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BRIEF COMMUNICATIONS

Condensation of Diphenylguanidine and Hexamethylenediamine

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Abstract—Reaction of condensation of diphenylguanidine with hexamethylenediamine was performed. It is shown that the resulting condensate is a selective ion exchanger.

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It is known that long-chain alkylguanidines and resins containing guanidine functions are anion exchangers and have high capacity and relative selectivity for gold [1, 2]. The alkylation of guanidine and introduction of a guanidine function into the polymer chain pose a difficult technological problem. It has been shown previously how the water-soluble polymer polyhexamethyleneguanidine can be converted to a water-insoluble form [3].

The readily available and inexpensive domestically manufactured low-basic 1*N*,3*N*-diphenylguanidine (pK_a 10.12) is to be used to obtain water-insoluble ion exchangers with guanidine functions [4, 5].

Because of the noticeable solubility in water, diphenylguanidine itself cannot be used as an ion exchanger. One of ways to render diphenylguanidine insoluble is to make larger its molecular mass by, e.g., performing its condensation with hexamethylenediamine.

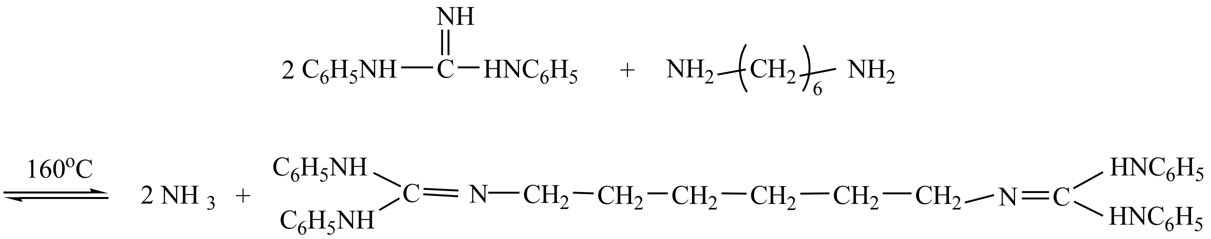
It is known that fusion of guanidine with hexamethylenediamine at temperatures of up to 180°C yields an oligomer of polyhexamethyleneguanidine [6, 7]. Because no reaction of this kind with 1*N*,3*N*-diphenylguanidine has been carried out, it seems advisable to perform the condensation reaction with hexamethylenediamine. The condensation of diphenylguanidine is also an issue of current interest because it has been found that gold can be quantitatively eluted from low-basic ion exchangers with guanidine functions [2].

EXPERIMENTAL

Interaction of 1*N*,3*N*-diphenylguanidine with hexamethylenediamine. To 4.2 g (0.02 mol) of 1*N*,3*N*-diphenylguanidine and 2.5 g (0.021 mol) of hexamethylenediamine were added 10 mL of glycerol and two drops of phosphoric acid. The mixture was heated to 160°C, with ammonia bubbles starting to be evolved, as judged from the staining of litmus paper. The temperature was gradually raised to 170°C, the mixture was kept for 1 h and, when the gas evolution ceased, it was cooled and poured over with an alkali solution. The precipitated resin was washed with water and dried at 50°C. According to the ^{1}H NMR spectrum, a complex mixure of roducts was thus obtained.

As in the case of polyhexamethyleneguanidine synthesis [6–9], performing the reaction of 1*N*,3*N*-diphenylguanidine with hexamethylenediamine by fusion of reagents at temperatures of 180°C and more is impossible because 1*N*,3*N*-diphenylguanidine decomposes at temperatures higher than 170°C [10].

The condensation reaction in a dimethyl sulfoxide solution yielded a pure product. For this purpose, 4.2 g (0.02 mol) of 1*N*,3*N*-diphenylguanidine and 1.2 g



$$2\,C_6H_5NH-\overset{\overset{NH}{\|}}{C}-HNC_6H_5 + NH_2-(CH_2)_6-NH_2 \xrightleftharpoons{160^oC} 2\,NH_3 + (C_6H_5NH)_2C{=}N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-N{=}C(HNC_6H_5)_2$$

Scheme. Formation scheme of 1.6-[di-21*N*(11*N*,31*N*-diphenylguanidine)]hexane.

(0.01 mol) of hexamethylenediamine were dissolved under heating in 10 mL of dimethyl sulfoxide. Ammonia bubbles started to evolve already at 140°C; with the temperature raised to 160°C, the ammonia evolution intensity increased and the reaction was complete in 1 h. The reaction mass was poured into an aqueous solution of an alkali. The resulting sticky resin was dissolved in dichloroethane, the organic phase was washed with water and dried with $CaCl_2$, and the solvent was evaporated to give 5.0 g of a transparent yellowish resin. Its IR spectrum (in KBr) was recorded with a Specord 75-IR instrument, and the NMR spectrum, with a Bruker Avance III 600 NMR spectrometer (1H: 600.13 MHz) in deuteroacetone.

Synthesis of an ion exchanger. To impart a developed surface, 1.6 g of the condensate was dissolved in 5 mL of dichloroethane. The solution was poured onto 5.6 g of BAU-A carbon substrate and it was dried at 50°C. Samples (0.05 g each) of the resulting ion exchanger were poured over with 50 mL of a solution of complex gold cyanide (97.5 mg L^{-1}) and iron cyanide (337.5 mg L^{-1}), and the mixture was agitated with a magnetic rabble for 0.5 h. The content of gold in the aqueous phase was monitored by the atomic-adsorption method with an AAS-30 instrument.

The occurrence of a reaction between 1*N*,3*N*-diphenylguanidine and hexamethylenediamine can be judged from the evolution of ammonia from a heated mixture of reagents. Apparently, the condensation mechanism is similar to that in which Mannich bases are formed.

This conclusion is supported by an analysis of the IR spectrum (dichloroethane). The spectrum contains strong bands at 2857, 2931, and 3058 cm^{-1}, characteristic of stretching vibrations of aromatic and aliphatic C–H bonds. The presence of a broad strong band at 3200–3450 cm^{-1} means that N–H bonds are present in the condensation product.

The ^1H NMR spectrum of the condensate in $(CD_3)_2CO$ contains broadened signals of methylene protons at 1.37 ppm, two central aliphatic CH_2 groups 94H) (see scheme), and two neighboring CH_2 groups (4H) at 1.60 ppm. The signal at 3.32–3.43 ppm should be attributed to methylene groups bonded to nitrogen atoms (4H). A multiplet associated with protons of amino groups is recorded at 6.6–6.7 ppm (4H), and the signal of aromatic protons is recorded as a multiplet at 6.9–7.4 ppm (20H). The signals are assigned in accordance with the tables [11].

Thus, it can be stated that, under the conditions described, 1*N*,3*N*-diphenylguanidine reacts with hexamethylenediamine to give 1.6-[di-21*N*(11*N*,31*N*-diphenylguanidine)]hexane insoluble in water and an aqueous solution of an alkali.

Because the compounds with a guanidine function are widely used as anion exchangers, the product synthesized in the study was tested as such. The tests demonstrated that, at pH 8, 8.4, 9.2, 9.6, and 9.9, gold can be recovered with the condensate brought in a 0.5-h contact with an alkaline cyanide solution containing 97.5 mg L^{-1} of gold and 337.5 mg L^{-1} of iron in amounts of 92.5, 72.5, 40.0, 17.5, and 5.0 mg L^{-1}, respectively. It should be noted that the whole amount of iron remains in solution in this case. Gold is desorbed by the known method [2] with an aqueous solution of an alkali in the presence of sodium benzoate.

CONCLUSIONS

The condensation of 1*N*,3*N*-diphenylguanidine with hexamethyleneguanidine was performed for the first time. The condensate rather effectively sorbs gold and shows a noticeable selectivity for iron ions.

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