oxidation of salicylaldehyde,[4] particularly when small scale syntheses were undertaken. Due to interfering ions, lead acetate could not be used in the recovery. Instead, the catechol thus formed was precipitated directly from the reaction mixture with barium hydroxide and regenerated from the resulting salt with a small quantity of dilute, aqueous hydrochloric acid. Ether extraction gave yields comparable to those noted in the described synthesis. For excellent purity the crude product was vapor distilled with bromobenzene.[5]

Experimental

Catechol from *o*-Aminophenol.—To a solution of 35.6 g. (0.363 mole) of sulfuric acid in 50 ml. of water cooled to −10° was added with constant stirring 15.8 g. (0.145 mole) of *o*-aminophenol. The final solution was brought to about 10% by dilution with ice and then added at a moderate rate to a boiling solution of 50 g. (0.2 mole) of cupric sulfate pentahydrate in 50 ml. of water contained in a flask equipped for distillation. The catechol formed was steam distilled until the distillate gave only a faint test with alcoholic ferric chloride. To this distillate was added a 10% aqueous solution of normal lead acetate until precipitation was complete. The lead catecholate was then collected on a buchner funnel, washed thrice with cold water, then twice with small portions of acetone and finally sucked dry. The dry material was transferred to a 300-ml. round bottom flask, covered with 200 ml. of benzene and then treated with a rapid stream of dry hydrogen chloride. In 15 to 20 minutes the decomposition was complete, leaving a residue of lead chloride which was filtered off. The filtrate was then placed on a steam-bath and distilled at atmospheric pressure until the distillate appeared clear. The remainder of the benzene was evaporated *in vacuo*, leaving a brownish, crystalline residue of catechol which was transferred to a 50-ml. distilling flask, covered with 25 ml. of bromobenzene and vigorously distilled through an air condenser into a flask cooled to 0°. The separating product was filtered by suction and the filtrate returned to the distilling flask which contained undistilled catechol. This was likewise distilled, giving an additional amount of pure material in the distillate, and the process repeated until all the catechol was carried over. In this manner, 2.32 g. (9.7%) of colorless plates, m.p. 104°, was obtained.

Catechol from Salicylaldehyde.—Directions for this preparation, scaled down to 0.05 mole, were employed as noted above.[4] To the final reaction mixture, adjusted to a *p*H of approximately seven with acetic acid and warmed to 40°, was added a solution of 9.45 g. (0.03 mole) of barium hydroxide octahydrate in 30 ml. of water at 80°. Greenish-gold leaflets of barium catecholate separated and were immediately filtered by suction. The funnel and contents were transferred to a clean filter flask, washed with cold water until the washings appeared clear, then twice with acetone and allowed to dry by suction. To the first filtrate was added a solution of 6.30 g. (0.02 mole) of barium hydroxide octahydrate in 20 ml. of water, whereupon more material separated out. This was filtered and washed in a similar manner. The combined quantities of dry salt were crushed, placed in a 100-ml. round bottom flask and covered with 25 ml. of a hydrochloric acid solution containing 2.74 g. (0.075 mole) of hydrogen chloride. The mixture was then warmed on the steam-bath until complete solution was effected and the contents transferred quantitatively to a separatory funnel and extracted with two 100-ml. portions of ether. The ether extract in turn was washed with two 25-ml. portions of 5% potassium bicarbonate, dried for one-half hour over anhydrous magnesium sulfate, filtered and evaporated *in vacuo*, leaving 3.91 g. (71%) of impure, crystalline catechol. Repeated distillation with bromobenzene, as described in the above experiment, gave 3.72 g. (68%) of colorless plates, m.p. 104°.

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[4] H. D. Dakin, "Organic Syntheses," Coll. Vol. I, 2d Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 149.

[5] N. Elliott, U. S. Patent 1,912,628 (1933).

Conductance of Aluminum Chloride in Sulfuryl Chloride on Adding Benzophenone or Sulfur Monochloride[1]

BY A. R. PRAY AND C. R. MCCROSKY

RECEIVED APRIL 28, 1952

Kraus, Van Dyke and their collaborators have recently reported studies on the complexes formed by some aluminum (or gallium) halides with other molecules in several non-aqueous solutions.[2] These solutes are of especial interest as their solutions are electrically conducting, the conductance changing in a marked way as the complexing agent is added.

We here report a somewhat similar study on aluminum chloride dissolved in sulfuryl chloride, using benzophenone and sulfur monochloride as complexing agents.

Experimental

Materials.—Sulfuryl chloride[3] was distilled immediately before use. The distilling apparatus, of ordinary kind with ground glass joints, was flushed out with a portion of the fraction boiling at 69° before collection of the portion to be used. The solvent so obtained had a specific conductance of 4×10^{-8} mho.

Aluminum chloride, anhydrous, of reagent grade, was purified by sublimation, the method resembling that given by Archibald[4] but simplified in detail.

Benzophenone was recrystallized three times from alcohol, dried in a current of warm air, and stored over barium oxide.

Sulfur monochloride was twice distilled from excess sulfur. The middle portion of the fraction boiling at 138° was used.

Apparatus and Procedure.—Conductance measurements were made on an assembled apparatus following the circuit of Jones and Josephs.[5] The conductance cell was immersed in an oil thermostat of 20-l. capacity maintained at 25 ± 0.05°. The conductance cell was a test-tube, 15 by 2.5 cm., fitted with a hard rubber cover. Through this cover two parallel glass tubes holding the electrodes passed. The electrodes were shiny platinum plates, about 1 cm. square and separated by about 1 mm. The glass tubes were separated by a glass spacer at the electrode end. The hard rubber cover was drilled to provide entry for a buret tip, by means of which the complexing agent was added. The buret was of 10-ml. volume, graduated in 0.05 ml. It was calibrated at each ml. It was found convenient to fit the top with a microcapillary to restrict air entry.

The addition of complexing agent to the aluminum chloride was carried out as follows. Twenty ml. of sulfuryl chloride was distilled into the conductance cell. From 0.3 to 1 g. of aluminum chloride was weighed out into the cell. The liquid was warmed slightly to hasten solution. The cell was closed with the cap holding the electrodes and immersed in the thermostat. About 10 g. of the complexing agent was weighed into a small (10–25 ml.) calibrated volumetric flask. The flask was made up nearly to the mark with sulfuryl chloride, allowed to stand in the thermostat, and finally adjusted to volume. The contents were then transferred to the buret. The initial conductance of the solution was then measured and discrete amounts of com-

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[1] Presented at the 118th National Meeting of the American Chemical Society in Chicago, September 3–8, 1950.

[2] (a) Aluminum bromide with methyl ether in methyl bromide solution, W. J. Jacober and C. A. Kraus, THIS JOURNAL, **71**, 2409 (1949); (b) Aluminum bromide with other molecules in nitrobenzene solution, R. E. Van Dyke and C. A. Kraus, *ibid.*, **71**, 2694 (1949), and R. E. Van Dyke, *ibid.*, **73**, 398 (1951); (c) gallium chloride with other molecules in nitrobenzene solutions, R. E. Van Dyke, *ibid.*, **72**, 2823 (1950); (d) aluminum bromide with other molecules in benzonitrile solution, R. E. Van Dyke and T. S. Harrison, *ibid.*, **73**, 402, 571 (1951); (e) aluminum chloride with other molecules in nitrobenzene solution, R. E. Van Dyke and H. E. Crawford, *ibid.*, **73**, 2018, 2022 (1951).

[3] Kindly furnished by the Hooker Electrochemical Co., Niagara Falls, New York.

[4] E. H. Archibald, "Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1932.

[5] G. Jones and R. J. Josephs, THIS JOURNAL, **50**, 1049 (1928).

plexing agent were added, in solution. The solution in the cell was agitated by gentle rotation of the hard rubber cover. After each addition a new reading was made until finally a large molar excess of complexing agent had been added. The cell constant was determined at the beginning and end of each set of observations.

Benzophenone.—The conductance of aluminum chloride in sulfuryl chloride, as benzophenone was added, was studied for three concentrations of aluminum chloride: 0.129, 0.323 and 0.564 molar. For the first of these, benzophenone solution of 0.632 molarity was added; for the second, of 0.711 molarity, and for the third, 1.034. Data for these three additions are plotted in Fig. 1; a brief summary is given in Table I. It will be seen that the conductance of aluminum chloride is initially low and rises, as benzophenone is added, to a maximum at a molar ratio for benzophenone to aluminum chloride around 0.6–0.7; the conductance then falls markedly to a minimum for the molar ratio of (nearly) unity, and rises again thereafter.[6] This behavior is somewhat similar to that observed by Van Dyke and Harrison for the addition of pyridine to aluminum bromide in benzonitrile and in nitrobenzene[2d] as well as to that observed by Van Dyke and Kraus for the addition of methyl ether to aluminum bromide in nitrobenzene,[7] and that observed by Jacober and Kraus for the addition of methyl ether to aluminum bromide, methyl aluminum bromide and dimethyl aluminum bromide in methyl bromide.[2a]

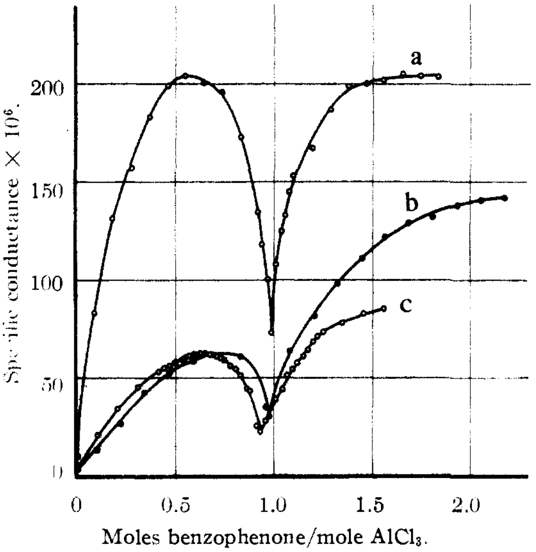

Fig. 1.—Conductance of aluminum chloride in sulfuryl chloride on addition of benzophenone at 25°: a, 11.25 millimoles $AlCl_3$, 1.035 molar benzophenone; b, 2.58 millimoles $AlCl_3$, 0.632 molar benzophenone; c, 6.86 millimoles $AlCl_3$, 0.711 molar benzophenone.

Sulfur Monochloride.—The conductance of aluminum chloride in sulfuryl chloride as sulfur monochloride was added was studied for two concentrations of aluminum chloride: 0.189 and 0.498 molar. The added sulfur monochloride had a molarity of 4.11. Data for these two additions are plotted in Fig. 2. It will be seen that the conductance of aluminum chloride in sulfuryl chloride is initially low and rises rapidly, as sulfur monochloride is added, to a maximum at a molar ratio for sulfur monochloride to aluminum chloride around 0.2; the conductance then falls rapidly to a minimum for the molar ratio of 0.5 ($S_2Cl_2/AlCl_3$), remaining constant thereafter.[8] As the addition of sulfur monochloride

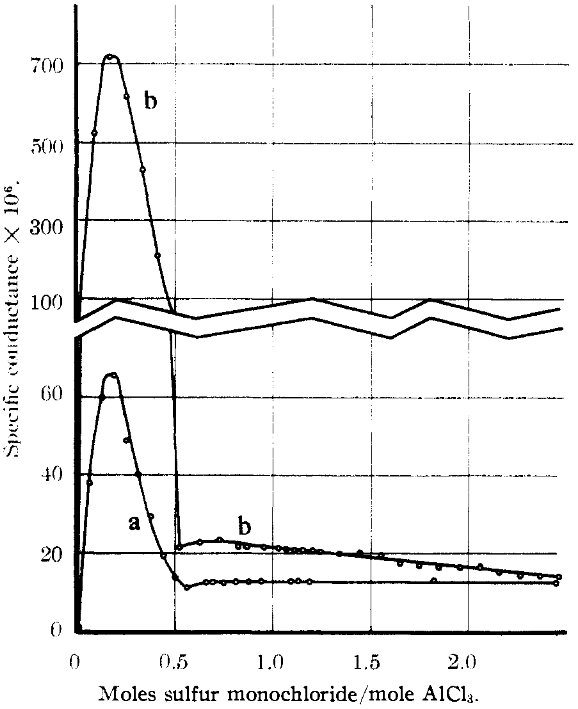

Fig. 2.—Conductance of aluminum chloride in sulfuryl chloride on addition of sulfur monochloride at 25°: a, 3.28 millimoles $AlCl_3$, 4.11 *M* S_2Cl_2; b, 9.96 millimoles $AlCl_3$, 4.11 molar S_2Cl_2.

TABLE I

THE CONDUCTANCE OF ALUMINUM CHLORIDE IN SULFURYL CHLORIDE ON THE ADDITION OF BENZOPHENONE

Curve a Ms. $AlCl_3$ = 0.01125 M. $C_{13}H_{10}O$ = 1.035 *K* × 10^6, mhos	Mole ratio $C_{13}H_{10}O/AlCl_3$	Curve b Ms. $AlCl_3$ = 0.00258 M. $C_{13}H_{10}O$ = 0.632 *K* × 10^6, mhos	Mole ratio $C_{13}H_{10}O/AlCl_3$	Curve c Ms. $AlCl_3$ = 0.00686 M. $C_{13}H_{10}O$ = 0.711 *K* × 10^6, mhos	Mole ratio $C_{13}H_{10}O/AlCl_3$
10.0	0.00	2.86	0.00	2.86	0.00
130.9	.184	41.7	.343	34.3	.207
203.6	.552	61.4	.710	53.3	.414
172.9	.828	34.6	.955	58.6	.493
117.5	.943	80.6	1.201	62.4	.673
72.9	.989	111.1	1.447	50.6	.829
125.1	1.035	128.7	1.690	22.48	.932
187.0	1.288	138.3	1.935	53.6	1.093
201.6	1.564	142.1	2.180	72.8	1.250
203.8	1.840	149.0	2.425	85.4	1.555

TABLE II

THE CONDUCTANCE OF ALUMINUM CHLORIDE IN SULFURYL CHLORIDE ON THE ADDITION OF SULFUR MONOCHLORIDE

Curve a Ms. $AlCl_3$ = 0.00328 M. S_2Cl_2 = 4.11 *K* × 10^6, mhos	Mole ratio $S_2Cl_2/AlCl_3$	Curve b Ms. $AlCl_3$ = 0.00996 M. S_2Cl_2 = 4.11 *K* × 10^6, mhos	Mole ratio $S_2Cl_2/AlCl_3$
1.03	0.00	8.35	0.00
37.8	.063	524	.0825
65.5	.188	719	.1649
40.3	.314	432	.330
19.3	.438	212	.412
11.28	.564	21.6	.515
12.72	.752	21.6	1.031
12.78	1.129	19.6	1.546
12.86	1.818	16.3	2.060
12.78	2.445	14.4	2.473

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[6] Benzophenone is itself a conductor in sulfuryl chloride; the conductivity of a molar solution is about $5 \times 10^{-[illegible]}$ mho, as compared to the pure solvent, ca. $4 \times 10^{-[illegible]}$ mho.

[7] R. E. Van Dyke and C. A. Kraus, THIS JOURNAL, **71**, 2694 (1949).

[8] Sulfur monochloride is itself a non-conductor in sulfuryl chloride solution.

proceeds from the start, there precipitates out of the conductance vessel a white, crystalline solid with a composition corresponding to $Al_2Cl_6 \cdot S_2Cl_2$.[9] After the molar ratio ($S_2Cl_2/AlCl_3$) of 0.5 is reached, this compound ceases to precipitate and no further change in the solution is apparent. A brief summary of the data corresponding to Fig. 2 is given in Table II.

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[9] Found for $Al_2Cl_6S_2Cl_2$: 13.3% Al, 70.4% Cl. Calcd.: 13.48% Al, 70.89% Cl.

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The Aluminum Chloride-Catalyzed Condensation of γ-Butyrolactone with Benzene

BY WILLIAM E. TRUCE AND CECIL E. OLSON

RECEIVED APRIL 14, 1952

The condensation of γ-butyrolactone with benzene in the presence of aluminum chloride has been reported by Christian.[1] We have independently studied this reaction and observed several differences. A higher yield of γ-phenylbutyric acid was realized and α-tetralone was obtained as a product. The relative amounts of the two products can be greatly altered by varying the amount of aluminum chloride as shown in Table I.

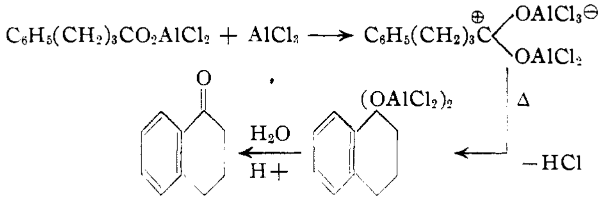
TABLE I

Molar ratio $AlCl_3$/lactone	Yield of α-tetralone, %	Yield of γ-phenylbutyric acid %
1.25	11	73
1.67	32	43
2.50	66	..

The formation of a ketone by the condensation of a lactone with benzene does not appear to have been reported previously. It is submitted as a convenient preparation of γ-tetralone and possibly it could be extended to the preparation of related cyclic ketones.

The following steps and intermediates for the reaction are suggested.

$$C_6H_6 + (CH_2)_3CO_2 + AlCl_3 \longrightarrow C_6H_5(CH_2)_3CO_2AlCl_2 + HCl$$



$$C_6H_5(CH_2)_3CO_2AlCl_2 + AlCl_3 \longrightarrow C_6H_5(CH_2)_3\overset{\oplus}{C}\begin{matrix} OAlCl_3^{\ominus} \\ OAlCl_2 \end{matrix}$$

Recent work by Birch and co-workers,[2] and later by Snyder and Werber,[3] in which γ-phenylbutyric acid was condensed to α-tetralone with various strong acids, lends support to the above proposal.

Experimental

The three reactions described below were carried out in a 500-ml., three-neck, round-bottom flask equipped with a reflux condenser (capped with a drying tube), mechanically-driven, sealed stirrer and a 125-ml. erlenmeyer flask connected to the reaction flask by flexible tubing.

Reaction No. 1.—To a well-stirred solution of benzene (200 ml., 176 g., dried over CaH_2) and γ-butyrolactone (20.8 g., 0.24 mole), C.P. anhydrous aluminum chloride (40.2 g., 0.3 mole) was added at a rate that kept the solution refluxing (about one hour). The solution was heated at reflux temperature until the evolution of hydrogen chloride had nearly ceased (about four hours).

The mixture was cooled to room temperature and poured over 200 g. of ice drenched in concentrated hydrochloric acid. The organic layer was separated and washed twice with water. The aqueous part was combined with the washings, washed twice with ether and discarded. The ether washings and the organic layer were combined, dried and distilled under reduced pressure. The first product was a colorless liquid, α-tetralone; b.p. 120–124° (10 mm.) (lit.[4] 128° (12 mm.)); $n^{20}D$ 1.5691, (lit.[3] 1.5688); semicarbazone, m.p. 214–216° (lit.[3] 216°), and yield 4.0 g. (11%). The second product was a waxy crystalline solid, γ-phenylbutyric acid, b.p. 148–155° (10 mm.) (lit.[1] 120–125° (1 mm.)), m.p. 47–48° (lit.[1] 48–49°), and yield 28.5 g. (73%).

Reaction No. 2.—The same amounts of benzene and γ-butyrolactone were used as in Reaction No. 1 with 53.6 g. (0.4 mole) of aluminum chloride and under the same conditions. The yield of α-tetralone was 11.1 g. (32%) and the yield of γ-phenylbutyric acid was 17.0 g. (43.3%).

Reaction No. 3.—Following the same procedure but using 80 g. (0.6 mole) of aluminum chloride, the yield of α-tetralone was 23.2 g. (66%). No phenylbutyric acid was isolated from the brown residue in the distilling flask.

Acknowledgment.—The authors are grateful to the Procter and Gamble Co. for financial support in this work.

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[1] R. V. Christian, Jr., THIS JOURNAL, **74**, 1591 (1952).

[2] A. J. Birch, R. Jaeger and R. Robinson, *J. Chem. Soc.*, 582 (1945).

[3] H. R. Snyder and F. X. Werber, THIS JOURNAL, **72**, 2965 (1950).

[4] H. Luther and C. Wächter, *Chem. Ber.*, **82**, 161 (1949).

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Ionophoresis in Non-aqueous Solvent Systems

BY M. H. PAUL AND E. L. DURRUM

RECEIVED MARCH 26, 1952

Recently there has been renewed interest in what Tiselius[1] has termed "Zone Electrophoresis." Electrophoresis on paper, particularly, has become a convenient and useful method for the separation of an ever increasing number of charged substances. Although considerable data had been amassed about the properties of non-aqueous solvent systems by Walden,[2] a search of the recent literature uncovered no references to electrophoretic separations in non-aqueous solvents with the exception of a paper[3] on the mobility of carbon black particles suspended in kerosene.

A preliminary study on the application of non-aqueous systems to filter paper ionophoresis was undertaken in an attempt to effect resolution of mixtures of certain biological compounds which are insoluble in aqueous electrolytes, such as cholesterol, higher fatty acids and steroid hormones.

The movement of dyes on filter paper was studied first because their migration is conveniently followed. Paper strips (30 × 1.5 cm.) cut from "Whatman 3 MM" filter paper were suspended in a glass and bakelite electrophoresis cell (apex height—13 cm.) similar to that previously described.[4]

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[1] A. Tiselius, Abstracts, XII International Congress of Pure and Applied Chemistry, New York, N. Y., Sept., 1951, p. 67.

[2] P. Walden, "Electrochemie Nichtwässriger Lösungen," Barth, Leipzig, 1924.

[3] M. Hayek, *J. Phys. Colloid Chem.*, **55**, 1527 (1951).

[4] E. L. Durrum, THIS JOURNAL, **72**, 2943 (1950).