$$RCOOCH_3 + OH^- \longrightarrow RCOOH + OCH_3^- \quad (9)$$

must be considered.

In two cases, that of 2,6-dimethylbenzoic and that of 3,5-dibromo-2,4,6-trimethylbenzoic acid, the reaction of equation (8) is clearly incomplete. In both cases increase in solute concentration or in water concentration (shown by low value of *t* in column 1 of Table I) leads to smaller values of *i*. In the latter case this apparently can be reduced to the neighborhood of 2 but not lower. This suggests strongly that the process of equation (8) occurs not in the single step written but in two non-overlapping steps

$$RCOOH + H_2SO_4 \rightleftharpoons RCO_2H_2^+ + HSO_4^- \quad (10)$$

$$RCO_2H_2^+ + H_2SO_4 \rightleftharpoons RCO^+ + OH_3^+ + HSO_4^- \quad (11)$$

reaction (10) being just as complete with those acids which are capable of further reaction to form the acyl ion as it is with benzoic acid and other acids which show no evidence of the latter process.

The present data clarify many of the structural factors which affect the formation of the acyl ion. The process is favored by substitution of methyl for hydrogen, whereas electron attracting substituents like Br and NO_2 are unfavorable (note especially the effect of bromine substitution on trimethylbenzoic acid). The effect of a methyl group is in the same direction in the ortho and para positions, unlike its effect on the acidic ionization of benzoic acid, and it is so much stronger in the ortho position that the formation of acyl ions has been observed only with derivatives of 2,6-dimethylbenzoic acid. Neither two nor three methyl groups suffice when only one is in the ortho position, but a third methyl in the para position does increase the extent of the effect observed with the 2,6-dimethyl compound. A di-ortho substitution is insufficient when one or both of the groups are of the electron attracting type; the process does not therefore appear to be related to the kinetic steric hindrance which di-ortho substituted compounds in general exhibit. Finally the aliphatic trimethylacetic acid, which possesses many similarities to the di-ortho substituted benzoic acid derivatives, fails to show the effect.

Summary

Further cryoscopic studies of organic oxygen compounds in sulfuric acid have been carried out with an improved apparatus. Nitrobenzene has been found to be incompletely ionized. Completely ionized monoacid bases have been shown to exhibit minor deviations from ideal behavior. An entirely new type of reaction with strong sulfuric acid has been found to occur with 2,6-dimethylbenzoic acid and two of its derivatives. This involves the formation of acyl ions of the type RCO^+ in addition to the normal ionization as a base forming ions of the type $RCO_2H_2^+$. The structural factors which determine the appearance of this ionization process have been clarified. The methyl ester of an acid which forms acyl ions in sulfuric acid has been found to be hydrolyzed instantaneously in sulfuric acid.

NEW YORK, N. Y. RECEIVED JULY 12, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Partial Pressures of Hydrogen Chloride from Benzene Solutions at 30°

BY JOHN H. SAYLOR

The distribution of hydrogen chloride between benzene and water at 20° has been determined by Knight and Hinshelwood.[1] Wynne-Jones[2] has pointed out that the peculiar shape of the curve expressing their results is not to be expected from theoretical considerations and that the concentrations of the hydrogen chloride in the benzene layer are not even approximately proportional to the partial pressures of the aqueous solutions.

Wynne-Jones carried out a few experiments with benzene at 25° over a small concentration range and found that the behavior of hydrogen chloride in the benzene was quite normal. He also determined the distribution of hydrogen chloride between water and nitrobenzene at 25° and found hydrogen chloride to be a normal solute in the nitrobenzene. He concluded that Knight and Hinshelwood's results are probably subject to some experimental error.

The purpose of the present investigation was to study the behavior of hydrogen chloride in benzene solutions by determining its partial pressure

---

(1) Knight and Hinshelwood, *J. Chem. Soc.*, 470 (1927).

(2) Wynne-Jones, *ibid.*, 1064 (1930).

directly from dry benzene and from benzene simultaneously saturated with hydrogen chloride and water.

Experimental

The apparatus used is shown in Fig. 1. It is a modification of the apparatus used by Dolezalek[3] to determine the partial pressures of hydrogen chloride from aqueous solutions and that of Klemenc and Nagel[4] used to determine the partial pressures of nitric acid from concentrated aqueous solutions.

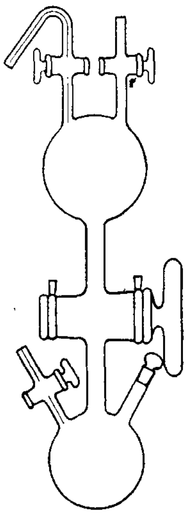

Fig. 1.—Vapor pressure apparatus.

The two bulbs were connected by a mercury-sealed, graphite-lubricated stopcock having a bore of 10 mm. The volume of the top bulb between the stopcocks was found to be 292.6 ± 0.2 cc. by determining the weight of water necessary to fill it at 30°. The volume of the bottom bulb was approximately 200 cc.

In making a determination the central stopcock was closed and dry benzene siphoned into the lower bulb. A rubber stopper bearing a glass tube was then placed into the tube leading from the bulb and dry hydrogen chloride bubbled into the benzene. After a sufficient time had elapsed the gas inlet tube was removed and the ground glass stopper inserted. The top and bottom bulbs were then partially evacuated, the apparatus allowed to stand for a few minutes, the large stopcock opened and the apparatus placed in a thermostat regulated to 30 ± 0.02°. After remaining in the thermostat for five to seven days, the stopcock between the two bulbs was closed and the apparatus removed from the thermostat. The bent tube on the upper bulb was inserted in a beaker of water and the stopcock opened when water was drawn into the bulb absorbing the hydrogen chloride. By suitably tilting the apparatus the solution could be poured out through the other stopcock and the bulb rinsed several times with water. The hydrogen chloride was titrated with carbonate-free sodium hydroxide with methyl red as the indicator. All titrations were made with weight burets. The sodium hydroxide was standardized with constant boiling hydrochloric acid. The partial pressure of the hydrogen chloride was calculated from the volume of the upper bulb, the temperature and the number of moles of gas found to be present.

A sample of the benzene solution was obtained by clamping the apparatus upside down and connecting a weighed evacuated weight pipet to the stopcock on the solution bulb by means of a short piece of rubber tubing. The weighed sample was run underneath the surface of an excess of water, the pipet well rinsed and the solution titrated with sodium hydroxide. In some cases methyl orange was used as the indicator and in others methyl red.

In the determination of the partial pressure of hydrogen chloride from benzene saturated with water, a mixture of benzene and water was placed in a large test-tube and hydrogen chloride passed into the water layer, after which a portion of the benzene layer was siphoned into the vapor pressure apparatus.

Three different samples of benzene were used. Two were Baker Analyzed and one was from Kahlbaum. They were purified by the method of Richards and Shipley,[5] fractionated in efficient all-glass stills using calibrated thermometers and stored over sodium. The boiling ranges of the fractions used were 80.07–80.13°, 80.12 ± 0.02° and 80.19–80.20°. The hydrogen chloride was generated by dropping sulfuric acid onto a good grade of ammonium chloride.

Results

The results are given in Table I. In Fig. 2 is plotted the logarithm of the partial pressure of the

TABLE I

THE PARTIAL PRESSURES OF HYDROGEN CHLORIDE FROM BENZENE SOLUTIONS AT 30°

Moles HCl/1000 g. C_6H_6	Pressure HCl, mm.
0.0006	1.5
.0022	6.2
.0171	51.4
.0391	78.0
.111	211
.172	321
.188	393
.275	510
.297	585
.302	570
Benzene saturated with water	
0.0579	109
.132	244
.205	395
.282	579

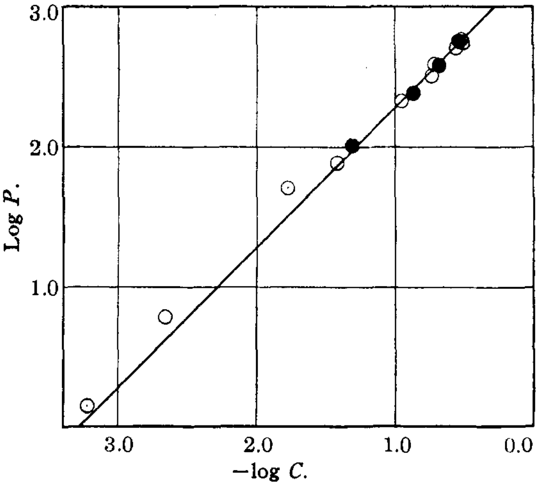

Fig. 2.—Plot of the logarithm of the partial pressure of hydrogen chloride against the logarithm of its concentration in benzene: ●, benzene saturated with water.

---

[3] Dolezalek, *Z. physik. Chem.*, **26**, 321 (1898).

[4] Klemenc and Nagel, *Z. anorg. allgem. Chem.*, **155**, 262 (1926).

[5] Richards and Shipley, THIS JOURNAL, **36**, 1828 (1914).

hydrogen chloride against the logarithm of its concentration in the benzene. The black circles represent the cases in which the benzene was saturated with water. The straight line is drawn with a slope of unity which it must have if hydrogen chloride obeys Henry's law. The plot indicates that hydrogen chloride is a normal solute in benzene and that it is not affected if the benzene is simultaneously saturated with water.

Summary

The partial pressures of hydrogen chloride from benzene solutions have been determined directly and the results indicate that it is a normal solute in dry benzene and in benzene simultaneously saturated with water.

DURHAM, N. C. RECEIVED JULY 6, 1937

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FORDHAM UNIVERSITY]

Studies on Pyrimidines. I. The Preparation of 2-Methyl-6-oxypyrimidine-5-acetic Acid and Some of its Derivatives

BY LEOPOLD R. CERECEDO AND FRANK D. PICKEL

Once the structure of vitamin B_1 had been established by the research groups of Williams, of Windaus, of Todd, and of others, it became clear to us that the problem of the synthesis might be attacked by condensing 2-methyl-5-chloromethyl-6-aminopyrimidine with 4-methyl-5-β-hydroxyethylthiazole. If we keep in mind the similarity between the chemical properties of thiazole and pyridine, an abundance of prototypes of this synthesis may be found in the field of pyridine chemistry.

Our experiments on the thiazole moiety of the vitamin will be the subject of a separate communication. As regards the pyrimidine required for the synthesis, it was realized that 2-methyl-6-oxy-5-hydroxymethylpyrimidine would be a key substance in its preparation. Several methods for the synthesis of this compound suggested themselves. The most convenient one appeared to be the direct introduction of the hydroxymethyl or chloromethyl group into the corresponding pyrimidine. The investigation of this phase of the problem is still in progress. Another method which was considered was the preparation of 2-methyl-6-oxy-5-aminomethylpyrimidine by the degradation of 2-methyl-6-oxypyrimidine-5-acetic acid and the subsequent conversion of the amine into the alcohol. For the degradation of the acid, the two well-known methods of Hofmann and of Curtius suggested themselves. The degradation by the Hofmann reaction caused difficulties which so far have not been overcome. On the other hand, our experiments with the Curtius method were successful. From ethyl 2-methyl-6-oxypyrimidine-5-acetate we prepared the corresponding hydrazide. Degradation of this hydrazide according to Lindemann's modification of the Curtius method yielded the amine containing one less carbon atom. From the amine the corresponding alcohol was obtained. During the course of this work a number of interesting observations regarding the chemistry of pyrimidines have been made which we have not yet had time to study in all their ramifications. They will be reported as the work progresses.

It would have been surprising if others working in the same field would not have experimented along similar lines. Thus, after the main part of the work to be described in the present report had been completed, a paper by Todd and his associates[1] appeared in which they described the preparation of several compounds that had been synthesized independently in this Laboratory. It is a source of gratification to us that our data confirm and supplement those of the English workers. Likewise, Williams and his associates[2] state in a recent paper that the three modes of attack for the preparation of the pyrimidine mentioned above were, among others, also considered by them.

Experimental Part

Ethyl 2-Methyl-6-oxypyrimidine-5-acetate (I).—Acetamidine hydrochloride, freshly distilled ethyl formylsuccinate, and sodium hydroxide were mixed in equimolar amounts with enough cold water to just dissolve the sodium hydroxide. The mixture was kept in a cold place

---

(1) Todd, Bergel, Fraenkel-Conrat and Jacob, *J. Chem. Soc.*, 1601 (1936).

(2) Cline, Williams and Finkelstein, THIS JOURNAL, **59**, 1052 (1937).