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REACTION OF DIHALOALKANES WITH INORGANIC SULFIDES

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The reaction of dihaloalkanes with inorganic sulfides is commonly used in the preparation of thioethers [1]. Only a few kinetic studies have been carried out on the many methods for performing such reactions.

EXPERIMENTAL

Chromatographically pure samples of dichloroethane, 1,3-dichloropropane, dichloroisobutane, and dibromoethane were used. Samples of Na_2S, Na_2S_2, Na_2S_4, and the starting reagents were purified according to Karyakin [2] and Weissberger [3]. The experiments were run according to our previous work [4] in a medium consisting of ethanol and water taken in equal amounts. The reactions were monitored by periodic removal of probes and determination of Na_2S_X by a polarographic method and of the HS groups by potentiometric titration [5]. The IR spectra were taken on a UR-20 spectrophotometer.

RESULTS AND DISCUSSION

The nature of the dihaloalkane (DHA) affects the rate of the reaction with Na_2S (Fig. 1). Comparison of the kinetic curves 3 and 4 shows that an increase in the electronegativity of the halide in DHA accelerates the reaction. The nature of the DHA also determines the type of reactions which occur in this system. Thus, the polymer yield is only 2% in the case of 1,3-dichloropropane while virtually no polymer formation is found in the reaction with dichloroisobutane. The reaction rate also depends on the nature of the inorganic sulfide. In the case of polysulfides (Fig. 2), the reaction rate increases significantly due to an increase in monomer nucleophilicity. The nature of the cation does not affect the kinetics and yield of the reaction products.

Powderlike products are obtained containing 51.6% S when using inorganic monosulfides while rubberlike products containing disulfide (1.97 sulfidity) and polysulfide (3.87 sulfidity) bonds.

The polythioether formation reaction was studied quantitatively in the case of the reaction of dichloroethane (DCE) and Na_2S. Linearization of the kinetic curves in plots for 1/C vs time indicated that the reaction has overall second-order kinetics. The rate of Na_2S consumption increases linearly with increasing DCE concentration up to a 20-fold excess. The graphically determined reaction activation energy is equal to 23.6 kcal/mole. However, this kinetic parameter does not reflect the entire complexity of the reactions in this system. Analysis of the composition of the reaction mixture showed that crystalline, gaseous, and water-soluble products are formed in the polycondensation of DCE and Na_2S along with polyethylene sulfide. The crystalline product with mp 110-112°C was isolated by treatment of the powderlike product with benzene. Comparison of the IR spectra of this product and authentic 1,4-dithiane and the absence of a mixed melting point depression indicate the identity of this product. The IR spectrum of the gaseous product with bp 14°C has a strong doublet at 1610-1640 cm^{-1} and broad band at 930 cm^{-1}. The doublet may be assigned to C=C aliphatic bond stretching modes and the broad band, to C–H vibration. The spectrum has high frequencies for the CH stretching bands at 3110 and 3140 cm^{-1} and a strong band at 720-740 cm^{-1} assigned to C–C bonds, indicating that this product is vinyl chloride. The formation of this product may

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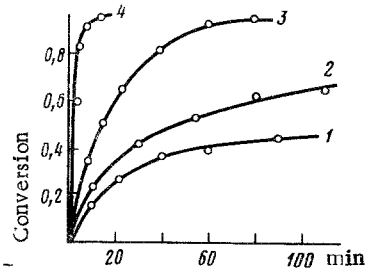

Fig. 1

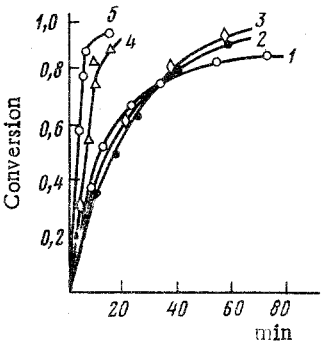

Fig. 2

Fig. 1. The effect of the nature of the dihaloalkane on the rate of reaction with Na_2S: 1) dichloroisobutane, 2) 1,3-dichloropropane, 3) dichloroethane, and 4) dibromoethane at 70°C in 1:1 water–ethanol.

Fig. 2. The effect of the nature of the inorganic sulfide on the rate of reaction with dichloroethane: 1) $(NH_4)_2S$, 2) Na_2S, 3) K_2S, 4) Na_2S_2, 5) Na_2S_4 at 70°C in 1:1 water–ethanol.

be attributed either to partial dehydrochlorination of DCE by analogy with the well-known method for preparing vinyl chloride by means of alcoholic alkali or by the formation of dichlorodiethyl sulfide in the reaction mixture and its splitting to the olefin in the presence of alkali [5]. The water-soluble reaction products are sulfur mercaptide and inorganic sulfides.

CONCLUSIONS

1. A study was carried out on the reaction of dichloroethane with sodium monosulfide. In addition to polyethylene sulfide, dithiane and vinyl chloride are formed in the reaction system.

2. The nature of the dihaloalkane and the inorganic sulfide determine the rate of their polycondensation and the composition of the reaction products.

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