Chemistry

M. S. Barvinok, V. S. Kuprin, V. V. Mazurek, and G. I. Semenov

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Abstract

Full Text

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Physicochemical Investigation of the Process of Formation of Furfural–Aniline Resins

(Presented by Academician I. V. Tananaev, January 29, 1960)

The preparation of furfural–aniline resins has long been described in the literature ([1]). They have found application in the preparation of varnishes and in the chemical stabilization of soils ([2]). However, the chemistry of the process of resin formation from furfural and aniline has not been covered in the literature. To study this process we used methods of physicochemical analysis in combination with chemical and physical methods of investigation. In doing so we considered the light-absorbing properties of the system, its viscosity, and its thermal effect. The starting substances were: aniline, furfural, acetone, and toluene (analytical grade), and hydrochloric acid (chemically pure). The light absorption of acetone solutions was measured with an SF-4 photoelectric spectrophotometer, viscosity with a Höppler viscometer (model for precision measurements), and the thermal effect in a calorimeter ([3]). Infrared spectra were recorded on an automatic IKS-2 spectrometer. In order to follow the interaction of furfural with aniline at the beginning of the resin-formation process, the system furfural—aniline—acetone—HCl was investigated, the sum of furfural and aniline being 20 mole %, and HCl 0.0015 mole %.

The light absorption of the system was studied. Acetone solutions of furfural and aniline were mixed in various ratios. HCl was added in the form of concentrated hydrochloric acid to solutions of aniline in acetone. The light absorption of the solutions was measured half an hour after mixing, when it had acquired a value that remained unchanged for a prolonged period of time.

The results of the measurements are presented in Fig. 1. On the optical-density—composition curve (curve 1, $\lambda = 560$ mμ) there is observed a special point corresponding to the interaction of furfural with aniline in the molar ratio 1 : 1, which is most clearly manifested in the spectral region 530–560 mμ. The formation of a compound from 1 mole of furfural and 1 mole of aniline at the first stage of resin formation corresponds to furfuranylide (I) ([4])

$$C_6H_5NH_2 + O{=}CH{-}C_4H_3O \rightarrow C_6H_5N{=}CH{-}C_4H_3O + H_2O.$$

(I)

For the study of a deeper stage of resin formation, the system furfural—aniline—HCl—acetone was investigated, the sum of furfural and aniline being 20 mole %, and HCl 0.012 mole %.

In this case, however, before preparation of the acetone solutions, mixtures of furfural—aniline—HCl of various compositions were heated at 40° for 7 hours. Heating of furfural-aniline mixtures and an increase in the HCl concentration promote deepening of the resin-formation process. The optical-density—composition diagram in this case (curve 2, $\lambda = 565$ mμ) has a more complex character. On the optical-density—composition curves there are observed notable points corresponding to molar ratios 2 : 1, 1 : 1, 1 : 2, and 1 : 4. These points are confirmed on the optical-density—composition diagram in the study of a section with the sum of furfural and aniline equal to 40 mole % (curve 3, $\lambda = 570$ mμ).

The viscosity of the investigated system furfural—aniline—HCl (HCl 0.012 mol. %) was measured at 60°, when the furfural-aniline resins are in a viscous-fluid state.

On the viscosity—composition curves there is observed a singular point in the form of a sharp maximum, corresponding to the interaction of furfural and aniline in a molar ratio of 1 : 2 (curve 4). The viscosity of the system at this point exceeds the viscosity of the initial components by almost a thousandfold. This singular point does not change its abscissa (composition) upon addition of an indifferent substance—toluene—although the viscosity of the system decreases.

To construct the heat-effect—composition diagram, the system furfural—aniline—HCl (HCl 0.048 mol. %) was studied. At a lower HCl content the resin-formation process proceeds slowly, which makes measurement of the heat effects difficult. On the heat-effect—composition curve (curve 5) there is observed a singular point corresponding to the interaction of furfural with aniline in a molar ratio of 1 : 2 (the heat effect is expressed in calories per mole of mixture). Thus, the singular point corresponding to the interaction of furfural with aniline in a molar ratio of 1 : 2 is confirmed on composition—property diagrams in the study of a series of properties: light absorption, heat effect, and viscosity. The resins corresponding to this singular point are the best stabilizers of soils (^{2}).

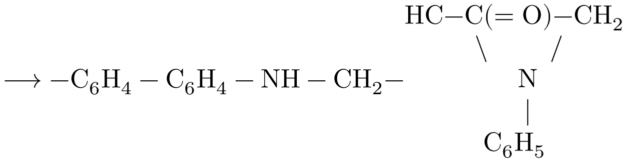
By methods of chemical investigation (analysis, synthesis, quantitative hydrogenation) and by study of the infrared spectra, we established that this singular point corresponds to two chemical compounds, of which one is converted into the other by cyclization.

On the basis of the scheme indicated, the deeper stage of resin formation may be represented as follows:

$$C_6H_5NH_2 + \text{furfural-anil} \xrightarrow{\text{HCl}}$$

$$\longrightarrow -C_6H_4 - NH - CH_2 - CH{=}CH - C(=O) - CH{=}N-$$

(II)



$$\longrightarrow -\mathrm{C_6H_4}-\mathrm{C_6H_4}-\mathrm{NH}-\mathrm{CH_2}-\begin{array}{c}\mathrm{HC{-}C({=}\,O){-}CH_2}\\ \backslash \quad\quad / \\ \mathrm{N} \\ | \\ \mathrm{C_6H_5}\end{array}$$

(III)

Fig. 1

Compound III was isolated by us from the resin in the form of colorless crystals with m.p. 144°. It should be noted that such a compound had earlier been obtained under somewhat different conditions by Mac Gowan. The latter assigned to it

structure with a tetrahydropyridine ring (^{5}). However, when we studied the IR spectrum of this compound and of the product of its hydrogenation (with 1 g-mol H_2), it turned out that the absorption frequency of $C = O$ shifts from the normal value for unstrained rings (1712 cm^{-1}) to a value characteristic of five-membered rings (1742 cm^{-1}), with simultaneous disappearance of the $C = C$ frequency. The stretching vibration frequency of $C = O$ in III is affected by two effects: on the one hand, the conjugation effect, which lowers the frequency, and on the other, the strain of the five-membered ring, which raises it. Therefore the $C = O$ frequency in III has a normal value and does not show conjugation. In the UV spectrum of compound III, weak conjugation is observed (at $\lambda = 300$ mμ, the extinction coefficient decreases from 9100 for III to 4660 for the product of its hydrogenation).

Compound III could not be isolated from the resin, but the product of its hydrogenation (with 1 g-mol H_2) was obtained in the form of almost colorless crystals (light brown) with m.p. 83—83.5°. The elemental analysis and molecular weight correspond to the formula $C_{17}H_{18}ON_2$.

The hydrogenation product of III, corresponding to the same empirical formula, has m.p. 114.5—115°. Hydrogenation in both cases was carried out under identical conditions: catalyst $Pd/CaCO_3$, solvent ethyl acetate, normal pressure, temperature $\sim 18°$.

As a result of the investigation carried out, it may be considered that furfural-aniline resins (composition 1:2) are a mixture of low-molecular compounds II and III, the crystallization of which is hindered by the noncyclic form II.

The investigation performed by us demonstrates the fruitfulness of an integrated approach to the study of systems by methods of physicochemical analysis in combination with other research methods.

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