[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Reaction of Cyclohexanol and Hydrogen Chloride

BY A. G. GASSMANN[1] AND R. J. HARTMAN

Hinshelwood and Legard,[2] Smith[3] and others have recognized that hydrogen chloride cannot be used as a catalyst for all esterifications because of its reactivity with alcohols. The interaction of hydrogen chloride with methyl, ethyl and propyl alcohols has been studied by Hinshelwood[4] and Kilpi.[5] The possibility of interaction of cyclohexanol and hydrogen chloride used as catalyst in esterification studies by Hartman, Storms and Gassmann[6] prompted the present investigation.

Experimental

Pure cyclohexanol was first dried by the method of Bjerrum and Lund[7] and then by refluxing over calcium oxide. Carefully dried hydrogen chloride gas was passed into the purified cyclohexanol to obtain the anhydrous cyclohexanol–hydrogen chloride solution. This solution was then diluted to approximately 0.10 normal since this was the catalyst concentration used in the esterification studies.[6] The exact concentration was determined by titration with barium hydroxide solution. The reaction was carried out in sealed tubes in constant temperature baths maintained at 60.00 and 80.00 ± 0.05° and 90.00, 100.00 and 110.00 ± 0.10°. Analysis throughout the reaction was made by titration with barium hydroxide solution.

Results and Discussion

The change in acid concentration with time at the five temperatures studied is shown in Fig. 1. From Fig. 1 it is seen that there is practically no reaction at 60° and only approximately 15% reaction after 120 hours at 80°. Since the esterification studies of Hartman, Storms and Gassmann[6] involved time intervals of less than 120 hours and a maximum temperature of 75°, it is apparent that the interaction of cyclohexanol and hydrogen chloride is not sufficient to cause a significant change in the concentration of the hydrogen chloride catalyst.

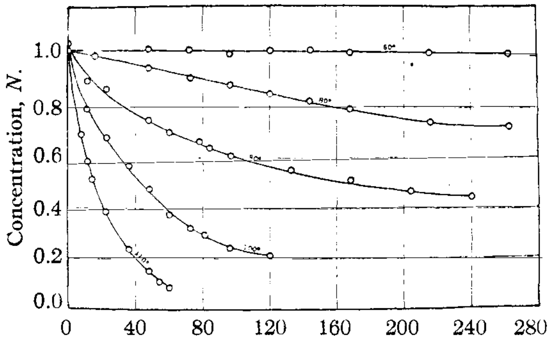

Fig. 1.—Change in hydrogen chloride concentration with time.

The reaction of hydrogen chloride with cyclohexanol is retarded by the water formed. An approximate initial rate can be obtained from Fig. 1 and the energy of activation subsequently obtained is 27,100 calories. This value compares favorably with that of 26,000 calories found for the reaction of methyl alcohol with hydrogen chloride by Hinshelwood.[4] The energy of activation is significantly higher than any of the activation energies found for the formation of carboxylic esters[6] and indicates a different mechanism of alicyclic halide formation than for ester formation. This has been conclusively proven by Roberts and Urey[8] who have shown that the hydroxyl group is detached from the acid and the hydrogen is detached from the alcohol in ester formation. In alicyclic halide formation, however, the hydroxyl group must be detached from the alcohol and replaced by the halogen.

Summary

The interaction of cyclohexanol and hydrogen chloride has been studied. No appreciable reaction was found to occur at 60° and after 120 hours at 80° only 15% reaction had occurred. The activation energy of formation of alicyclic halide is greater than that found for carboxylic ester formation, indicating a different mechanism for the two reactions.

BLOOMINGTON, INDIANA RECEIVED APRIL 26, 1941

---

[1] This paper represents a part of a thesis presented by Albert George Gassmann to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(2) Hinshelwood and Legard, *J. Chem. Soc.*, 587 (1935).

(3) Smith, THIS JOURNAL, **62**, 1136 (1940).

(4) Hinshelwood, *J. Chem. Soc.*, 599 (1935).

(5) Kilpi, *Z. physik. Chem.*, **141A**, 424 (1929); **166A**, 285 (1933).

(6) Hartman, Storms and Gassmann, THIS JOURNAL, **61**, 2167 (1939).

(7) Bjerrum and Lund, *Ber.*, **64B**, 210 (1931).

(8) Roberts and Urey, THIS JOURNAL, **60**, 2391 (1938).