ELECTRONIC SPECTROSCOPY OF SOLUTIONS OF HETEROCYCLIC COMPOUNDS IN SULFURIC ACID

I. INVESTIGATION OF THE STABILITY OF FURAN COMPOUNDS IN SULFURIC ACID

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The behavior of furan derivatives in strongly acidic media was investigated by means of electronic spectroscopy. It is shown that at concentrations of 10^{-5} to 10^{-6} mole/liter a number of the investigated compounds are stable in sulfuric acid of any concentration because of a decrease in the probability of polymerization processes.

Considering the contradictions encountered in the problem of the acidophobic character of furan and its derivatives [1,2], we investigated the behavior of furan compounds in sulfuric acid solutions by means of electronic spectroscopy. From the character of the shift of the intense K band of the allowed $\pi-\pi^*$ transition peculiar to all of the compounds of the furan series, electronic spectroscopy makes it possible to identify the substances and to observe their chemical and physicochemical transformations. Resinification, sulfonation, ionization, and solvation are included among such potential transformations of furans in sulfuric acid.

We studied the UV spectra of furfural and its 5-methyl, 5-nitro, 5-dimethylamino, 5-bromo, and 5-iodo derivatives in concentrated sulfuric acid. The spectra of all of the compounds except 5-iodo- and 5-nitrofurfurals do not change when the compounds are allowed to stand at 95°C in sulfuric acid for 6 h (Fig. 1). In addition to the band at 367 nm, which corresponds to the spectrum of the solution at the start of thermostatting, a band with $\lambda_{\max}$ 320 nm gradually developed in the spectrum of 5-iodofurfural; after 4 h, the intensity of this band surpassed that of the starting band. The spectrum of 5-nitrofurfural changes considerably in the very first hour: the K band at 318 nm vanishes. A secondary spectral band corresponding to a decomposition product, which also vanished immediately, was also observed for a certain time on the boundary with the far UV.

Thus the stability of the furfurals varies considerably in strongly dilute solutions of them in sulfuric acid. The complete retention of the spectra of furfural and 5-methyl-, 5-bromo-, and 5-dimethylaminofurfural indicates their stability in this medium, i.e., neither polymerization (the conditions for which are unfavorable here), sulfonation, nor ring opening occur. Under these conditions, 5-dimethylaminofurfural exists in the protonated form with the ammonium group acting as an electron acceptor with respect to the furan ring. In this case, a definite behavioral analogy with 5-nitrofurfural should show up; however, this is not in fact observed.

One explanation for the change in the spectrum of 5-iodofurfural may be the ability of the iodine atom to undergo complexing – in particular, to form strong hydrogen bonds with sulfuric acid. However, the fact that the observed process occurs relatively slowly also makes it possible to assume the possibility of more profound transformations.

Using cryoscopic titration [3] in acetic acid, we found that furfural interacts with sulfuric acid to form 2 : 1 adducts. We previously [4] obtained the same results by an electrical conductivity method. This behavior indicates the probability of the formation of associates, particularly through the carbonyl group:

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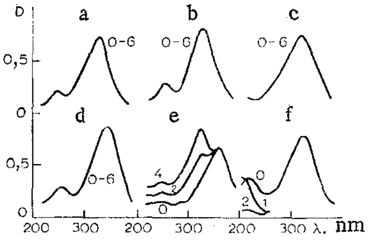


Fig. 1. Spectra of solutions of 5-substituted furfurals in sulfuric acid (thermostatted at 95°C): a) furfural; b) 5-methylfurfural; c) 5-dimethylaminofurfural; d) 5-bromofurfural; e) 5-iodofurfural; f) 5-nitrofurfural (the numbers on the curves are the thermostatting times in hours).

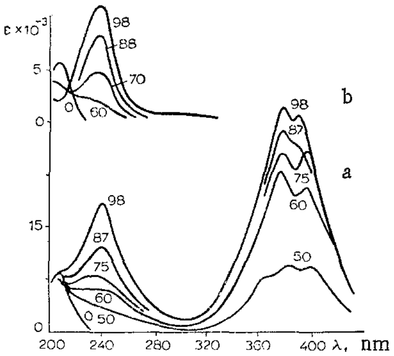


Fig. 2. Electronic spectra of furan (a) and silvan (b) in aqueous sulfuric acid solutions (the numbers on the curves are the sulfuric acid concentrations in water in volume %).

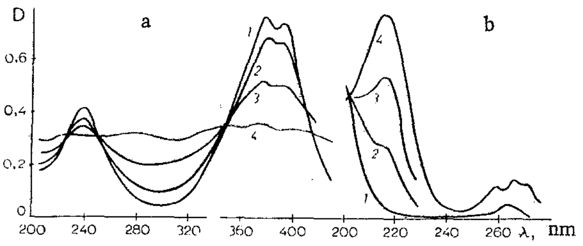
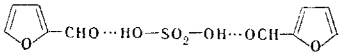


Fig. 3. Change in the spectra of furan (a) and benzene (b) in concentrated sulfuric acid. a: 1) Spectrum of a freshly prepared solution; 2) 2 h (at 20°) after preparation of the solution; 3) 24 h at 20°; 4) 2 h at 95°. b: 1) Spectrum of a freshly prepared solution; 2-4) 10, 20, and 40 min (at 20°) after preparation of the solution.



A substituent in the 5 position may display independent functionality, as observed in the case of 5-iodo- and 5-nitrofurfurals.

The spectral properties of furan, α-methylfuran, and – for comparison – benzene in sulfuric acid were specially examined. At various sulfuric acid concentrations, the spectra of furan and α-methylfuran (Fig. 2) have bands that characterize an acid–base equilibrium in the solutions. The spectrum of furan has two bands, both of which are of considerably higher intensity than in neutral solution. The spectrum of α-methylfuran has only one band, which is also peculiar to furan. The pK_a values for furan (−6.0) and α-methylfuran (−5.7) were calculated on the basis of this band via the method in [5]. This is in agreement with the data on the low basicity of the compounds under consideration [6]. The nature of the long-wave band in the spectrum of furan, which is absent in the spectrum of 2-methylfuran, is not completely clear. It is possibly determined by the peculiarity of the ionization of this compound.

Solutions of furan in sulfuric acid are relatively unstable: the characteristic spectral bands are lost at 95° in 2 h (Fig. 3a).

In contrast to furan, benzene does not give a long-wave shift of the K band in sulfuric acid. The changes are manifested only in the disappearance of the fine structure of the B band (Fig. 3b). By recording the spectrum at 200-225 nm every 5-10 min, we observed the gradual formation of a new band at 215 nm directly in the solutions in the cuvette. Dilution of this solution with water gave the spectrum of a substance with λ_{max} 210 nm, which corresponds to benzenesulfonic acid [7].

The results of the present experiments demonstrate that the problem of the acidophobic character of furan derivatives is to a considerable extent associated with their concentrations in acid solutions. The increase in the stability of dilute solutions of these compounds in sulfuric acid is apparently determined by the change in the character of the intermolecular interaction. Polymerization of the substances under the conditions selected does not occur because of the low probability of collision of the molecules. We did not observe sulfonation, and it must be noted that, according to the literature [8,9], furan derivatives are usually sulfonated with sulfur trioxide (in oleum or pyridine–sulfur trioxide complex) rather than with sulfuric acid.

EXPERIMENTAL

A method that excludes primary contact of the substance with sulfuric acid was developed for the preparation of solutions of furan derivatives in sulfuric acid. For this, 0.1-0.3 ml of a 1-2% solution of the preparation in acetic acid or ethanol was dissolved in 100 ml of concentrated sulfuric acid with vigorous stirring (the concentration of the compound was 1-4 · 10^{-5} mole/liter).

The preservation of the substance in sulfuric acid was confirmed by identification from the spectral characteristics of aqueous solutions after dilution of the samples with water. Isolation of the substance from neutralized solutions by extraction with ether was used in the case of aldehydes. The spectra of furfural and 5-methylfurfural in sulfuric acid were in agreement with the data in [10].

The experiments were performed with SF-4a and VSU2-P spectrophotometers with 1-cm-thick quartz cuvettes. "Pure" sulfuric acid with transparency up to 200 nm with the VSU2-P spectrometer was used; prior dilution was performed in glacial acetic acid and specially purified ethanol.

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