

	Calculated for $C_{16}H_{14}O_8$.	Found. I.
Carbon.....	75.58	74.99
Hydrogen.....	5.51	5.65

This compound, anisoyl benzoyl methane, was also readily formed when sodium ethylate was used instead of methylate. There appeared to be no difference in the yield, but the product was darker colored when ethylate was employed.

Bromine acts upon this diketone with formation of substitution products. When six and one-half grams (two molecules) of bromine were added to a solution of ten grams (one molecule) of the diketone in 150cc. of ether, a vigorous reaction took place with evolution of considerable hydrogen bromide. On evaporation of the ether, a white, crystalline product resulted; this crystallized from methyl alcohol in well-defined white prisms, and melted at 127° to 128° . This compound is probably anisoyl benzoyl dibromomethane, $C_{16}H_{12}O_8Br_2$, and will be further examined.

When piperonal acetophenone dibromide¹ is treated with sodium methylate according to the above-described process, a compound is obtained which crystallizes in small yellow needles, and melts at 86.5° . This substance is at present under investigation.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.
No. 48.]

THE ELECTROLYTIC OXIDATION OF SUCCINIC ACID.

BY CHARLES H. CLARKE AND EDGAR F. SMITH.

Received July 21, 1899.

THE oxidizing action of the current on organic bodies is sure to yield most interesting results. Indeed, the whole organic field remains practically open to investigation along this line. Turn in any direction and ample material will be found for such study. We selected succinic acid as the subject of our investigation. It is, indeed, true that in the past this acid and its salts have engaged the attention of chemists in the electrolytic way, but unfortunately their results are contradictory. No attention was given to the important conditions of current density, voltage, temperature, etc., with the consequence that

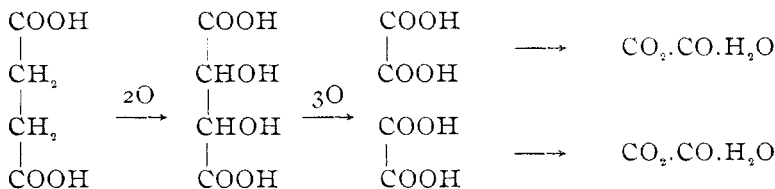
¹ St. v. Kostanecki and Schneider: *Ber. d. chem. Ges.*, 29, 1892.

what has been done electrolytically upon this acid, and, indeed, upon nearly all the acids which have been exposed to the influence of the current, has very little scientific value.

Our aim has been to learn the influence of electrolytic oxygen upon succinic acid. What the products of reduction may be we have not at the present taken pains to ascertain. That is a problem for the future. We have also striven to carefully record the conditions under which we operated and by which our products were produced so that others, if they choose, may repeat and verify them.

The different experiments were conducted in a rather large beaker-glass, using a good porous cup as a diaphragm. The succinic acid was dissolved in definite amounts of sodium hydroxide and known volumes of alcohol. This mixture constituted the anode liquor and it was placed in the porous cup, while the beaker-glass contained sodium hydroxide alone. In those trials in which attention was given to the collection of gases, the mouth of the porous cup was closed with a rubber stopper carrying a small condenser, the latter being suitably connected with a delivery tube leading into an inverted flask or jar, serving as the gasometer.

In considering what the possible result might be in the moderated oxidation of succinic acid, the question naturally arose,—can tartaric acid possibly be produced and then oxalic acid?



Almost every electrolytic study of the acids has made mention of the presence of carbon dioxide, and with us the thought of its possible antecedents was constantly present; hence, we sought to produce and isolate both the tartaric and the oxalic acid.

It may be here remarked that the current used in all the experiments varied from 0.024 to 1.55 ampere for 100 sq. cm. of anode surface. The period of action, as will be seen, ranged from one to ninety-eight hours. When the trial was concluded

the anode liquor had a red color and an aromatic odor. It was acidified with hydrochloric acid, when a great deal of carbon dioxide was evolved. After cooling the liquid was extracted with ether and the watery layer removed by a separatory funnel. Portions both of the ethereal and of the aqueous layers, after the removal of silica and alumina, were carefully freed from other impurities and tested for tartaric acid and oxalic acid. In the first instance recourse was had to the production of the silver mirror, and in the second to the formation of calcium oxalate. The ether extracts of the two experiments showed the mirror, and one of them calcium oxalate. Traces of these acids, therefore, were undoubtedly present. We next endeavored to discover some better means of obtaining and identifying them. During the process of the oxidation, milk of lime was cautiously introduced into the anode chamber. At the expiration of eighteen hours a voluminous precipitate was present. This was filtered out, washed and treated with acetic acid. Much carbon dioxide was evolved, but there remained a precipitate, white in color, which proved to be calcium oxalate. This was then treated with dilute sulphuric acid, filtered and warmed, while potassium permanganate was run into the acid liquid. In this way the presence of 0.0814 gram of oxalic acid was proved.

The coloring-matter of the ethereal extract was isolated. In the purifying process much of it was lost, and the remainder, unfortunately, was also lost through a mishap in making the combustion. The substance, whatever it may prove to be, never appeared in large quantities. It is undoubtedly aromatic in its nature. It melted at 178° , and re-solidified at 169° C.

The gases collected in certain of the oxidations were in the early periods mainly oxygen and carbon monoxide, which later increased in volume and were accompanied by ethylene, methane, and hydrogen.

The appended tables show the working conditions and the corresponding results. To summarize, we may say that the electrolytic oxidation of succinic acid in a divided cell gave *tartaric acid, oxalic acid, some aromatic bodies, oxygen, carbon monoxide, carbon dioxide, ethylene, and methane.*

Experiment number.	Succinic acid, Grams.	Sodium hydroxide, Grams.	Alcohol, cc.	Water, cc.	Time, Hours.	N, D, 100°.	Volts.	Temperature, Degrees.	Remarks.
1	2	4	75	—	9	0.465	3.74	62	Trace of reducing substance in ether extract.
2	2	6	75	—	8	0.361	4.19	65.5	
3	22	46	75	100	5	0.505	2.28	63	
4	17	33	—	100	39	0.461	2.10	22	Obtained tar, although no alcohol was present.
5	12	24	50	10	18	0.409	2.90	22	Ether extract did not react with $C_6H_5NHNH_2$.
6	10	20	50	10	21	0.359	3.00	22	
7	5	10	50	10	1	0.177	2.74	22	
8	5	50	50	50	18	0.144	2.37	22	
9	5	50	50	50	65	0.024	1.30	22	Muslin cell.
10	5	50	—	50	24	0.035	2.57	23	" "
11	5	50	—	50	24	0.046	2.55	24	" "
12	5	50	—	50	113	0.049	2.55	23	Trace of oxalic acid in water solution.
13	5	50	50	50	12	1.000	3.52	25	
14	5	35	50	65	19	0.262	2.87	24	Trace of oxalic acid in water solution.
15	5	25	50	50	23	0.287	3.22	27	
16	5	50	50	50	20	1.410	4.93	37	Obtained 0.1046 gram $(COOH)_2 \cdot 2H_2O$.
17	5	50	—	50	47	0.321	2.82	25	Traces of oxalic acid in water solution and ether extract.

¹ Twenty per cent. soda solution used hereafter.

18	5	50	50	100	18	0.420	3.42	29	Obtained 0.0075 gram $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$.
19	5	—	—	—	14	0.685 1.912	1.98	26	Used acetic acid solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ with lead electrodes. Negative results.
20	5	50	50	50	37	0.757 1.501	3.57	35	Trace of tartaric acid in ether extract. (See Gas Analysis table.)
21	5	50	—	100	19	1.545	3.27	29	See Gas Analysis table.
22	5	50	—	100	21	1.483	3.50	29	See Gas Analysis table.
23	5	50	50	100	55	0.540	3.58	25	
24	5	50	50	100	65	0.212	2.55	23.5	
25	10	100	50	50	38	0.780	2.88	24	
26	10	100	50	50	29	0.286	4.25	23	See Gas Analysis table.
27	10	100	50	50	39	0.773	3.08	24	
28	10	100	50	50	24	0.064	2.57	22	Current varied from 0.038–0.899. Nickel electrodes, muslin cell, no tar.
29	10	—	50	—	98	0.555	2.00	24	
30	10	100	50	50	24	0.756	2.69	28	
31	10	100	50	50	28	0.357	1.83	26	
32	10	100	75	75	55	0.746	2.89	28	See Gas Analysis table.
33	10	100	75	75	68	0.916	2.59	25	See Gas Analysis table.
34	10	100	100	100	82	0.753	2.91	30	See Gas Analysis table.
35	10	100	50	100	70	0.909	2.03	28	
36	10	40	40	—	48	0.737	3.43	29	Two cells { Outer lost 2.72 NaOH = 14.62 per cent. } Ratio $\frac{1.000}{0.777}$. Middle lost 2.868 NaOH = 11.37 per cent. }
37	10	35	35	—	112	0.729	4.30	26	Two cells { Outer lost 6.04 NaOH = 27.55 per cent. } Ratio $\frac{1.000}{0.746}$. Middle lost 7.24 NaOH = 20.57 per cent. }

¹ By this is meant that the cup containing the anode liquor was placed within a larger, similar vessel, and the latter in a large beaker containing the cathode solution.

GAS ANALYSES.

Experi- ment number.	Sample number.	Oxygen. Per cent.	Ethylene. Per cent.	Carbon monoxide. Per cent.	Methane. Per cent.	Hydro- gen. Per cent.
20	1	15.6	9.8	1.3	—	—
21	1	18.0	16.0	4.4	—	—
21	2	79.6	—	—	—	—
22	1	66.7	—	1.0	—	—
25	1	17.2	1.0	10.0	—	—
32	1	3.06	1.96	6.55	44.11	17.90
32	2	3.18	2.72	12.84	24.40	35.88
33	1	77.5	—	3.2	—	—
34	1	18.5	—	1.0	—	—
34	2	2.4	3.1	9.5	31.2	28.9
34	3	41.0	1.0	4.0	—	—
36	1	28.2	3.6	—	—	—
36	2	75.4	5.0	9.6	5.00	0.8
36	3	39.4 ¹	14.2	—	—	—
36	4	83.5	7.2	4.3	—	—
37	1	31.0	3.6	3.6	—	—
37	2	60.8	5.8	—	—	—
37	3	66.7	4.6	2.8	—	—
37	4	77.4	2.0	2.6	—	—

NOTES ON THE DETERMINATION OF SULPHUR IN PIG IRON.

BY M. J. MOORE

Received August 4, 1899.

MUCH has been said regarding the inaccuracy of the volumetric method for the determination of sulphur in pig iron, and many good reasons too well-known to mention here, have been given by way of explanation. I will refer, however, to one article by Phillips² which illumines some of the dark places admirably.

The writer is not aware that any mention has ever been made that physical treatment was responsible for a great portion of the error, such treatment of course, changing the chemical composition of the iron. It is the practice of nearly all if not all, steel and furnace plants to pour the molten metal into water, this being called a "shot sample." The shot thus formed are taken to the laboratory and crushed in a steel mortar and passed

¹ It was found that the pyrogallic acid was exhausted; hence this discrepancy.

² This Journal, 17, 891.