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SUBJECT: The Reaction between Sulfuric Acid and Aliphatic Hydrocarbons.
Amsco 125-82

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FROM: Willis H. Baldwin

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Abstract

Concentrated sulfuric acid is regularly used to remove unsaturated hydrocarbon impurities from saturated aliphatic hydrocarbons. The reaction between concentrated sulfuric acid and saturated aliphatic hydrocarbons is not so well known. A survey of the chemical literature has been found to include studies that show several relatively slow reactions. Isotopic exchange with D_2SO_4 , racemization of optically active alkanes, isomerization, cleavage to alkanes of lower molecular weight, combination to compounds of higher molecular weight and the formation of SO_2 have been recognized.

Amsco 125-82, the diluent that is used in the solvent extraction activities of the laboratory, reacts with sulfuric acid forming sulfur dioxide and low boiling hydrocarbon fragments. The overall reaction probably results in the formation of more stable hydrocarbons by rearrangement. The sulfuric acid treatment can thus produce a more desirable diluent.

Introduction

Olefins are soluble in 99% sulfuric acid as the result of a chemical reaction. This reaction has been and still is used extensively for the removal of olefins from saturated aliphatic hydrocarbons. Saturated hydrocarbons also react with sulfuric acid at a slower rate and in a different way. The rate of the reaction depends upon the structure of the hydrocarbon; tertiary hydrogens react faster than primary or secondary hydrogens. The structure of the remainder of the molecule has a measurable influence on the relative rates of reaction of tertiary hydrocarbons.

Amsco 125-82, one of the diluents that has been used in solvent extraction processes at the laboratory, contains several branched, saturated aliphatic hydrocarbons (1). It has been stated that the washing of Amsco with sulfuric acid has resulted in a diluent that is more desirable for use in processing (2). Decontamination factors are improved and the physical behavior of the solvent mixture is more favorable after the Amsco has been treated with sulfuric acid. It has been demonstrated in our laboratory that sulfuric acid produced more extensive changes than mere removal of olefins.

Long contacting (several days) of Amsco 125-82 with 95% sulfuric acid resulted in the darkening of the sulfuric acid layer, the formation of SO_2 and the formation of 9 new hydrocarbons that boiled lower than any of the components of the starting material. All of the original components of the starting Amsco were found in the final product; that is, no major component was removed completely by the treatment. The relative amounts of the components had been altered by the treatment. These observations were based upon qualitative tests of the solvent (before and after treatment) by gas phase chromatography.

Several pertinent observations about these reactions were found in the chemical literature. Birch and Dunstan (3) found that 2, 3, 4 trimethyl pentane was cleaved into smaller fragments by sulfuric acid at a faster rate than 2, 2, 4 trimethyl pentane, 2, 2, 3 trimethyl pentane, 2, 2, 5 trimethyl hexane or 2, 3 dimethyl butane.

Whitmore and Johnson (4) stirred 2, 2, 4 trimethyl pentane with 95% sulfuric acid, at 25°C for 10 days. Gaseous products included sulfur dioxide and hydrocarbons. Less than 25% of the starting hydrocarbon was recovered unchanged. More than 35% of the liquid product boiled lower and 25% boiled higher than the starting material. A black powder was obtained from the acid layer when it was

diluted with water. The overall reactions included scission and combination of the hydrocarbon chains.

Caesar and Francis (5) heated 2, 4 dimethyl pentane at 50°C with 97% sulfuric acid and found that 15% had been isomerized to 2, 3 dimethyl pentane. Marschner and Carmody (6) found 2, 2, 4 trimethyl pentane to be reactive while n pentane and n heptane were but little affected by sulfuric acid at 24°C for 6 hours.

Isotopic hydrogen exchange between the hydrocarbons and sulfuric acid has been applied to the study of this reaction (7,8,9,10,11,12) as well as the use of optically active hydrocarbons (8,9,10). In summary the results of these studies show the following:

1. Compounds with a tertiary hydrogen (C_3CH) show deuterium-hydrogen exchange at a faster rate than other hydrocarbons: n octane exchanged at a rate that was 1% of the rate found for 2- or 3- methyl heptane (8).

2. Primary hydrogens on methyl groups attached to the tertiary carbon also exchange with the proton of the sulfuric acid (11).

3. Oxidative mechanisms are involved in isotopic exchange since non-oxidizing acids (H_3PO_4) do not show exchange (7). Sulfur dioxide is a product of the reaction between sulfuric acid and the hydrocarbons.

4. The rate of racemization of optically active (+) 3 methyl heptane was found to be 7% of the rate of isotopic exchange (8).

5. Isomerization was slower than racemization (8).

6. Burwell, et al (10) have proposed a mechanism that is based on that of Otvos, et al (11) and Stevenson, et al (12). A chain reaction has been proposed that includes:

(a) chain initiation by oxidation (in the following illustrations only the carbon skeletons and essential hydrogens have been used)

(b) the carbonium ion (I) is the chain carrier that reacts by isomerization,

(c) or by intermolecular exchange (the abbreviated ion, II, has been used merely to symbolize a different cation)

the chain is terminated by the reaction of the chain carrier to form an unreactive compound.

The reactions of carbonium ions that include scission and combination as well as isomerization have been summarized by Whitmore (13).

The observation (2) that washing of Amoco with sulfuric acid produces a product that is more desirable in solvent extraction processes can be explained by the isomerization of the hydrocarbons under the influence of the sulfuric acid. The compounds that are most reactive toward sulfuric acid are most reactive in the solvent extraction environment. The effect of the sulfuric acid is to isomerize them to less reactive compounds.

Experimental

Amsco 125-82 (6 ml.) was placed in a glass stoppered tube with 1.2 ml 95% sulfuric acid. The mixture was treated at 25°C as described below. After each treatment an aliquot (0.5 ml) of the organic phase was removed, washed with water and 10 λ portions of the organic phase were examined by gas chromatography to follow the course of the reaction.

The Amsco-sulfuric acid mixture was tumbled end over end for one hour. The acid layer had turned yellow but no change was detected in the hydrocarbon.

After an additional 16 hours of tumbling end over end the acid layer was much darker and low boiling components were detected by gas chromatography.

The mixture was allowed to stand without agitation for two weeks. The acid layer was black; the odor of SO₂ was detected but there was no difference from the preceding sample when chromatographed.

The mixture was next tumbled end over end for an additional 5 days. The low boiling components were now more numerous and were present in larger amounts. The chromatographic analysis has been reproduced in Figure 1. At least 9 new components are present. No attempt was made to collect gaseous products.

The gas chromatograph (Perkin-Elmer model 154) was operated with a column 1 meter long, that had been packed with dinonyl phthalate on 30-60 mesh Celite (0.3 g. ester per g. solid). The column was heated at 125°C while 50 ml helium per minute was passed through. The results, reproduced in Figure 1, have been selected to show the Amsco before and after treatment with sulfuric acid and known hydrocarbons have been included for standardization.

The hydrocarbons shown in Figure 1 appear from the column as a function of boiling point. There are no specific interactions that lead to specific separations. Therefore, the known hydrocarbons can be used as standards to estimate

the boiling points of other components.

Quantitatively, the weight percentage composition of the mixtures is nearly proportional to the areas under the curves. In the case of the Amsco, however, the resolution is so poor that the estimation of the composition becomes quite laborious.

It becomes quite evident by a comparison of the Amsco before and after treatment that all of the major components are still represented. None of the major components has been removed completely by the sulfuric acid treatment. The original components have reacted at different rates so that the ratios of the major components have been altered.

The olefin content of Amsco 125-82 is so low as to make the methods of the determination of the olefin quite unreliable. The extent of the decomposition represents changes in the number of molecules that are many times greater than the apparent olefin content.

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Figure 1

Gas-Liquid Chromatographic Analysis of Amsco
Before and After Reaction with H_2SO_4