

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 $C_6(COOH)_3(COOK)_3 \cdot 6H_2O$, 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 $15 \times 15 \times 5$ 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

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

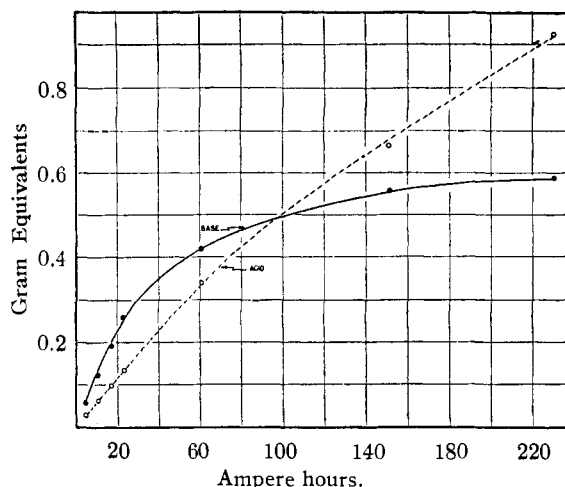


Fig. 1.—Electrolytic decomposition of potassium acid mellitate: ———, base; ---, acid.

consistently in electrolyses of solutions of the ammonium salt for preparation of mellitic 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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Chloromethylation of Acetone

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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-butane-sulfonate, 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-

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

2-methylbutanenitrile, converted by alcoholysis to ethyl 4-chloro-2-hydroxy-2-methylbutanoate.

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Experimental

2-Chloroethyl Methyl Ketone (I).—Paraformaldehyde (240 g., 8 moles) suspended by stirring in refluxing acetone (1174 ml., 16 moles) was treated with dry hydrogen chloride at such a rate as to maintain boiling of the mixture. When all paraformaldehyde had dissolved (about two hours), the mixture was stirred two hours more, cooled, treated with anhydrous calcium chloride to saturation, and left for several hours. The upper layer was separated, rapidly distilled at about 50 mm., stripped of most of its acetone by heating at atmospheric pressure, washed with water, dried and distilled *in vacuo* to yield 350 g. (41%) of I, boiling at 53° at 20 mm., 64° at 30 mm., 72° at 40 mm., 78° at 50 mm., or 123° (dec.) at 740 mm. (literature 53°² or 53.5°³ at 15 mm.). The identity of I was confirmed by its chlorine content (calcd., 33.29%; found, 33.21%), its molecular refraction (n_D^{20} 1.4284, d_4^{25} 1.068; *MR* calcd. 25.55, *MR* found, 25.68), and its conversion to 3-methyl-1-phenylpyrazoline, m.p. 74–76° (literature 76–77°⁴), with phenylhydrazine. Slow distillation alone gave 50, or with diethylamine² 65%, of methyl vinyl ketone.

Similar experiments with methyl ethyl ketone gave less than 1% 1-chloro-2-methyl-3-butanone, b.p. 58° at 20 mm. Paraldehyde, formalin and hydrogen chloride likewise produced only a very little β -chloropropionaldehyde.

I was converted by the method of Marvel and Sparberg⁵ to sodium 3-oxo-1-butanedisulfonate⁶ in 16% yield.

Anal. Calcd. for C₄H₇O₄SNa: Na, 13.2. Found: Na, 13.1, 13.5.

Coupling of I with potassium thiocyanate in alcoholic solution by the method of Shriner⁷ gave an uncharacterized viscous yellowish-red liquid with a foul odor, decomposing on distillation at 5 mm.

I formed the expected addition compound upon shaking with a concentrated aqueous solution of sodium bisulfite.

Anal. Calcd. for C₄H₉O₃SClNa: Na, 10.9. Found: Na, 10.2.

The cyanohydrin was prepared by the method of Bucherer and Grolee.⁸ I (106.5 g., 1 mole) and sodium bisulfite (105 g., 1 mole) were shaken together in 200 ml. of water, and potassium cyanide (65.1 g., 1 mole) in 100 ml. of water was added in portions. The 4-chloro-2-hydroxy-2-methylbutanenitrile, which separated as a layer, was removed at once, and dried: crude yield, 46%. Vacuum distillation gave the pure nitrile, b.p. 104–106° at 13 mm., n_D^{20} 1.4448, d_4^{25} 1.125.

Anal. Calcd. for C₅H₉ONCl: N, 10.5; *MR*, 31.4. Found: N, 10.2; *MR*, 31.5.

The nitrile was best hydrolyzed by allowing it to stand with excess concentrated hydrochloric acid.⁹ Evaporating to dryness, extracting with benzene, and removing the benzene produced a liquid that could not be crystallized and gave a fading end-point when titrated with base; it was considered to be the lactide of 4-chloro-2-hydroxy-2-methylbutanoic acid.

For alcoholysis, 60 ml. of the cyanohydrin in 100 ml. of absolute ethanol was saturated with hydrogen chloride at 0°. The mixture was refluxed for four hours, diluted with water, refluxed for one-half hour more, cooled, neutralized with sodium bicarbonate, and extracted with ether. Drying and distilling gave 25 ml. (30%) of ethyl 4-chloro-2-hydroxy-2-methylbutanoate, b.p. 105–107° at 23 mm., n_D^{20} 1.4385, d_4^{25} 1.106.

Anal. Calcd. for C₇H₁₃O₂Cl: Cl, 19.6; *MR*, 42.6. Found: Cl, 19.1; *MR*, 42.8.

(2) E. E. Blaise and M. Maire, *ibid.*, [4] 3, 265 (1908).

(3) J. Decombe, *Compt. rend.*, **202**, 1685 (1936).

(4) M. Maire, *Bull. soc. chim.*, [4] 3, 272 (1908).

(5) C. S. Marvel and M. S. Sparberg, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 558.

(6) A. Lapworth, *J. Chem. Soc.*, **85**, 1214 (1904).

(7) R. L. Shriner, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 366.

(8) H. Bucherer and A. Grolee, *Ber.*, **39**, 1225 (1906).

(9) K. N. Gajnd, *J. Indian Chem. Soc.*, **14**, 13 (1937).

Methanolysis proceeded similarly but gave two incompletely separated fractions. The one boiling at 68° at 20 mm. contained about 1% chlorine, evidently as impurity, and probably consisted chiefly of methyl 2-hydroxy-2-methyl-3-butenate, produced by loss of hydrogen chloride from the expected ester. The latter, b.p. 98–100° at 24 mm., contained slightly less than the theoretical amount of chlorine for methyl 4-chloro-2-hydroxy-2-methylbutanoate for the same reason.

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On the Products of the Maillard Reaction¹

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Before measurable carbon dioxide is evolved or color developed in the Maillard reaction, it is apparent that there is an interaction between simple sugars and amino acids. In the most recent contribution, Haugaard, Tumerman and Sylvestri² conclude that at alkaline pH, the initial product is a Schiff base.

In later stages, carbon dioxide, carbonyl compounds and humin-like material are observed. Wolfrom, Schuetz and Cavalieri³ isolated hydroxymethylfurfural (HMF) from heated glucose-glycine mixtures. Gottschalk and Partridge⁴ have demonstrated chromatographically two reaction products in heated mixtures of glucose and amino acids under alkaline conditions. The products were assumed to be N-glycosides. They were capable of reacting with ninhydrin and had lower *R_f* values in butanol-acetic acid than the original amino acid. Reaction mixtures after some fractionation were hydrolyzed with acetic acid and chromatographed, revealing a compound which co-chromatographed with authentic HMF.

In this paper, results are reported of further study of the glucose-glycine reaction. Some of the numerous reaction products have been separated by chromatography and their relation to the original reactants determined by radiographic techniques.

Experimental

Solutions described in the previous paper⁵ were analyzed for reaction products, the reaction being studied at 56.5° and at 100°. The reaction at 100° was allowed to proceed for two hours, equivalent in terms of color development to 250 hours at 56.5°, whereas the reaction at 56.5° was continued for 453 hours. The mixture at the lower temperature was sampled at the beginning and end of the run. Samples (0.1 ml.) were withdrawn from the 100° mixture at 0, 2, 4, 16, 40, 64, 85 and 128 min.

Aliquots for chromatograms were prepared as follows: The 0.1-ml. sample was transferred to a 1-ml. volumetric flask and diluted to volume. Aliquots (20 μ l.) of this diluted solution were applied to papers and chromatographed two-dimensionally for amino acids, sugar, non-volatile organic acids and for autoradiographs. Water-saturated phenol and water-saturated butanol-acetic acid were used for the amino acids; phenol-water and butanol-ethanol-water (52-32-15) for the sugars; butanol-formic acid and

(1) Presented at the XII International Chemical Congress, New York, 1951.

(2) G. Haugaard, I. Tumerman and H. Sylvestri, *THIS JOURNAL*, **73**, 4594 (1951).

(3) M. L. Wolfrom, R. D. Schuetz and L. F. Cavalieri, *ibid.*, **71**, 3518 (1948).

(4) A. Gottschalk and S. J. Partridge, *Nature*, **165**, 684 (1950).

(5) F. H. Stadtmann, C. O. Chichester and G. Mackinney, *THIS JOURNAL*, **74**, 3194 (1952).