tetroxide, the etherate of aluminum triethyl exhibits the reducing properties which are characteristic of metal hydrides and alkyls.

The general trend of the results reported herein indicates that the etherate of aluminum triethyl should be a convenient substitute for the free aluminum triethyl, since the etherate behaves in a manner to be expected for metal alkyls, but is less difficult to handle.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHEASTERN UNIVERSITY]

Acids and Bases. IX. Conductance of Aluminum Bromide and Stannic Chloride in Thionyl Chloride on Addition of Pyridine and Quinoline[1]

BY LEON E. D. PEASE, JR., AND W. F. LUDER

RECEIVED MAY 29, 1953

Conductance curves are presented for the addition of the bases pyridine and quinoline to the acids aluminum bromide and stannic chloride dissolved in thionyl chloride. Explanations for the differing shapes of the curves are suggested.

I. Introduction

In an earlier paper of this series[2] the behavior of aluminum chloride, ferric chloride and stannic chloride as acid catalysts in the reaction of metals with thionyl chloride according to the electronic theory of acids and bases[3] was described. This paper reports additional properties of two aprotic acids in the same aprotic solvent, as determined by the methods of Van Dyke and Kraus.[4]

II. Experimental

Materials.—C.P. aluminum bromide and stannic chloride were distilled into weighed, fragile bulbs, employing the technique of Kraus and Nelson.[5] Pyridine was purified according to the method of Burgess and Kraus.[6] Quinoline was fractionated off aluminum oxide. Thionyl chloride was purified as in the previous paper.[2] The specific conductance of that used in runs was between 5×10^{-8} and 12×10^{-8} mho.

Apparatus.—The bridge has been described previously.[7] The cell was constructed from a 250-ml. erlenmeyer flask employing the method of Hnizda and Kraus.[8] It was fitted with a ground cap, into which a 5-ml. micro-buret was sealed. A side arm was attached, through which the cell could be evacuated and filled with dry nitrogen. The cell constant was 0.3926. An oil thermostat was employed to maintain the temperature of the cell at 25 ± 0.01°.

Procedure.—After the estimated amount of thionyl chloride for a concentration between 0.05 and 0.2 molal was weighed in the cell, a fragile bulb containing a weighed amount of acid was dropped in. Usually the bulb broke with the impact; if it did not, it was crushed with a glass tube. Because considerable heat was evolved during the solution of aluminum bromide, the cell was cooled in ice before the ampule was added. A tube from a source of dry nitrogen was attached to the side arm, so that whenever the cell was open a slow stream of nitrogen flowed out the top.

The micro-buret, filled with liquid base through the tip, was then attached to the cell. After the cell had been in the thermostat for 10 minutes the first increment of base was added. For 30 seconds, the cell was agitated to mix the solution without removing from the thermostat. The final resistance reading was taken four minutes from the time the base was added.

III. Results

Although many more runs were made, typical results obtained by this procedure are shown in Figs. 1–4.

Early in the investigation it was noted that the resistances on the far acid side (left) of the break-point shown in the figures changed slowly with time, although they became constant close to the break-point and were constant on the basic side. Therefore several time runs were made using a fixed concentration of either acid or base alone in the solvent. The resistance of the basic solutions remained constant. The resistances of the acid solutions decreased about 100% over a period of several hours before coming to a constant value.

Several addition runs were then made over different time intervals, some as rapidly as possible and others over periods of 12 hours or more. In all the runs the break occurred at the same mole ratio for a given pair.

Apparently, a slow reaction occurs between the acid and the solvent. The slowness of this reaction is not entirely unexpected, because of the high acidity of the solvent, as indicated by the curves in Figs. 1–4 and by the previous investigation.[2] However, the fact that the same break is obtained and that the resistances become constant as the break is approached and remain so on the basic side indicates that the reaction between the acid and the base takes precedence over the reaction of the acid with the solvent, as is to be expected. Consequently, when readings are taken at similar time intervals for a given acid and base, rapid runs can be made, from which smooth curves, all showing a break at the same ratio, are obtained.

When aluminum bromide is added to thionyl chloride a deep red color is produced, which disappears as the break-point is approached at a 1–1 molal ratio of base to acid. No precipitate is formed during the addition of base. On the other hand, when either base is added to stannic chloride solution a white precipitate is formed.

IV. Conclusion

The shape of the curves in Fig. 1 may be explained as follows. Addition of pyridine to the aluminum bromide solution first forms the addition

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[1] Abstracted from a thesis submitted by Leon E. D. Pease, Jr., to the faculty of Northeastern University in partial fulfillment of the requirements for the M.S. degree, June, 1952.

[2] R. A. Hubbard, Jr., and W. F. Luder, THIS JOURNAL, **73**, 1327 (1951).

[3] W. F. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946.

[4] R. E. Van Dyke and H. E. Crawford, THIS JOURNAL, **73**, 2022 (1951), and the preceding papers in the series.

[5] C. A. Kraus and W. K. Nelson, *ibid.*, **56**, 198 (1934).

[6] D. S. Burgess and C. A. Kraus, *ibid.*, **70**, 706 (1948).

[7] W. F. Luder, *Rev. Sci. Instruments*, **14**, 1 (1943).

[8] V. F. Hnizda and C. A. Kraus, THIS JOURNAL, **71**, 1565 (1949).

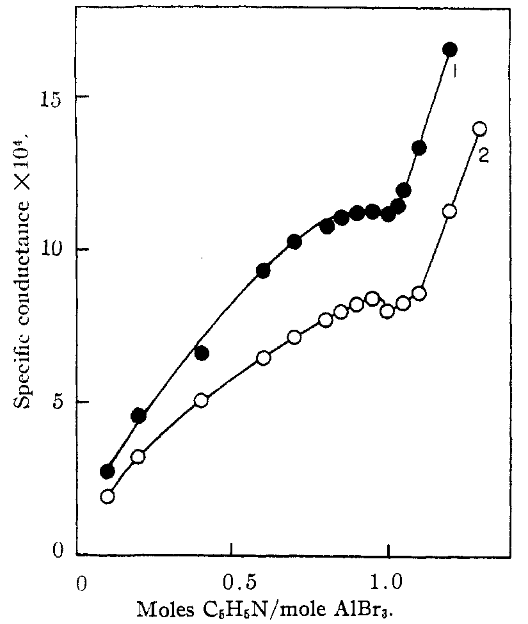

Fig. 1.—Conductance of aluminum bromide in thionyl chloride upon addition of pyridine: curve 1, 0.2219 molal; curve 2, 0.1725 molal.

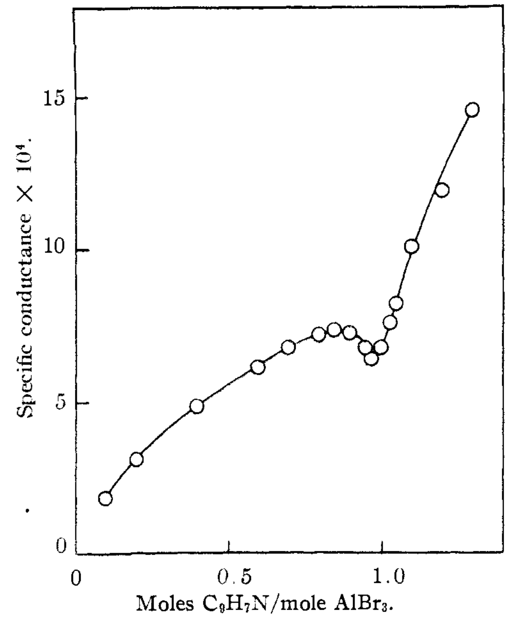

Fig. 2.—Conductance of aluminum bromide in thionyl chloride upon addition of quinoline: $AlBr_3$, 0.1408 molal.

compound $C_5H_5N{:}AlBr_3$,[9] which, because of the low conductance, must ionize only slightly, probably according to the equation

$$C_5H_5N{:}AlBr_3 \rightleftharpoons C_5H_5N{:}AlBr_2^{+1} + Br^{-1}$$

The falling off from linearity as more addition compound is formed is apparently the familiar mass-action effect in decreasing the ionization of a weak electrolyte.

To obtain additional information on the rapid rise in conductance above the 1-1 ratio, separate dilution runs were made on pyridine alone. Comparison showed that the rise in Fig. 1 is much more rapid than it would have been if caused only by the addition of pyridine. Therefore, the pyridine must now be reacting with the 1-1 compound to produce another compound which has a higher degree of ionization. The obvious conclusion that this compound is $(C_5H_5N{:})_2AlBr_3$ is supported by the work in nitrobenzene reported by Van Dyke and Harrison.[9] Probably the ionization is

$$(C_5H_5N{:})_2AlBr_3 \rightleftharpoons (C_5H_5N{:})_2AlBr_2^{+1} + Br^{-1}$$

Because of the larger size of this positive ion compared with the size of the positive ion from the 1-1 compound, and because four orbitals in the alumi-

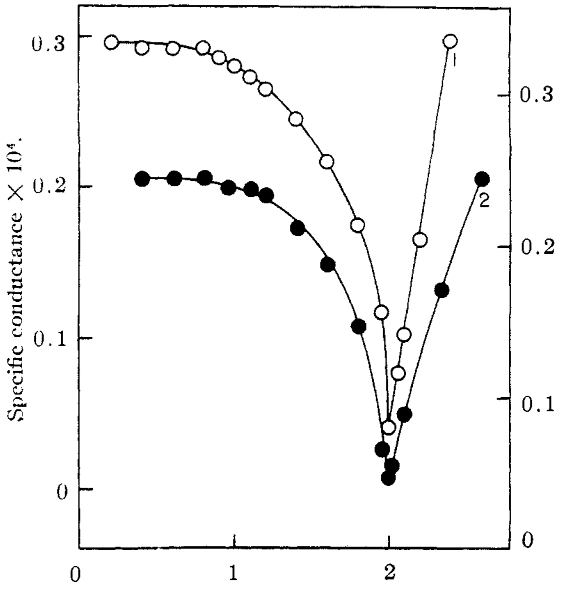

Fig. 3.—Conductance of stannic chloride in thionyl chloride upon addition of pyridine: curve 1, 0.1090 molal; curve 2, 0.0555 molal (use right-hand scale for (2)).

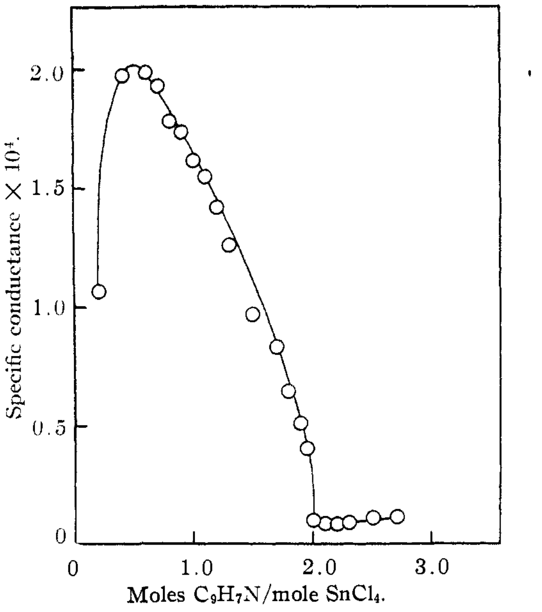

Fig. 4.—Conductance of stannic chloride in thionyl chloride upon the addition of quinoline: $SnCl_4$, 0.1178 molal.

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[9] R. E. Van Dyke and T. S. Harrison, THIS JOURNAL, **73**, 575 (1951).

num atom are occupied instead of three, one would expect a higher degree of ionization as indicated in Fig. 1.

The behavior of quinoline toward aluminum bromide apparently is similar to that of pyridine as shown by curves of similar shape and magnitude illustrated by the example in Fig. 2.

On the other hand, the behavior of quinoline and pyridine toward stannic chloride shows more difference than one might expect. Although Figs. 3 and 4 indicate that one mole of stannic chloride is neutralized by two moles of either base, two differences are evident: the higher conductance to the left, and the lower conductance to the right, of the break-point in Fig. 4.

To the left of the break-point in Figs. 3 and 4, the shapes of the curves, the formation of the precipitates, and the break at the 2–1 ratios indicate two equilibria, such as

$$C_5H_5N + SnCl_4 \rightleftarrows C_5H_5N{:}SnCl_3^{+1} + Cl^{-1} \qquad (1)$$

$$C_5H_5N + C_5H_5N{:}SnCl_3^{+1} + Cl^{-1} \rightleftarrows (C_5H_5N{:})_2SnCl_4 \qquad (2)$$

white precipitate

The higher conductance of the quinoline compound is probably due to the larger size of the positive ion.

In Fig. 3 to the right of the break, the conductance increases at the same rate as it does when pyridine is added to thionyl chloride alone. Therefore, no further reaction is occurring. But in Fig. 4, the increase in conductance is much less than is caused by the addition of quinoline to thionyl chloride alone. In trying to account for this puzzling behavior several runs were made to higher molar ratios, one beyond 5–1. The same slight increase was observed in all the runs. Apparently the only explanation is that the quinoline must be combining with the precipitate.

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[CONTRIBUTION NO. 1164 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The High Field Conductance of Aqueous Solutions of Carbon Dioxide at 25°. The True Ionization Constant of Carbonic Acid[1]

BY DANIEL BERG AND ANDREW PATTERSON, JR.

RECEIVED JUNE 3, 1953

High field conductance measurements have been performed on solutions of carbon dioxide in water at 25.00°, approximately 0.15–0.16 M. At a field of 200 kv./cm. the high field conductance quotient is 4.6%. These data have been interpreted to obtain the true ionization constant, $K(0)_1$, of carbonic acid. This constant was found to have the value $1.32 \pm 0.05 \times 10^{-4}$ at 25°.

Of the several weak acids available to the chemist for study, one of the most interesting is carbonic acid. It is a common constituent of the atmosphere, a disturbing factor in many conductance measurements, and of vital importance in physiological processes. It is all the more interesting because only a small fraction of dissolved carbon dioxide is in the hydrated form and because the equilibrium between hydrated and unhydrated forms is attained only slowly. Because of this slow attainment of equilibrium, we have felt that it should be possible to use the high field conductance measurements, which of necessity must be performed in a short period of time (a few microseconds) to obtain the true constant of the first ionization

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^- \qquad (1)$$

$$K(0)_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad (2)$$

We present herewith the results of high field conductance measurements on solutions of carbon dioxide and show how it is possible to use these results to obtain $K(0)_1$ for carbonic acid.[2]

Experimental

The experimental procedure was identical with that of Gledhill and Patterson,[3] employing a differential pulse transformer (DPT) bridge circuit and accessory equipment for the production and observation of brief high voltage pulses. For these measurements the pulse duration was four microseconds. Solutions of carbon dioxide were prepared by bubbling purified carbon dioxide into a volume of degassed conductivity water in the conductance cell until the resistance declined to a value of about 1400 ohms. The cell resistance then slowly fell to about 1000 ohms and remained at this equilibrium value. The concentration of carbon dioxide was determined by adding an excess of standard barium hydroxide to a measured sample of the cell solution and back-titrating carefully with standard hydrochloric acid using chlor phenol red as indicator. Three titrations were performed for each cell solution studied; the concentrations were determined with an average deviation of 3%. At low fields, conductance measurements were made with the DPT bridge by substitution of a suitable resistance and parallel capacitance for the second cell. For the high field measurements the reference cell contained a solution of hydrochloric acid of appropriate resistance, and concentration near 10^{-4} M; these measurements are thus relative to hydrochloric acid, and any high field conductance due to free ions is effectively compensated. The temperature was maintained at 25 ± 0.015°, referred to a recently calibrated platinum resistance thermometer.

Results

The results are shown in Fig. 1. The triangles pertain to 0.0165 M, the crosses to 0.0163 M, and the filled circles to 0.0152 M aqueous solutions of carbon dioxide. At 200 kv./cm. the fractional high field conductance quotient is 4.6%, compared

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[1] This material is taken from a dissertation submitted by Daniel Berg to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1953.

[2] By the term $K(0)_1$ is meant the first ionization constant at zero field. All terms and symbols used in this paper and not defined herein are defined by F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4428 (1952), or by H. S. Harned and B. B. Owen, ref. 4.

[3] J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, **56**, 999 (1952).