SO_4 is used as the solvent: in this case the intensity of the band at 380 mμ decreases. With increasing concentration of sulfuric acid, a further decrease occurs in the intensity of the absorption band at 380 mμ, an inflection appears on the absorption curve at 295 mμ, and the maximum of the band at 245 mμ shifts to 255 mμ (Fig. 1).

In 95% H_2SO_4 the absorption band with a maximum at 380 mμ almost completely disappears. This process is reversible: if a solution of *p*-N,N-dimethylaminophenyldiazonium borofluoride in concentrated H_2SO_4 is diluted with water, then the spectrum of this solution becomes analogous to the spectrum of the substance in dilute acids—as the concentration of H_2SO_4 decreases, the intensity of the band at 380 mμ increases, the band at 295 disappears, and the maximum of the short-wavelength absorption band again becomes 245 mμ.

The family of curves obtained for solutions with different concentrations of sulfuric acid has isosbestic points at 270 and 312 mμ (Fig. 1); this indicates that only two forms exist in solutions of different acidity.

The described change in the spectral characteristics of *p*-N,N-dimethylaminophenyldiazonium borofluoride is evidently connected with the transition of the quinoid structure of the *p*-N,N-dimethylaminophenyldiazonium cation into a benzenoid one, with simultaneous protonation of the amino-group nitrogen and formation, in strongly acidic media, of a doubly charged cation:

$$(CH_3)_2\overset{+}{N}H{-}C_6H_4{-}\overset{+}{N}\equiv N$$

To confirm the latter assumption, we synthesized *p*-trimethylammoniumphenyldiazonium dichloride, whose molecule contains an unquestionably benzenoid ring, and studied the UV spectra of its aqueous solution:

$$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix} > N^+ - \text{benzene ring} - N^+ \equiv N + 2Cl^-$$

It turned out that the spectrum of an aqueous solution of this compound is analogous to the spectrum of *p*-N,N-dimethylaminophenyldiazonium borofluoride in

Fig. 2. UV spectra of an aqueous solution of
p-trimethylammoniumphenyldiazonium dichloride (1), and of
p-N,N-dimethylaminophenyldiazonium borofluoride in 95% H_2SO_4 (2).

Figure 2: Fig. 2. UV spectra of an aqueous solution of *p*-trimethylammoniumphenyldiazonium dichloride (1), and of *p*-N,N-dimethylaminophenyldiazonium borofluoride in 95% H_2SO_4 (2).

95% H_2SO_4 (Fig. 2). The data obtained are evidence for the existence, in concentrated sulfuric acid, of a doubly charged cation with a benzenoid structure for *p*-N,N-dimethylaminophenyldiazonium borofluoride.

We also investigated the IR spectra of *p*-N,N-dimethylaminophenyldiazonium borofluoride in the solid state and of its solutions in water and concentrated sulfuric acid. In the solid state, *p*-N,N-dimethylaminophenyldiazonium borofluoride has two bands in the absorption region of triple and cumulated double bonds, namely at 2246 and 2166 cm^{-1}.

According to the data of Wetsel et al. [(6)] and Nuttel [(9)], in the IR spectra of *p*-N,N-dimethylaminophenyldiazonium chloride and borofluoride two absorption bands are also observed: one, intense, lies in the region 2251-2281 cm^{-1}, and a band of low intensity is located above 2200 cm^{-1}, at 2268 cm^{-1}. In aqueous solution we observed only a band at 2156-2161 cm^{-1}; in the region above 2200 cm^{-1} only asymmetry at $\sim$ 2251 cm^{-1} is observed. In concentrated sulfuric acid only one band is observed at 2300 cm^{-1}, which corresponds to absorption of the $-\overset{+}{N} \equiv N$ bond for diazocations having such strong electron-acceptor groups as nitro or carbethoxy groups [(3)]. In the IR spectrum of solid *p*-trimethylammoniumphenyldiazonium dichloride in this region there is also only one absorption band at 2302 cm^{-1}.

Fig. 2. UV spectra of an aqueous solution of *p*-trimethylammoniumphenyldiazonium dichloride *(1)*, and of *p*-N,N-dimethylaminophenyldiazonium borofluoride in 95% H_2SO_4 *(2)*.

Thus, on the basis of investigation of the UV and IR spectra, it may be concluded that the cation of *p*-N,N-dimethylaminophenyldiazonium itself in aqueous solutions, dilute solutions of HCl and H_2SO_4, and concentrated HCl exists only in one form—the quinoid form (or one close to it); in concentrated H_2SO_4 this cation is capable of being protonated, exhibiting the properties of a weak base.

Experimental Part

p-N,N-Dimethylaminophenyldiazonium borofluoride was synthesized by the procedure of [(10)]. *p*-Trimethylammoniumphenyldiazonium dichloride was obtained by diazotizing an alcoholic solution of the dichloride of the corresponding aniline with isoamyl nitrite. In the solid state the diazonium chloride was isolated from the alcoholic diazo solution by addition of ether.

$C_9H_{13}Cl_2N_3$. Found, %: diazo nitrogen 11.90; 11.87
Calculated, %: diazo nitrogen 11.95

The dichloride of the starting aniline was synthesized through *p*-trimethylammonium iodide acetanilide, obtained by the procedure of [(11)].

UV absorption spectra were recorded on an SF-4 spectrophotometer in standard cuvettes with an absorbing-layer thickness of 1 cm.

IR spectra were recorded on an IKS-12 spectrophotometer with a LiF prism. Spectra of the solid substance were recorded in the form of a suspension in Vaseline oil.

Using UV and IR spectra, the behavior of *p*-N,N-dimethylaminophenyldiazonium borofluoride was studied over a broad range of concentrations of the acids HCl and H_2SO_4. It was shown that the *p*-N,N-dimethylaminophenyldiazonium cation in water, dilute H_2SO_4, and conc. HCl has the same structure, close to the quinoid one, in contrast to the other aryldiazonium cations, which have mainly a benzene structure. It was proved that the *p*-N,N-dimethylaminophenyldiazonium cation is a weak base and adds a proton in concentrated sulfuric acid, becoming a doubly charged cation with a benzenoid structure.

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