Chemistry

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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STUDY OF THE DIAZONIUM CHLORIDE-DIAZOIMIDE EQUILIBRIUM FOR *p*-N-BENZENESULFONYLAMINOPHENYLDI CHLORIDE

In 1900 Morgan and co-workers (1) published a study on *p*-N-benzenesulfonylaminophenyldiazonium chloride and its diazoimide. He established that these compounds are readily isolated and relatively stable. On the basis of a study of their chemical properties, Morgan put forward assumptions concerning the structure of this diazonium chloride and the corresponding *p*-diazoimide, but no direct evidence for the hypotheses was provided (1–3).

We have carried out a systematic study of the UV and IR spectra of the *p*-benzenesulfonylaminophenyldiazonium cation and its *p*-diazoimide.

Fig. 1. UV spectra:
1 –$PhSO_2NHC_6H_4N_2Cl$ in H_2O;
2 –($PhSO_2NHC_6H_4N_2Cl$ in H_2O) + NH_4OH;
3 –$PhSO_2NC_6H_4N_2$ in H_2O;
4 –$PhSO_2NC_6H_4N_2$ in 0.1 N HCl

Fig. 2. UV spectra of $PhSO_2NHC_6H_4N_2Cl$ in buffer solutions.
1 –pH 1.1; 2 –pH 2.0; 3 –pH 3.5; 4 –pH 4.8

A solution of *p*-N-benzenesulfonylaminophenyldiazonium chloride in ordinary distilled water has two long-wavelength absorption bands in the UV spectrum, with absorption maxima at 327 and 372 mµ (Fig. 1). We assumed that these bands belong to the diazonium chloride (327 mµ) and its diazoimide (372 mµ), which in aqueous solution are present as an equilibrium mixture.

Upon careful alkalization the diazonium chloride solution turns yellow, and in its UV spectrum only one long-wavelength absorption band is observed, at 372 mµ. It is known that the diazoimide is isolated from an aqueous solution of the diazonium chloride upon alkalization with CH_3COONa and NH_4OH as a yellow crystalline precipitate.

The UV spectrum of a solution of the diazoimide in water has an absorption band with a maximum at 372 mµ, and the solution is yellow in color. A solution of the diazoimide in 0.1 N HCl becomes colorless; in the UV spectrum an absorption band is observed only at 327 mµ. The experimental data obtained indicate that the *p*-N-benzenesulfonylaminophenyldiazonium cation and

the corresponding *n*-diazoimide have different absorption in the UV region of the spectrum, and the presence of an isosbestic point indicates that we are dealing with an equilibrium of two forms—the diazonium and diazoimide forms. Thus, UV spectra make it possible to study the process of transition from the diazonium cation to the *n*-diazoimide and to determine the regions of existence of both forms. For this purpose, *n*-N-benzenesulfonylaminophenyldiazonium chloride was studied in buffer solutions with different pH values (Fig. 2). As is seen from Fig. 2, *n*-N-benzenesulfonylaminophenyldiazonium chloride exists completely in the diazonium form at $\mathrm{pH} \leq 1.1$, and completely in the diazoimide form at $\mathrm{pH} \geq 4.8$. In the interval between acidity values (pH 1.1—4.8) there is an equilibrium of the two forms (Fig. 2). All measurements in buffer solutions were carried out for diazonium chloride concentrations of 10^{-4} and 10^{-5} mole/liter.

Such constancy of concentration during measurements is necessary because the transition of the *n*-N-benzenesulfonylaminophenyldiazonium cation into the *n*-diazoimide occurs not only under the influence of a change in the medium, but also upon dilution: at a concentration of 10^{-1} mole/liter, in the spectrum of *n*-N-benzenesulfonylaminophenyldiazonium chloride in CH_3OH only a slight inflection is observed in the region of 372 $m\mu$ on the main absorption curve; at a concentration of 10^{-5} mole/liter there is already only one band of the *n*-diazoimide, with a maximum at 372 $m\mu$. At an intermediate concentration, both forms exist in solution (Fig. 3).

Fig. 3. UV spectrum of $PhSO_2NHC_6H_4N_2Cl$ in CH_3OH at different concentrations:
$1 - C = 10^{-1}$; $2 - C = 10^{-2}$; $3 - C = 10^{-4}$; $4 - C = 10^{-5}$ mole/liter.

The different absorption of these compounds in the UV region is consistent with the yellow color of the *n*-diazoimide, in contrast to the colorless diazonium chloride.

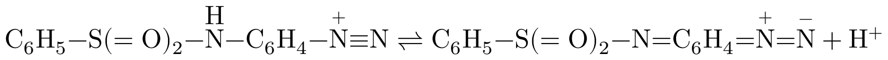
In the IR spectra, the frequency of the absorption band corresponding to the valence vibrations of the diazonium group in solid $C_6H_5SO_2C_6H_4N_2$ has the value 2181 cm^{-1}, which corresponds more to absorption by cumulated bonds

$$C = \overset{+}{N} = \overset{-}{N},$$

than to the absorption frequency of the CN_2 group in diazonium chloride, equal to 2259 cm^{-1}, which corresponds to the absorption region of the diazonium group

$$C-\overset{+}{N}\equiv\overset{-}{N}.$$

Thus, on the basis of the study of UV spectra it has been shown that the transition of the n-N-benzenesulfonylaminophenyldiazonium cation into the n-diazoimide is a dissociation reaction of a weak acid and occurs already in an acidic medium (pH 1.1–4.8).



$$C_6H_5{-}S(=O)_2{-}\overset{H}{N}{-}C_6H_4{-}\overset{+}{N}{\equiv}N \rightleftharpoons C_6H_5{-}S(=O)_2{-}N{=}C_6H_4{=}\overset{+}{N}{=}\overset{-}{N}+H^+$$

Studies of the UV and IR spectra of n-N-benzenesulfonylaminophenyldiazonium chloride and its n-diazoimide have shown that the structure of the former is benzenoid, and that of the latter quinoid, although with some displacement of electron density in both cases.

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