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EFFECT OF THE STRUCTURE OF METHYL-SUBSTITUTED CARBOXYLIC ACIDS AND ANHYDRIDES ON THEIR ACTIVITY IN GAS-PHASE OXIDATION

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Methyl-substituted phthalic and maleic anhydrides and phthalic acids are products of the incomplete oxidation of polyalkylbenzenes. Information on the effect of the structure of these compounds on their reactivity would indicate ways of increasing the reaction selectivity and providing optimal conditions for the gas-phase oxidation.

We studied the gas-phase oxidation of 2,4-dimethylisophthalic and 2,5-dimethylterephthalic acids as well as methyl-substituted phthalic and maleic anhydrides on V_2O_5 .

Figures 1 and 2 show that the major product of the oxidation of 2,4-dimethylisophthalic and 2,5-dimethylterephthalic acids is pyromellitic dianhydride. The yield of this dianhydride at the optimal reaction temperature is 37% for 2,4-dimethylisophthalic acid and 85% for 2,5-dimethylterephthalic acid. As shown in our earlier work [1, 2], durene under identical conditions gives 66% pyromellitic dianhydride, while 4,5-dimethylphthalic acid undergoes 50% conversion to its anhydride. Significant amounts of up to 18% methyltrimellitic acid were found in the products of the oxidation of 2,4-dimethylisophthalic acid. The yield of this product decreases with increasing temperature (see Fig. 2, curve 2). The total conversion of these acids differs, especially at low temperatures. At 400°C the amount of 2,4-dimethylisophthalic acid not reacted is 10 times greater than the analogous amount of 2,5-dimethylterephthalic acid though the conversion of this latter acid is sharply increased at 430°C.

Figure 3 shows that the amounts of unreacted phthalic anhydride, its monomethyl derivatives, and 4,5-dimethylphthalic anhydride vary in different manners with increasing temperature. The high resistance of 4,5-dimethylphthalic anhydride towards oxidative transformations which is comparable to that of the unsubstituted anhydrides is of special note. Although the methyl groups in 4,5-dimethylphthalic anhydride are favorably located for the formation of the anhydride ring, the selectivity for the conversion of this compound into pyromellitic dianhydride is low.

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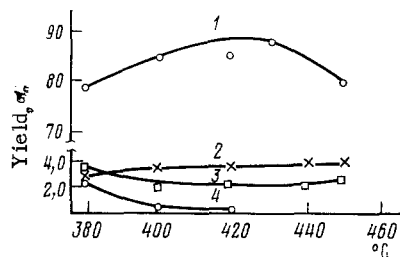


Fig. 1

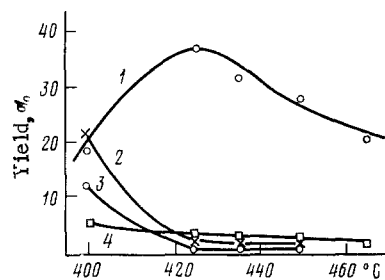


Fig. 2

Fig. 1. Gas-phase oxidation of 2,5-dimethylterephthalic acid: 1) pyromellitic dianhydride, 2) maleic anhydride, 3) trimellitic anhydride + trimellitic acid, 4) 2,5-dimethylterephthalic acid.

Fig. 2. Gas-phase oxidation of 2,4-dimethylisophthalic acid: 1) pyromellitic dianhydride, 2) methyltrimellitic anhydride + methyltrimellitic acid, 3) 2,4-dimethylisophthalic acid, 4) trimellitic anhydride + trimellitic acid.

By analogy with 4,5-dimethylphthalic anhydride, we might have expected high stability of dimethylmaleic anhydride. In order to check this hypothesis, we performed the oxidation of maleic anhydride and its monomethyl and dimethyl derivatives under identical reaction conditions (Fig. 4). The effect of structure on the yield of products of the oxidation of methyl-substituted phthalic anhydride is similar to that found in the oxidation of methyl derivatives of maleic anhydride. Under vigorous gas-phase oxidation conditions, dimethylmaleic anhydride is oxidized to a lesser extent than methylmaleic anhydride and displays stability similar to that found for unsubstituted aromatic anhydrides. In the range from 350° to 450°C, dimethylmaleic anhydride is more stable than pyromellitic dianhydride.

According to our previous data [3], we might have expected the same reactivity of 2,4-dimethylisophthalic and 2,5-dimethylterephthalic acids, in which a methyl group is adjacent to the carboxyl group. The differences found in the behaviors of these acids are probably the consequence of the different capacities of these compounds for adsorption on the catalyst surface.

The plane-parallel orientation to the V_2O_5 surface predominates due to structure features in the adsorption of 2,5-dimethylterephthalic acid. As a result, both methyl and the

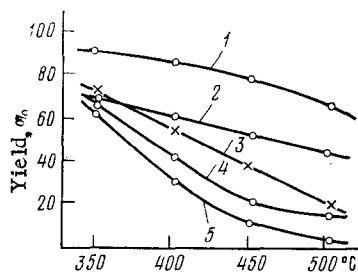


Fig. 3

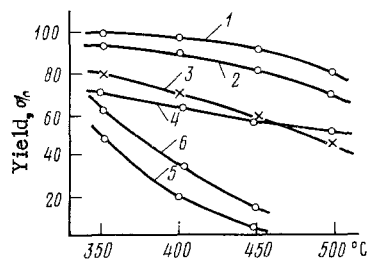


Fig. 4

Fig. 3. Amount of unconverted starting compound in the products of the oxidation of 4,5-dimethylphthalic anhydride relative to the other anhydrides: 1) phthalic anhydride, 2) pyromellitic dianhydride, 3) 4,5-dimethylphthalic anhydride, 4) 3-methylphthalic anhydride, 5) 4-methylphthalic anhydride.

Fig. 4. Resistance to the oxidative decomposition of dimethylmaleic anhydride relative to the other anhydrides: 1) maleic anhydride, 2) phthalic anhydride, 3) dimethylmaleic anhydride, 4) pyromellitic dianhydride, 5) methylmaleic anhydride, 6) trimellitic anhydride.

carboxylic acid group are brought close to the surface, thus facilitating the formation of anhydride rings and by-passing intermediates. This proposal is supported by the small amounts of trimellitic and methyltrimellitic anhydrides in the oxidation product mixture. As a result of structural asymmetry, 2,4-dimethylisophthalic acid may be adsorbed predominantly by means of the carboxyl groups. In this case, the oxidation of the methyl groups is somewhat hindered.

An analogous situation is found in the oxidation of 4,5-dimethylphthalic and dimethylmaleic acids, leading to a predominantly perpendicular molecular orientation of these compounds relative to the catalyst surface. IR bands characteristic for the carboxylic ion in the salts of organic acid [4] were found in the spectra of adsorbed phthalic and maleic anhydrides.

By analogy, we may assume that saltlike compounds are also formed upon the adsorption of the anhydride group of 4,5-dimethylphthalic and dimethylmaleic anhydrides on the catalyst surface.

EXPERIMENTAL

Analytical-grade samples of phthalic and maleic anhydrides were used. Samples of 3- and 4-methylphthalic anhydrides were prepared by the condensation of maleic acid with piperylene and isoprene, respectively, and subsequent dehydrogenation of the adducts according to Diels and Alder [5]. This method was also used for the preparation of 4,5-dimethylphthalic anhydride from 2,3-dimethyl-1,3-butadiene and maleic anhydride. A sample of 2,4-dimethylterephthalic acid was isolated from the "tail" fractions of durene oxidation products. A sample of 2,4-dimethylisophthalic acid was obtained by the oxidation of 2,4-bis-methoxymethyl-m-xylene using 36% HNO₃. After purification, the product indices corresponded to literature data.

The oxidation was carried out in a laboratory system [6] using fused V₂O₅ (3 × 5 mm particle size). The reaction products were analyzed by gas-liquid chromatography and polarography.

The gas-liquid chromatographic analysis was carried out on a Shimadzu CC-1 chromatograph after prior esterification of the oxidation products with methanol in the presence of H₂SO₄ and dimethyl sulfate. The column had 1.1 m packing length and 3 mm inner diameter. The column was packed with 5% SE-30 stationary liquid phase on silanized 60-80 mesh Chromosorb W. A flame ionization detector was used. The detector temperature was 280°C and the injector temperature was 300°C. Helium gas carrier was used. The analysis was carried out with linear programming from 80° to 260°C at 8 deg/min [7].

The polarographic analysis was performed on an LP-60 Czechoslovak recording polarograph in a thermostatted cell at 21°C. A capillary with 4.16 m^{2/3}τ^{1/6} was used. All the potentials were relative to the saturated calomel electrode. The polarograms were taken with 0.01 N HCl base electrolyte [8]. Comparison of the data obtained from the chromatograms and polarograms showed the same results.

CONCLUSIONS

A comparative study was carried out for the oxidation of methyl-substituted phthalic and maleic anhydrides and phthalic acids on V₂O₅ and the effect of structure on the oxidation product yields was found.

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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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