Determination of the Content of Tautomeric Ions in Solutions of *n*-Aminoazobenzene and Its Derivatives

1962

SovietRxiv

Fig. 1. Absorption spectra of sulfuric-acid solutions of *n*-aminoazobenzene. ($C = 5 \times 10^{-5}$ mol/l; cuvette length 1 cm). Sulfuric acid concentration: 1—4.8; 2—12.2; 3—23.7; 4—34.3%

Figure 1: Fig. 1. Absorption spectra of sulfuric-acid solutions of *n*-aminoazobenzene. ($C = 5 \times 10^{-5}$ mol/l; cuvette length 1 cm). Sulfuric acid concentration: 1—4.8; 2—12.2; 3—23.7; 4—34.3%

Abstract

Full Text

Chemistry

Yu. L. Kaminskii, I. Ya. Bershtein, and O. F. Ginzburg

Determination of the Content of Tautomeric Ions in Solutions of *n*-Aminoazobenzene and Its Derivatives

(Presented by Academician M. I. Kabachnik on 26 I 1962)

Salt formation of *n*-aminoazobenzene (AAB) and its derivatives is accompanied by the appearance of two tautomeric ions (II) and (III), which in concentrated solutions of strong acids are converted into the doubly charged cation (IV). These transformations may be represented by the following scheme ([1,2]):

[Displayed chemical scheme with structures labeled (I), (II), (III), and (IV), connected by reversible protonation arrows marked H^+.]

In solutions in which the base (I) and the doubly charged ions (IV) are practically completely absent, the ratio between the tautomers (II) and (III) is not constant and depends on the acid concentration ([1,3]). This is indicated, in particular, by the absorption spectra of AAB in sulfuric acid solutions of various concentrations shown in Fig. 1. It should be noted that it is not possible to obtain solutions containing only one of the tautomers. In the spectra shown in Fig. 1, the absorption maximum at a wavelength

Fig. 1. Absorption spectra of sulfuric-acid solutions of *n*-aminoazobenzene. ($C = 5 \times 10^{-5}$ mol/l; cuvette length 1 cm). Sulfuric acid concentration: 1—4.8; 2—12.2; 3—23.7; 4—34.3%.

Fig. 2. Optical densities of sulfuric-acid solutions of *n*-aminoazobenzene at wavelengths of 318 and 497 mμ. Acid concentration: 1—0.2; 2—4.8; 3—12.2; 4—23.7; 5—34.3%.

497 mμ is due to the presence in the solutions of quinoid cations (II), and at a wavelength of 318 mμ to ammonium ions (III) (2,4). In this case tautomer

Fig. 2. Optical densities of sulfuric-acid solutions of *n*-aminoazobenzene at wavelengths of 318 and 497 mμ. Acid concentration: 1—0.2; 2—4.8; 3—12.2; 4—23.7; 5—34.3%

Figure 2: Fig. 2. Optical densities of sulfuric-acid solutions of *n*-aminoazobenzene at wavelengths of 318 and 497 mμ. Acid concentration: 1 —0.2; 2—4.8; 3—12.2; 4—23.7; 5—34.3%

(II) practically does not absorb at the value λ_{max} of tautomer (III), and vice versa. The presence of an isosbestic point indicates that the concentrations of both tautomers are linearly dependent on one another. Therefore the points obtained by plotting the optical-density values of sulfuric-acid solutions of AAB at wavelengths of 318 mμ and 497 mμ lie on one straight line (Fig. 2). Extending this straight line to its intersections with the coordinate axes, we obtained the values of the optical densities that would be characteristic of AAB solutions if they contained only one of the tautomers. On the basis of the maximum values of the optical densities thus found, the molar absorption coefficients of each of the tautomers were calculated ($\varepsilon_{\mathrm{II}} = 5.22 \cdot 10^4$ at 497, $\varepsilon_{\mathrm{III}} = 1.82 \cdot 10^4$ at 318 mμ), as well as the concentrations of ions (II) and (III) in the solutions studied. The corresponding data are given in Table 1.

Table 1

Content of tautomeric cations (II) and (III) in sulfuric-acid solutions of AAB

Concentration of sulfuric acid, %	Ion content, %	Ion content, %	Ion content, %
	II	III	II + III
0.2	13.0	88.0	101.0
4.8	13.8	85.8	99.6
12.2	17.6	80.3	97.9
23.7	28.1	72.4	100.5
34.3	40.5	58.1	98.6

As is seen from examination of the data in Table 1, the error in this determination is comparatively small. Thus, in a number of cases, on the basis of comparison of the absorption spectra of solutions in which the ratio between the tautomers is not the same, it is possible to determine the molar absorption coefficient and the concentration of each of the tautomers in these solutions.

Leningrad Technological Institute
named after Lensovet

Received
19 I 1962

CITED LITERATURE

1. A. Hantzsch, A. Burawoy, Ber., **63**, 1760 (1930).

2. G. E. Lewis, Tetrahedron, **10**, 129 (1960).

3. E. Sawicki, J. Org. Chem., **21**, 605 (1956).

4. H. H. Joffe, S. Jung-yeh, J. Org. Chem., **22**, 128 (1957).

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