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Abstract

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Infrared Absorption Spectra of Oxybenzylamines

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According to the work of a number of investigators (^{1}), carried out on model mono- and disubstituted phenols, in the process of curing phenol-formaldehyde resins with hexamethylenetetramine, oxybenzylamines are formed–intermediate products of the curing reaction. Oxybenzylamines are polynuclear compounds in which the phenolic nuclei are linked by dimethyleneamine (—CH_2—NH—CH_2—)

Fig. 1. Infrared absorption spectra:

a –compound (I)

CH_3-substituted phenolic nucleus—CH_2—NH—CH_2—CH_3-substituted phenolic nucleus (I)

b –compound (II)

H_3C-substituted phenolic nucleus—CH_2—N(CH_3-substituted phenolic nucleus)—CH_2—CH_3-substituted phen (II)

and trimethyleneamine (N(CH_2—$)_3$) bridges. It is assumed that, during curing, these bridges, under the influence of thermal action, are converted into methylene and azomethine bridges.

It was of considerable interest to test the above ideas by using infrared spectroscopy methods. Despite the fact that infrared spectroscopy is one of the few methods that can be used for the structural investigation of infusible and insoluble curing products, very few works devoted to this question have been published. In the available works (^{2}), the spectra of

absorption of a number of substituted phenols and of certain novolac and resol resins. At the same time, there are no works dealing with the study of the processes of curing phenol-formaldehyde resins under the influence of hexamethylenetetramine.

In the present communication, results are given for a study of absorption spectra in the infrared region of certain oxybenzylamines obtained by the interaction of phenol and its mononuclear derivatives

Fig. 2. Infrared absorption spectra of polynuclear oxybenzylamines:

a –

$$HO{-}C_6H_3(CH_3){-}\left[CH_2{-}NH{-}CH_2{-}C_6H_3(OH)(CH_3)\right]_n CH_2{-}NH{-}CH_2{-}C_6H_3(OH)(CH_3)$$

b –

$$HO{-}C_6H_3(C(CH_3)_3){-}\left[CH_2{-}NH{-}CH_2{-}C_6H_3(OH)(C(CH_3)_3)\right]_n CH_2{-}NH{-}CH_2{-}C_6H_3(OH)(C(CH_3)_3)$$

c –

$$HO{-}C_6H_3(Cl){-}\left[CH_2{-}N(CH_3){-}CH_2{-}C_6H_3(OH)(Cl)\right]_n CH_2{-}N(CH_3){-}CH_2{-}C_6H_3(OH)(Cl)$$

with hexamethylenetetramine. In Fig. 1 are presented the absorption spectra of two model substances: 2,2′-dioxy-3,5,3′,5′-tetramethyldibenzylamine (I) and the corresponding trioxybenzylamine (II):

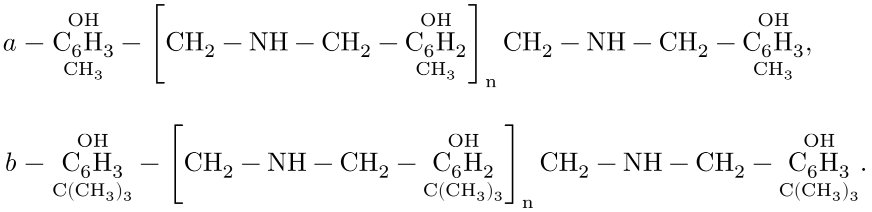
$$HO{-}C_6H_2(CH_3)_2{-}CH_2{-}NH{-}CH_2{-}C_6H_2(CH_3)_2{-}OH \qquad (I)$$

$$\left[HO{-}C_6H_2(CH_3)_2{-}CH_2\right]_3N \qquad (II)$$

These products were obtained from 2,4-xylenol by the method described in work (^{3}).

On the basis of the available literature data (^{2}), it is possible to identify some of the most intense bands in the absorption spectra of these compounds. Thus, the absorption band in the region of $11.6\,\mu$, present in the spectra of both compounds, should be assigned to the structure of tetrasubstituted benzene. The intense band in the region of $8.3\,\mu$ is usually

Fig. 3. Infrared absorption spectra of high-molecular-weight oxybenzylamines:



$$a - \underset{CH_3}{\overset{OH}{C_6H_3}} - \left[CH_2 - NH - CH_2 - \underset{CH_3}{\overset{OH}{C_6H_2}}\right]_n CH_2 - NH - CH_2 - \underset{CH_3}{\overset{OH}{C_6H_3}},$$

$$b - \underset{C(CH_3)_3}{\overset{OH}{C_6H_3}} - \left[CH_2 - NH - CH_2 - \underset{C(CH_3)_3}{\overset{OH}{C_6H_2}}\right]_n CH_2 - NH - CH_2 - \underset{C(CH_3)_3}{\overset{OH}{C_6H_3}}.$$

Fig. 3. Infrared absorption spectra of high-molecular-weight oxybenzylamines: a —polymer with methyl-substituted phenolic rings; b —polymer with tert-butyl-substituted phenolic rings.

Figure 1: Fig. 3. Infrared absorption spectra of high-molecular-weight oxybenzylamines: a —polymer with methyl-substituted phenolic rings; b —polymer with tert-butyl-substituted phenolic rings.

assigned to deformation vibrations of O—H. In addition to these bands, the fairly intense bands we found in the region of 11.8 and 11.92 μ are of great interest. The first of them is present in the spectrum of dibenzylamine, the second in the spectrum of tribenzylamine; moreover, both bands are located close to the intense band characteristic of the structure of tetrasubstituted benzene.

Figure 2 gives the absorption spectra of polynuclear oxybenzylamines. These oxybenzylamines are obtained by heating to 140—160° a thoroughly ground mixture of the corresponding phenol with hexamethylenetetramine and are comparatively low-molecular-weight compounds (4). In addition to the absorption bands indicated above, corresponding to tetrasubstituted benzene and hydroxyl, the spectra of polynuclear oxybenzylamines contain intense bands in the region of 12.2 μ, corresponding to a trisubstituted benzene ring—the terminal groups of these compounds. In the spectra of all oxybenzylamines obtained on the basis of phenol and its *p*-substituted derivatives, there is an absorption band in the region of 11.84 μ, corresponding to the dimethyleneamine bridge —CH_2—NH—CH_2—, whereas in the spectrum of the polymer obtained on the basis of

of *o*-chlorophenol, an absorption band is observed in the region of 11.92 μ, corresponding to the trimethyleneamine bridge $N(CH_2—)_2$. These results agree with the data of a number of authors (1), according to whom *p*-substituted phenols react with hexamethylenetetramine with the formation predominantly of dibenzylamines, whereas *o*-substituted phenols form predominantly tribenzylamines.

Figure 3 presents the absorption spectra of high-molecular-weight oxybenzylamines obtained by the interaction of phenols with hexamethylenetetramine in diphenyl solution; these spectra essentially repeat the absorption spectra of polynuclear oxybenzylamines shown in Fig. 2. In the absorption spectra of polyoxybenzylamines, the bands in the region of 12.2 μ, corresponding to terminal groups, are considerably weakened, but do not disappear completely, which, apparently, is due to the considerable branching of these polymers.

We see that the absorption bands characteristic of dimethyleneamine and trimethylene bridges also appear in the absorption spectra of polyoxybenzylamines shown in Fig. 3.

Thus, the absorption bands in the spectra of model oxybenzylamines in the regions of 11.84 μ and 11.92 μ, caused by the presence in them of dimethyleneamine and trimethyleneamine bridges, are also present in the spectra of polynuclear oxybenzylamines and in polyoxybenzylamines. This makes it possible to use these characteristic absorption bands for the structural investigation of curing processes of phenol-formaldehyde resins in those cases where curing proceeds through the stage of formation of oxybenzylamines.

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REFERENCES

[1] R. W. Martin, *The Chemistry of Phenolic Resins*, N. Y., 1956. [2] R. E. Richards, H. W. Thompson, J. Chem. Soc., 1947, 1260; H. W. Thompson, P. Torkington, Trans. Farad. Soc., 41, 246 (1945). [3] K. Hultzsch, Chem. Ber., 82, 16 (1949). [4] A. Zinke, G. Zigeuner, G. Weiss, W. Leupold-Löwenthal, Monatsh. Chem., 81, 1098 (1950).

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