anilide and the chloroacetanilide-Cl^{36} recrystallized from water; yield 23.8 mg. (28.6%).

δ-(*p*-Chlorophenyl)-hydantoic Acid-Cl^{36}.—Chloroacetanilide-Cl^{36} was hydrolyzed by heating under reflux with 0.5 ml. of concd. HCl and *p*-chlorophenyl isocyanate Cl^{36} was formed by the reaction of *p*-chloroaniline-Cl^{36} hydrochloride with phosgene in dioxane. Excess phosgene was removed by evacuation at 0° and the isocyanate reacted with glycine (30 mg.) in alkaline solution. Acidification precipitated δ-(*p*-chlorophenyl)-hydantoic acid-Cl^{36}; yield 17.6 mg. (15.6%). Non-radioactive hydantoic acid, prepared by this method, melted at 189–191° with decomposition.

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Synthesis of α-Aminocyclopropylacetic Acid

BY PETER H. LOWY

In a study of the biological effect of analogs of the naturally occurring amino acids, D,L-α-aminocyclopropylacetic acid was synthesized. It was prepared by a Strecker synthesis from cyclopropanecarboxaldehyde. The intermediate hydroxynitrile was aminated in methanolic ammonia.[1] Because of the instability of cyclopropane compounds toward acids the hydrolysis was carried out with barium hydroxide.[2] Like many other D,L-amino acids cyclopropylaminoacetic acid tastes slightly sweet. The structure was confirmed by oxidation with ninhydrin to cyclopropanecarboxaldehyde.

The amino acid did not affect the growth of wild type *Neurospora crassa* 25a on minimal medium[3] in concentrations of 10 and 40 γ per 3 ml.[4]

Experimental

Cyclopropylcyanide was prepared from γ-chlorobutyronitrile[5] by the method of Schlatter.[6]

Cyclopropane carboxaldehyde was prepared by reduction of cyclopropyl cyanide with one-quarter mole of lithium aluminum hydride according to Smith and Rogier.[7]

α-Aminocyclopropylacetic Acid.—A solution of 12.7 g. of ammonium chloride in 32 ml. of water was kept at 0–5° and stirred mechanically while 14 g. of cyclopropane carboxaldehyde, followed by a solution of 14.3 g. of potassium cyanide in 22 ml. of water, was added dropwise. The mixture was stirred for 2 hours at room temperature and allowed to stand overnight. It was extracted with six 30-ml. portions of ether. After removal of the ether by distillation, the residue of the combined ether extracts was dissolved in 80 ml. of methanol. The solution was saturated with dry ammonia at 0–5°, and allowed to stand for 4 days. Excess ammonia was driven off with an air stream and the solvent removed *in vacuo*. The residual crude cyclopropylaminoacetonitrile weighed 9.9 g.

18.5 g. of barium hydroxide octahydrate was dissolved in its crystal water (steam-bath). It was stirred mechanically at *ca.* 95° while the nitrile (thinned with 5 ml. of methanol) was added dropwise over 40 minutes. After heating and stirring for another 40 minutes, 100 ml. of hot water was added. The hot solution was saturated with carbon dioxide and filtered by suction with the aid of Super-Cel. The precipitate was extracted twice with 50 ml. of hot water while bubbling with carbon dioxide. The combined clear filtrates were concentrated *in vacuo* to 10–20 ml. 2.21 g. (9.3% based on the aldehyde) of the crude amino acid was obtained in several crops (directly from the aqueous concentrate and by precipitation with methanol or ethanol).

Anal. Calcd. for $C_5H_9O_2N$: C, 52.15; H, 7.88; N, 12.17. Found: C, 51.99; H, 7.66; N, 12.33.[8]

Degradation with Ninhydrin.—To 115 mg. of the amino acid dissolved in 5 ml. of hot water a solution of 700 mg. of ninhydrin in 20 ml. of 0.2 molar citrate buffer (*p*H 5) was added.[9] The mixture turned dark purple and was heated in a steam-bath for 20 minutes, while with a slow stream of nitrogen the volatile aldehyde was driven into a trap containing a solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The 2,4-dinitrophenylhydrazone alone as well as mixed with that prepared from authentic cyclopropanecarboxaldehyde melted at 186°.

(1) H. T. Clark and H. J. Bean, "Organic Syntheses," Coll. Vol. II, 2nd Printing, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 29.
(2) J. Ford, THIS JOURNAL, **67**, 876 (1945); *Org. Synth.*, **27**, 1 (1947).
(3) G. W. Beadle and E. L. Tatum, *Am. J. Bot.*, **32**, 678 (1945).
(4) Kindly tested by Phyllis B. Ellman.
(5) C. F. H. Allen, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 156.
(6) M. J. Schlatter, *Org. Syntheses*, **23**, 20 (1943).
(7) L. I. Smith and E. R. Rogier, THIS JOURNAL, **73**, 4047 (1951).
(8) Microanalysis by G. A. Swinehart.
(9) S. Moore and W. H. Stein, *J. Biol. Chem.*, **176**, 367 (1948).

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Ion Aggregation in Gallium(III) Chloride Solutions Containing Added Alkali

BY THERALD MOELLER AND GLENDALL L. KING

In an earlier communication,[1] it was reported that solutions of gallium(III) chloride, bromide, or nitrate may be treated with up to approximately 3 moles of hydroxyl ion per mole of gallium ion initially present without effecting precipitation of the hydrous oxide. Such solutions remain perfectly clear but flocculate sharply and completely upon addition of more alkali. Although appreciable delays in hydrous oxide or hydroxide precipitation are not particularly uncommon, lack of precipitation in the presence of essentially stoichiometric quantities of hydroxyl ion is unusual. Either excessive ion aggregation in solution due to added hydroxyl ion or peptization of the hydrous oxide by excess gallium ion may be regarded as a possible explanation.

Electrometric titration data[1] indicate that in the range prior to flocculation added hydroxyl ion is consumed without appreciable increase in *p*H, but they do not permit decision between an ion aggregation process and a peptization process. If, however, the diffusion current in a gallium(III) salt solution is proportional to gallium ion concentration and remains reasonably constant, polarographic data might permit such a decision. It seems reasonable that any ion aggregation resulting from binding of gallium ions by hydroxyl ions would manifest itself in a corresponding reduction in the magnitude of the diffusion current, whereas if the nature of the gallium species remained the same (as in peptization), no alterations in diffusion current would result when hydroxyl ion is added.

Zeltzer[2] reported that gallium(III) is reduced irreversibly at the dropping mercury electrode at a potential of −1.08 v. (*vs.* normal calomel electrode) from dilute solutions of its salts in 0.001 *N* hydrochloric acid. For solution of the present problem, irreversibility is of no consequence if level diffusion regions can be obtained. Experiment showed this to be possible in chloride solutions containing 0.05 *M* potassium chloride as supporting electrolyte. Corrected diffusion current values obtained by subtracting residual current values were found to be

(1) T. Moeller and G. L. King, *J. Phys. Colloid Chem.*, **54**, 999 (1950).
(2) S. Zeltzer, *Collection Czechoslov. Chem. Commun.*, **4**, 319 (1932).

proportional to gallium ion concentrations up to at least 4×10^{-4} M in chloride solutions.

Diffusion current data for 2.23×10^{-4} M gallium(III) chloride solutions 0.05 M in potassium chloride and containing varying quantities of added alkali, as corrected for dilution effects, are summarized in Table I. It is clear that as the quantity of hydroxyl ion increases, more and more gallium ion is tied up in solution. It may be concluded, therefore, that gallium–hydroxyl ion aggregates are built up in these solutions, thereby reducing the speed of diffusion of gallium ions to the electrode, and that peptization is not a factor of appreciable importance. It seems very reasonable to conclude that similar aggregation processes would characterize bromide and nitrate solutions under comparable conditions.

TABLE I

EFFECT OF ADDED HYDROXYL ION ON CORRECTED DIFFUSION CURRENT IN GALLIUM(III) ION REDUCTION

Mole ratio OH^-/Ga^{+3}	pH	Corrected current, microamperes
0.0	3.45	1.39
1.0	3.56	1.12
2.0	4.00	0.77
3.0[a]	5.40	0.00

[a] Flocculated.

Unfortunately, the data reported do not permit postulations as to the exact natures of the aggregates. Supplementary studies on the variations of the diffusion current with drop time and on the temperature coefficient of the current might permit such postulations.

Experimental

All materials used were chemically pure. Polarographic data were obtained with a Sargent Recording Polarograph. Polarographic reductions were run with samples thermostated to 25 ± 0.5° and freed of oxygen by bubbling nitrogen. All samples were 0.05 M in potassium chloride,

Initial studies were made upon gallium(III) chloride solutions of varying concentrations. To determine the effects of added alkali, solutions obtained by adding varying quantities of sodium hydroxide to fixed quantities of gallium chloride solution and adding sufficient potassium chloride were reduced polarographically. To ensure proper functioning of the dropping mercury cathode, control solutions containing no added hydroxyl ion were run immediately before and immediately after those containing alkali.

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5-Nitro-2-thiophenealdehyde

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Although the several nitrobenzaldehydes are well known, no mention has been made of their thiophene analogs. We have found that nitration of 2-thiophenealdehyde diacetate gives 72% of 5-nitro-2-thiophenealdehyde diacetate. This diacetate has been cleaved (76% yield) by steam distillation from dilute hydrochloric acid. The 5-nitro-2-thiophenealdehyde has been characterized as the semicarbazone and oxidized to 5-nitro-2-thiophenecarboxylic acid. The methyl ester of this acid melted at 76°, the recorded value for methyl 5-nitro-2-thiophenecarboxylate,[1] rather than at 99°, which is the recorded value for methyl 4-nitro-2-thiophenecarboxylate.[1] The 5-nitro-2-thiophenealdehyde also reacted with malononitrile in the presence of piperidine to give 93% of 5-nitro-2-thenalmalononitrile.

2-Thiophenealdehyde Diacetate.—To a mixture of 127 g. of acetic anhydride and 2 g. of stannous chloride dihydrate held below 10° by means of an ice-bath there was added over a forty-five-minute period 112 g. of 2-thiophenealdehyde. When the ice-bath was removed at the close of the addition, the temperature rose rapidly to 24° and reapplication of the ice-bath did not prevent a continuing rise in temperature. Therefore, the mixture was treated immediately with ice, water and then sodium bicarbonate. The copious precipitate was separated by filtration, washed with aqueous sodium bicarbonate and then with water and dried *in vacuo* at 30–40° for eight hours. After this precipitate was dissolved in benzene, the solution was filtered and evaporated to dryness. The residue was dried *in vacuo* at 40–50° for 5.5 hours to yield 167.5 g. (78%) of 2-thiophenealdehyde diacetate. An analytical sample was crystallized from a mixture of benzene and hexane, m.p. 66–68°.[2]

Anal.[3] Calcd. for $C_9H_{10}O_4S$: C, 50.5; H, 4.68. Found: C, 50.7; H, 4.91.

5-Nitro-2-thiophenealdehyde Diacetate.—Two solutions (A and B) were prepared. A consisted of 107 g. (0.5 mole) of 2-thiophenealdehyde diacetate in 200 cc. of acetic anhydride, and B consisted of 30 cc. of fuming nitric acid (d. 1.49–1.50) in 250 cc. of glacial acetic acid. Half of solution B was placed in a 1-l., three-necked flask fitted with a stirrer, a thermometer and a dropping funnel. The stirred mixture was cooled to 5–10° and then half of solution A was added dropwise over a 30-minute period. The temperature was held at 10–15° during the addition. The remainder of solution B was then added to the flask followed by dropwise addition of the balance of solution A over 30 minutes. The cooling-bath was removed, and the amber reaction mixture was stirred at room temperature (30°) for ninety minutes longer. The mixture was next poured into 1 l. of finely crushed ice, whereupon a yellow crystalline solid separated. The product was removed by filtration, washed with cold water, and pressed as dry as possible on the filter.

The crude product was dissolved in 350 cc. of benzene, filtered, and then washed with water until neutral. Water and 2 cc. of 85% phosphoric acid were added to the benzene solution and the mixture was steam distilled in an effort to hydrolyze the crude 5-nitro-2-thiophenealdehyde diacetate to the free aldehyde. This procedure was unsuccessful. Therefore, the crude product again was dissolved in benzene, washed with water, and distilled from a Claisen flask to give 92.9 g. (72% yield) of yellow liquid, b.p. 155–165° (1.5 mm.), which solidified in the receiver. A sample of the solid was recrystallized three times from ethanol and once from a benzene–hexane mixture to give pale yellow tablets, m.p. 71–75°.

Anal. Calcd. for $C_9H_9O_6NS$: N, 5.41. Found: N, 5.23.

5-Nitro-2-thiophenealdehyde.—Ten grams of the crude distilled 5-nitro-2-thiophenealdehyde diacetate was placed in a 1-l. Claisen flask with 500 cc. of 1 N hydrochloric acid and steam distilled. The first 200 cc. of distillate was a cloudy liquid from which 1.7 g. of long yellow thread-like needles deposited on chilling, m.p. 68–71°. Subsequent crops totalling 2.9 g., m.p. 72–75°, were obtained upon further distillation of some 1200 cc. Filtrates from the separation of these crops were returned to the distilland from time to time. The total yield of 5-nitro-2-thiophenealdehyde was 76% (4.6 g.). A sample of the first crop was crystallized twice from aqueous ethanol and finally from water, m.p. 75–76°.

Anal. Calcd. for $C_5H_3O_3NS$: C, 38.2; H, 1.92; N, 8.92. Found: C, 38.5; H, 2.02; N, 9.10.

The semicarbazone melted at 242–243° after one crystallization from nitrobenzene.

Anal. Calcd. for $C_6H_6O_3N_4S$: C, 33.6; H, 2.80. Found: C, 33.9; H, 2.73.

Methyl 5-Nitro-2-thiophenecarboxylate.—A few crystals of 5-nitro-2-thiophenealdehyde were suspended in water con-

(1) J. J. Rinkes, *Rec. trav. chim.*, [4] 51, 1134 (1932).

(2) All of the melting points are corrected.

(3) All of the analyses are microanalyses performed by Mr. Donald Stolts of these laboratories.