Chemistry

1963

SovietRxiv

Abstract

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Chemistry

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On the Interaction of Certain Amino Compounds with Dehydratable Silica Gels

(Presented by Academician V. A. Kargin, June 20, 1963)

Ordering of monomer molecules, i.e., a decrease in entropy in the reaction system, makes it possible to carry out the polymerization (polycondensation) of a number of substances that are not capable of these reactions under ordinary conditions ([1–4]). In our work ([5]) we showed that acetaldehyde molecules, ordered as a result of adsorption on the surface of silica gel dehydrated at room temperature, enter into a polycondensation reaction with the formation of polyene aldehydes.

The decrease in entropy of molecules upon adsorption will apparently be different for different kinds of surfaces and adsorbed molecules. For adsorbents of the silica-gel type, the decrease in entropy on transition to the adsorbed state should be especially large in the case of such bifunctional molecules as amino alcohols. It was therefore of interest to study the possibility of polycondensation of ethanolamine, ordered in the adsorption layer on the surface of silica gel, with formation of a polyamine (polyethylenimine) according to the reaction:

$$n(\mathrm{OH—CH_2—CH_2—NH_2}) \xrightarrow{-n\mathrm{H_2O}} \mathrm{OH—(—CH_2—NH—CH_2—)_n—NH_2}.$$

Such a study was all the more interesting because, in the liquid state, such a reaction apparently does not proceed, since an approximate calculation made by us shows that its heat effect is close to zero.

The experiments were carried out as follows. Monoethanolamine was adsorbed on silica gels of various porous structures from the gas phase or from a 5–10% aqueous solution. In individual cases the silica gels were impregnated with pure ethanolamine. After this, for 2–3 hours the samples were heated at a temperature of 120–160°C. In another series of experiments, silica gels that had adsorbed ethanolamine were kept for a long time at room temperature in a desiccator over ignited $CaCl_2$.

Both heating of the samples and keeping them over a desiccant led to removal of water from the system, as a result of which the equilibrium should shift toward formation of the reaction products. In all cases, under the indicated treatment,

Figure 1 and Figure 2 graphs

Figure 1: Figure 1 and Figure 2 graphs

the silica gels became colored yellow or yellow-brown, which is probably explained by partial oxidation of the reaction products by atmospheric oxygen. Such samples were evacuated for 2-3 hours at 100-150° and a pressure of 10^{-3} mm Hg in order to remove unreacted ethanolamine.

Extraction of the reaction products from the pores of macroporous silica gels was achieved by boiling them with several successive portions of distilled or acidified water, since the presumed product of polycondensation of ethanolamine –polyethylenimine–is soluble in water. The substance obtained after removal of water from the extracts was a light-yellow resin-like mass.

We recorded the IR spectra of this polymer and, for comparison, the spectra of liquid ethanolamine and of polyethylenimine obtained by polymerization

ethylenimine in aqueous solution. It turned out that in the spectrum of ethanolamine and of the product of its transformation on the surface of silica gel there are absorption bands at 1080 cm^{-1} and 1040 cm^{-1}, evidently associated with the vibration of C–O and the deformation vibrations of OH in the C–OH group, as well as with C–N vibrations in $-CH_2-NH_2$.

However, in the polymer obtained by polycondensation of ethanolamine, in the region of 1130 cm^{-1} a new band appears, absent from the spectrum of ethanolamine and present in the spectrum of polyethyleneimine obtained by polymerization of ethylenimine. This band apparently corresponds to valence vibrations of the C–N bond in polyethyleneimine molecules.

Fig. 1. Adsorption isotherms of methanol vapor on control (1), ethanolamine-treated (2), and ethylenimine-treated (3) silica gels.

Fig. 2. Adsorption isotherms of methanol vapor (1) and water vapor (2) on silica gels: control (a), treated with ethanolamine and boiled in water (b), treated with ethanolamine and heated in vacuum at 550°C for 2 hours (c), treated with ethanolamine and kept in 1 N NaOH solution in the cold for one week (d). Black points–desorption.

It is possible that the transformation of some part of the ethanolamine into polyethyleneimine on the surface of dehydrated silica gel proceeds through the stage of ethylenimine formation according to the reaction:

$$n(\mathrm{OH{-}CH_2{-}CH_2{-}NH_2}) \xrightarrow{-n\mathrm{H_2O}} n \begin{pmatrix} \mathrm{CH_2-CH_2} \\ \backslash \quad / \\ \mathrm{NH} \end{pmatrix} \xrightarrow{\mathrm{H^+}} (\mathrm{-CH_2{-}NH{-}CH_2-})_n,$$

since in a number of experiments the liberation of ethylenimine was observed.

The formation of polyethyleneimine on dehydrated silica gels is also confirmed by comparison of the structural-sorption characteristics (Fig. 1) of samples of coarse-pored silica gels obtained in the presence of ethanolamine and treated with ethylenimine vapors, which is capable of polymerizing on the surface of various adsorbents with formation of polyethyleneimine (cf. ([6])). As can be seen from Fig. 1, the methanol sorption isotherms on "ethanolamine" and "ethylenimine" silica gels coincide up to $P/P_s = 0.7$. This indicates that the surface of these adsorbents has the same nature. An elementary calculation from the change in total sorption capacity shows that the polyethyleneimine film formed both when the gel is treated with ethanolamine and when ethylenimine is adsorbed on it has approximately the thickness of a monolayer. The considerable decrease in the specific surface area of the treated samples is probably due to the fact that this monomolecular film makes the smallest pores of the adsorbent inaccessible to methanol molecules. On the other hand, the affinity of methanol for the polyethyleneimine film on the surface of silica gel will be less than the affinity

to the surface of pure silica, which will lead to an increase in the effective area occupied by the methanol molecule and, consequently, to a decrease in the specific surface of the sample calculated from the isotherm.

In contrast to the case of macroporous silica gels, finely porous adsorbents obtained from hydrogels washed with acidified water (pH 4), after impregnation with liquid ethanolamine and subsequent dehydration at 120–160°, acquire a number of unusual properties. Thus, for example, in contrast to ordinary silica gels, these samples do not dissolve in NaOH solutions at room temperature and dissolve in them only with difficulty upon prolonged boiling. Finely porous silica gels kept in ethylenimine vapor behave in exactly the same way, which once again indicates the conversion of ethanolamine in the pores into polyethyleneimine. The resistance to the action of alkali is evidently caused by blockage of the silica surface by a film of polyethyleneimine firmly adsorbed on it, whose impermeability even to OH^- ions is apparently due to hydrogen bonds formed between neighboring polymer molecules.

Finely porous "ethanolamine" silica gels also possess unusual adsorption properties: they sorb H_2O vapor fairly well and almost do not absorb benzene and methanol vapors. This is evident from the sorption isotherms of water and methanol vapor (Fig. 2) for samples treated by various methods. The desorption branches of the isotherms in the case of H_2O vapor run considerably higher than the adsorption branches, forming an unusually broad hysteresis loop. In addition, most of the sorbed water is not removed by evacuation at room temperature and can be desorbed only upon heating. The formation of polyethyleneimine on finely porous silica gels apparently leads to the appearance of interparticle, rather than intraparticle,[7] ultramicropores, which affects the features of water sorption by such samples.

It should be noted that the etherification of the silica-gel surface with the formation of $Si{-}O{-}CH_2{-}CH_2{-}NH_2$, proposed by the authors of work[8] for its

treatment with ethanolamine under analogous conditions, probably does not occur, as is evident from the results obtained in the present study.

We also studied the possibility of polycondensation of amino acids on dehydrated silica. It turned out that heating at 100° in vacuum of a macroporous silica gel containing glycocol and leucine in its pores leads to the formation of a product whose IR spectrum has bands characteristic of polypeptides. The formation of polypeptides in this case is also confirmed by other data.

It may be assumed that such polycondensation reactions of amino acids, concentrated by adsorption on the surface of silicas, could at one time have led to the formation of pre-proteins and played a rather important role in the process of the origin of life on Earth.

The authors are sincerely grateful to L. A. Kotorlenko and I. Ya. Kachkurova for their assistance with the spectral measurements.

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Received
19 VI 1963

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