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LABORATORY EXPERIMENTS ON THE PREPARATION OF

ADIPIC ACID AND ALKYLADIPIC ACID

In February, 1938, the first unit for the manufacture of adipic acid at Leuna was started. The following reaction conditions had been found to be the most advantageous. The best yield of about 87 - 89% of the theoretical yield was obtained when 1 mol. of cyclohexanol was added to 8 mols. of 62% nitric acid which had been previously heated to at least 140°F. Mixing of cyclohexanol with nitric acid is carried out under cooling in such a way that the reaction temperature does not, at any time, exceed 176°F. After all cyclohexanol has been added and the development of nitrous oxide has ceased, the adipic acid crystallizes out when the solution is cooled to 60°F. The solubility of adipic acid in the nitric acid which after the reaction has a concentration of about 20% HNO₃ is only 0.47%. After filtration, washing with ice water and recrystallization, a pure white acid is obtained which after drying has a melting point of 151°C.

In order to obtain information on the conversion of the nitric acid, laboratory experiments were carried out in a special apparatus which permitted to measure and analyze the gases formed in the course of the reaction. The nitrogen balance established on the basis of these experiments showed a total loss of 23.76% of nitrogen during the reaction which distributes itself as follows: 0.15% nitrogen in the adipic acid, 3.36% nitrogen in the form of nitrogen gas, and 20.24% nitrogen in the form of nitrous oxide. The remainder of the nitrogen is found either in the filtrate obtained on filtering the crystallized adipic acid or is present in the form of NO and NO₂. Since this filtrate contains the bulk of the nitrogen (about 70%), it seems possible to recover this nitrogen by passing nitrous oxide and air into the solution and thereby bringing the acid again to the required concentration, namely, 62%. It was shown in plant experiments that this procedure can be repeated until the concentration of succinic and glutaric acid becomes so high that it interferes with the crystallization and filtration of the adipic acid. When the concentration of these by-product acids in the filtrate reaches about 10 - 11% the filtrate has to be partly rejected and fresh 62% nitric acid has to be added.

The oxidation of alkylcyclohexanols takes place analogously so that a special discussion is not necessary.

Experiments on the Oxidation of Cyclohexane with Nitric Acid.

When cyclohexane was dropped into nitric acid of specific gravity of 1.38 at 176°F. (80°C.), no effect of the acid on the hydrocarbon was noted. Equally unsuccessful were experiments in which cyclohexane vapors were passed through hot nitric acid. The addition of mercury salts, iron nitrates, vanadium oxide and manganese oxide as catalysts also was without success. Increase in the concentration of nitric acid up to 99% did not result in satisfactory oxidation. Since oxidation experiments with cyclohexane were without success, the subsequent experiments were carried out with substituted cyclohexane which was supposed to be more reactive.

The oxidation of cyclohexylamine, however, was also not considered successful since it required exceedingly long reaction times (from 20 - 39 hours),

gave insufficient yields, could not be easily reproduced and required operation at temperatures above 195°F. (90°C.).

The use of cyclohexylchloride was equally unpromising since reaction conditions were similar to those with cyclohexylamine and yields were not high in this case either.

It was subsequently attempted to oxidize cyclohexene. 1 mol. of cyclohexene was stirred with 10 mols. of nitric acid (62% which contained 0.1% by weight of V_2O_5). The reaction temperature was 158°F. (70°C.). As before, the cyclohexene was added dropwise under stirring. The yield in these experiments was 31.4% of the theory.

The addition of MnO_2 , $Co(NO_3)_2 \cdot 6H_2O$ and $Hg(NO_3)_2 \cdot \frac{1}{2}H_2O$ had no noticeable effect on the course of the reaction. In all experiments yields between 30 and 33% of the theoretical yield were obtained. Experiments in which cyclohexene vapors were passed through hot nitric acid also did not give any better results. Since cyclohexyl esters can be prepared by the reaction of cyclohexene with organic acids, it was attempted to use this approach to the preparation of adipic acid. To solve the principal problem, cyclohexylacetate was prepared and oxidized with 62% nitric acid and the yield of adipic acid was 87.6% of the theory.

Cyclohexylacetate was subsequently prepared by the reaction of cyclohexene with glacial acetic acid in the presence of 98% sulphuric acid.

Since this procedure would not be technically feasible because of the difficulty of working up the spent acid which, besides nitric acid, would contain acetic acid, and because expensive 98% sulphuric acid is required for the preparation of the ester, another more advantageous solution to the problem was sought. Both of these difficulties could be avoided by the use of the dicyclohexyl ester of adipic acid. Experiments showed that this ester prepared from cyclohexanol and adipic acid could be easily oxidized. However, the direct preparation of the ester by reaction of cyclohexene with adipic acid in the presence of 98% sulphuric acid was not very successful. Experiments under pressure were even less satisfactory. Since the entire experimental work indicated that adipic acid esters are best prepared by using cyclohexanol as starting material, the preparation of cyclohexanol by hydration of cyclohexene was tried. The hydration of cyclohexene to cyclohexanol could be carried out successfully when the cyclohexene was treated with sulphuric acid in cyclohexane solution. The reaction was carried out at 86°F. (30°C.) with 80% sulphuric acid. The hydrocarbon and acid layers were treated with ice water and subsequently distilled with steam.