was distilled off. The solid colorless hydrazide thus obtained was filtered, washed with water, and recrystallized from slightly dilute ethanol. The yield was 1.5 g. (75%), m.p. 142–144°.

Anal. Calcd. for $C_{12}H_{16}N_2O_3$: C, 61.00; H, 6.83. Found: C, 60.79; H, 6.79.

2-(3,4-Dimethoxyphenyl)-cyclopropylmethylurethan.—The hydrazide just described (1.5 g.), dissolved in 100 ml. of 5% hydrochloric acid, was diazotized at 0° with 9 ml. of 5% sodium nitrite solution. The azide separated as an oil; it was extracted into toluene, and dried over sodium sulfate at 0°. Fifty milliliters of methanol was added, the solution was refluxed for five hours, and the solvents were removed under reduced pressure. The remaining oily urethan solidified on treatment with one drop of methanol. The yield of colorless crystals melting at 118–119.5° was 0.7 g. (46%).

Anal. Calcd. for $C_{13}H_{17}NO_4$: C, 62.13; H, 6.82. Found: C, 62.60, 62.62; H, 6.84, 6.60.

2-(3,4-Dimethoxyphenyl)-cyclopropylamine. (a)—2-(3,4-Dimethoxyphenyl)-cyclopropyl methylurethan (0.5 g.) was refluxed for 30 hours with 25 ml. of a saturated methanolic barium hydroxide solution, barium carbonate was filtered and the solvent evaporated under reduced pressure. The white residue was extracted with benzene, and the benzene was removed, yielding 0.2 g. of the amine. The compound was purified by sublimation and was identical with the amine obtained by procedure (b).

(b)—To a solution of 10 g. of 2-(3,4-dimethoxyphenyl)-cyclopropanecarboxylic acid (m.p. 105°) in 250 ml. of dry benzene was added 10 ml. of thionyl chloride, and the mixture was allowed to stand for three days at about 26°. Excess thionyl chloride and benzene was removed under reduced pressure at 55–60°, and dry xylene was added and stripped off to remove the last traces of thionyl chloride. A sample of the dark acid chloride was hydrolyzed with boiling water. The acid[6] thus obtained melted, after purification, at 103.5–105.5°.

The crude acid chloride was dropped into a stirred suspension of 15 g. of pulverized sodium azide in 50 ml. of xylene over a period of four minutes. Nitrogen evolution (78% conversion) ceased after 11 hours of refluxing. Most of the xylene was distilled off under reduced pressure, and the dark-red isocyanate was hydrolyzed by stirring with 75 ml. of 35% hydrochloric acid at 55–60° for three hours. The solution was concentrated under reduced pressure and neutralized with 10% sodium hydroxide solution. The amine was extracted with ether, dried, and the solvent was distilled off. The oily residue (2.2 g.) (25%) solidified on standing. Purification was achieved by distillation (b.p. 140–150° (1.6 mm.)), and sublimation of the solidified distillate (m.p. 63–64°) at 0.1 mm. The colorless sublimate melted at 68–70°.

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.86; H, 8.25; N, 7.28.

3,4-Dimethoxyphenylacetothiomorpholide.—Using the Schwenk and Bloch[7] modification of the Willgerodt reaction, a mixture of 37 g. of acetoveratrone, 10.3 g. of sulfur and 28.2 g. of morpholine was refluxed for 13 hours and poured onto ice. The oily thiomorpholide (37.5 g.) was extracted with benzene and crystallized on treatment with ether. After several recrystallizations from ethanol, the initially low-melting pale yellow product had m.p. 153–155°.

Anal. Calcd. for $C_{14}H_{17}NO_3S$: N, 4.98. Found: N, 5.05.

The thiomorpholide was hydrolyzed by refluxing with 10% potassium hydroxide solution for 10 hours. The solution was cleared with charcoal, acidified, and homoveratric acid (71% yield) was obtained. After two recrystallizations from benzene–petroleum ether it melted at 93–97°. Homoveratryl chloride was formed in 84% yield from the acid and thionyl chloride in benzene solution. It boiled at 145–149° (2 mm.).

N-[2-(3,4-Dimethoxyphenyl)-cyclopropyl]-homoveratramide.—A solution of 4.2 g. of homoveratryl chloride in 50 ml. of anhydrous ether was dropped slowly into a stirred solution of 2.5 g. of 2-(3,4-dimethoxyphenyl)-cyclopropylamine in 50 ml. of dry ether. The white precipitate which appeared immediately was filtered, washed with ice-water, and recrystallized from ethanol or benzene–isoöctane. The colorless crystals weighed 1.3 g. (27%), m.p. 115–117°.

Anal. Calcd. for $C_{21}H_{25}NO_5$: C, 67.91; H, 6.79. Found: C, 68.02; H, 6.82.

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Recovery of Mellitic Acid from its Salts by Electrolysis

BY MARGARET CARVER AND H. C. HOWARD

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The recovery in good yields of a non-volatile, water-soluble, organic acid, such as mellitic, from solutions of its salts, constitutes a difficult problem. Previous workers have resorted to double decomposition of barium, lead or silver salts with the appropriate acid.[1] Acidification with a mineral acid, followed by evaporation to dryness and soxhlet extraction of the solid, salt–organic acid mixture, is unsatisfactory due to acid salt formation and hence incomplete metathesis.[2,3] Liquid–liquid phase extraction of an acidified salt solution with an immiscible organic solvent is slow because of unfavorable distribution coefficients. Methyl ethyl ketone has been found one of the most satisfactory solvents for this purpose. The usefulness of electrolytic decomposition of aqueous salt solutions for the recovery of the water-soluble, organic acids from the oxidation of coal has been previously reported.[3]

In the present investigation a study has been made of the electrical efficiency and material yields in the electrolytic decomposition of aqueous solutions of the potassium and the ammonium salts of mellitic acid.

Experimental

Materials.—The mellitic acid was prepared by the oxidation of carbon black.[4] The ammonium salt of the acid was made as follows: Fifty grams of the crude acid was dissolved in 250 ml. of warm water, insoluble material filtered out, the filtrate cooled, poured into a liter of concentrated ammonium hydroxide, the mixture cooled to 0° and maintained at that temperature for an hour. The needle-like, crystalline precipitate of ammonium mellitate was filtered off on a buchner funnel, sucked dry and washed with a small amount of cold, concentrated ammonium hydroxide. The greater part of the ammonium hydroxide was removed by drying in a crystallizing dish on a steam-bath for about 30 minutes and the balance in vacuum over concentrated sulfuric acid at room temperature. The ammonium salt prepared by this procedure had the following approximate composition[5] $C_6(COONH_4)_6 \cdot 6H_2O$, molecular weight 552.3. The yield of salt was about 90% of the theoretical. The theoretical yield of mellitic acid from a gram-mole of this salt is 342.1 g. or 61.9% by weight.

The potassium acid salt was prepared by adding to a warm, aqueous solution of the free acid, prepared as above, 4 *N* potassium hydroxide until alkaline to litmus and then acidifying with glacial acetic acid. After standing for 12 hours the crystalline precipitate of the potassium acid salt

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[6] Strong decomposition occurred when the acid chloride was distilled in another run, and only a few drops of an oil, b.p. 165° (7 mm.) were obtained. Hydrolysis of this distillate gave the stereoisomeric acid of m.p. 107–108°.

[7] E. Schwenk and E. Bloch, THIS JOURNAL, **64**, 3051 (1942).

[1] W. Treibs, *Ges. Abhandl. Kenntnis Kohle*, **5**, 585 (1920).

[2] W. A. Bone, L. Horton, S. G. Ward, *Proc. Roy. Soc. (London)*, **A127**, 489 (1930).

[3] B. Juettner, R. C. Smith, H. C. Howard, THIS JOURNAL, **59**, 237 (1937).

[4] B. Juettner, *ibid.*, **59**, 1472 (1937).

[5] *Ibid.*, **59**, 208 (1937).

was filtered off on a buchner funnel, sucked dry, washed with a little cold, glacial acetic acid and dried in a current of air at room temperature. The salt prepared in this way is tribasic and has the approximate composition[6] $C_6(COOH)_3(COOK)_3 \cdot 6H_2O$, molecular weight 564.5. *Anal.* Calcd. loss on drying, 19.15%; equiv. wt. of anhydrous salt, 152.1. Found: loss on drying for 2 hr. at 100° *in vacuo*, 16.3%; equiv. wt. of anhydrous salt, 149.9. The yield of salt was about 50% of the theoretical. The theoretical yield of mellitic acid from a gram-mole of the salt is 342.1 g. or 60.6% by weight.

Apparatus.—The apparatus consisted of a ceramic ware, three-compartment cell, supplied by Maurice A. Knight, Akron, Ohio. Rubber gaskets were cemented to the edges of the cell sections, parchment diaphragms inserted, and the whole assembly made tight by compression. This was effected by end-plates pulled together with threaded rods and wing-nuts. The inside dimensions of each of the three compartments were approximately 15 × 15 × 5 cm. An 80-mesh platinum gauze anode, about 14 cm. square, with a 1 mm. diameter lead-in wire and similar reinforcing wire around the edges, was employed. The cathode consisted of 6.5 mm. diameter copper tubing about 130 cm. long, bent into loops. Cooling water was circulated through this copper cathode and through a similar glass coil immersed in the anode compartment. An ammeter, variable resistance and copper coulometer were connected in series with the cell and a voltmeter across the terminals.

Procedure.—Five hundred ml. of a solution of the salt to be decomposed, 10 to 20 g. per 100 ml., was placed in the central compartment, equal volumes of distilled water in the end compartments and a potential of 115 volts, direct current, was applied to the system. The resistance was high at first, but decreased rapidly as conducting ions migrated into the end compartments. By suitable adjustment of the external, series resistance, the current was limited to a maximum of 3.5 amperes. After the desired time interval, the current was interrupted, the contents of the anode and cathode compartments siphoned out, the migrated acid and alkali determined by titration, and the copper deposited in the coulometer weighed. The end compartments were then refilled with distilled water and the process continued.

Results and Discussion

Data for the decomposition of an aqueous solution containing 100 g. (1.063 equiv.) of the potassium acid mellitate, are plotted in Fig. 1. The slopes of the curves, gram-equivalents per ampere-hour, show the current efficiency of the process at any given stage. The theoretical value is 0.0373 equivalents per ampere-hour. The efficiency of separation of the acid is relatively constant at approximately 20% for the greater part of the decomposition and decreases to about 12% at the end. The efficiency of separation of the alkali starts at about 40% and decreases steadily, reaching a very low value as the decomposition approaches completion. With this cell, in the early stages of the decomposition, the fall in potential was 25 volts with a current of 3.5 amperes and increased to 55 volts with 1.0 ampere near the end.

Similar values of current efficiency were observed in the decomposition of solutions of the ammonium salt, but the fall in potential across the cell was approximately twofold at the same current densities, because of the poorer conductance of the ammonium salt solution.

The actual recoveries of mellitic acid, from electrolysis of solutions of two samples of the potassium acid salt were 86 and 87% of theoretical. In an experiment on decomposition of a solution of the ammonium salt the recovery was 94% and recoveries of approximately 90% have been obtained consistently in electrolyses of solutions of the ammonium salt for preparation of mellitic acid.

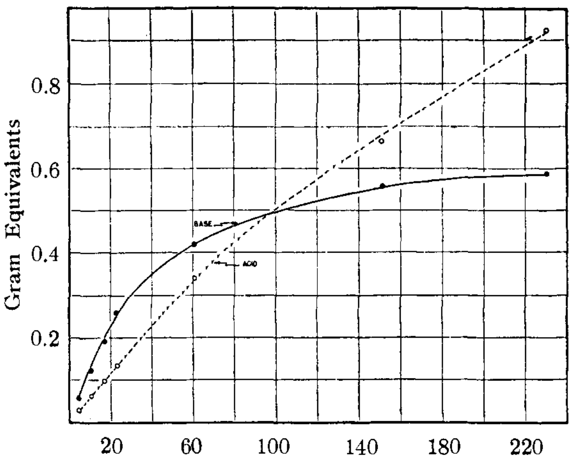

Fig. 1.—Electrolytic decomposition of potassium acid mellitate: ———, base; – – –, acid.

This process is slow—the output from a cell of this type using a current of 3 amperes is about 1 g. of mellitic acid per hour—the electrical efficiencies are low and large volumes of dilute solutions must be evaporated to recover the solid acid, but the operation requires little attention, material recoveries are excellent, and the product is free from inorganic impurities. A few tenths of a per cent. of silica have been found in some preparations. Unlike the electrolytic decomposition of solutions of salts of aliphatic acids, no evidence was found in the decomposition of this aromatic acid of any secondary anodic reactions. Operation of the cell by continuously feeding the salt into the central compartment and continuously withdrawing the solutions of acid and alkali from the end compartments, would improve the electrical efficiency.

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[6] Beilstein, "Handbuch der organische Chemie," Verlag von Julius Springer, Berlin, vierte Auflage, 1926, vol. IX, p. 1008.

Chloromethylation of Acetone

BY O. C. DERMER AND JACK NEWCOMBE

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The only recorded chloromethylation of carbonyl compounds as such is that by Colonge,[1] who used formalin, hydrogen chloride and zinc chloride to convert diethyl ketone, di-*n*-propyl ketone, and pinacolone to the α-chloromethyl derivatives. 2-Chloroethyl methyl ketone (I) has been obtained from acetone, paraformaldehyde, and hydrogen chloride in 41% yield, but only insignificant amounts of chloromethylated products were obtained from acetaldehyde and methyl ethyl ketone, and none at all from diisopropyl ketone. I couples with sodium sulfite to yield sodium 3-oxo-1-butanesulfonate, but not with cuprous cyanide or silver nitrite, and the reaction with potassium thiocyanate is complex. The sodium bisulfite compound of I with potassium cyanide gives 4-chloro-2-hydroxy-

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[1] J. Colonge, *Bull. soc. chim.*, [5] **3**, 2116 (1936).