

[CONTRIBUTION FROM THE ENGINEERING EXPERIMENT STATION AND THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## COBALTIC SULFATE AS AN OXIDIZING AGENT<sup>1</sup>

BY SHERLOCK SWANN, JR., AND THEODORE S. XANTHAKOS

RECEIVED JUNE 23, 1930

PUBLISHED FEBRUARY 9, 1931

Since the oxidation potential of cobaltic sulfate is the highest of any of the easily regenerated oxidizing agents which might be used as oxygen carriers in the electrolytic oxidation of organic compounds, a study of its behavior as an oxidizing agent seemed desirable.

By the use of organic compounds of varied susceptibilities to oxidation, such a study should give an indication of the feasibility of cobaltic sulfate as an oxygen carrier and should also indicate the type of oxidation for which cobaltic sulfate is best adapted. The work was undertaken with *these ideas in mind*.

The only reference found in a literature search where cobaltic sulfate was used as an oxidizing agent was in a paper by Conant and Aston<sup>2</sup> in which they showed that isobutyric aldehyde was oxidized to acetone and other products.

### Experimental

At the beginning of the investigation a method for the preparation of cobaltic sulfate was sought. That which suggested itself immediately was the electrolytic method described by Erich Müller,<sup>3</sup> which consisted in the oxidation of cobaltous sulfate in 8 *N* sulfuric acid at a platinum anode. The yields obtained were not entirely satisfactory under these conditions. A study was therefore undertaken to determine the optimum conditions for the preparation in the hope of improving the yield and shortening the time required.

The apparatus consisted of a large porous cup of 800 cc. capacity as the anode compartment which was placed in an 1000-cc. beaker. A platinum sheet of 80 sq. cm. area was used as the anode while a sheet of copper of about 300 sq. cm. area on the anode side which surrounded the porous cup served as the cathode.

The anolyte consisted of 500 cc. of a saturated solution of cobaltous sulfate in sulfuric acid. The catholyte was of the same composition. In all cases a current of 5 amperes was employed. The anode current density was therefore about 0.06 ampere per sq. cm. The temperature was controlled either by a cooling coil or an ice-bath.

Experiments were carried out at various temperatures and with different concentrations of sulfuric acid. The results are given in the tables.

The free acid concentration was determined electrometrically. The cobaltic sulfate prepared was always in suspension in the anode liquor, which was so viscous that a sample could not be taken by means of a

<sup>1</sup> Published by permission of the Director of the Engineering Experiment Station.

<sup>2</sup> Conant and Aston, *THIS JOURNAL*, 50, 2783 (1928).

<sup>3</sup> Erich Müller, "Elektrochemisches Praktikum," 4th ed., p. 210.

pipet. A quantitative analysis was therefore not possible. It was estimated by weight after filtration by suction through asbestos. The product was not dried further.

TABLE I

Free acid normality	EFFECT OF TEMPERATURE		Co <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> per 100 cc. of soln., g.
	Temp., °C.	Duration of oxidation in hours	
8	25	5.5	0
8	23	5.5	Very little
8	18	5.5	Very little
8	10	3.5	15
EFFECT OF FREE ACID CONCENTRATION			
8.3	10	2.75	33.2
9.55	10	3.5	47.7
10.7	10	2.5	40
11.9	10	3.67	21

This method of determining cobaltic sulfate is not accurate on account of the large amount of mother liquor retained by the crystals. The results should be comparable, however, because each determination was made in the same way.

In order to determine the effect of current density, some experiments were carried out in a much smaller cell. The method of analysis was different in this set of experiments. At the end of each run the anolyte was poured into a standard solution of *N*/10 sodium oxalate. The excess oxalate was titrated electrometrically with *N*/10 potassium permanganate. The results of these experiments are shown in the following table.

TABLE II

EFFECT OF CURRENT DENSITY ON YIELD

Amp.	Current density in amp. per sq. cm.	Duration of oxidation in hours	Yield of Co <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> , g.
0.7	0.0088	2.75	2.48
1.0	.043	2.75	4.00
0.7	.047	2.75	3.15
1.0	.073	2.75	3.75
1.0	.180	2.75	4.40
0.7	.350	2.75	2.97

The temperature in these experiments varied between 10–13°. It was noticed that the crystals of cobaltic sulfate became smaller with increase of current density until at 0.18 amp. per sq. cm. the solution could be drawn up into a pipet very readily. The optimum current density is roughly between 0.01 and 0.2 amp. per sq. cm.

Finally the current and material yields of cobaltic sulfate were determined. Since small crystals were obtained at a current density of 0.18 amp. per sq. cm., the current density used in this set of experiments was almost the same, 0.17 amp. per sq. cm. The current efficiency was determined as the oxidation progressed by an analysis of a 1-cc. sample of anode suspension drawn out by means of the pipet. The cobaltic sulfate was determined electrometrically as in the last set of experiments. The cobaltic sulfate

was present in the form of fine crystals which were distributed uniformly throughout the anode liquor. The results are shown in Table III.

TABLE III  
EFFECT OF DURATION OF OXIDATION ON CURRENT EFFICIENCY AND YIELD

Duration of oxidation	Amp.	Current efficiency, %	Material yield in % by wt.	Co <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , normality of anode suspension
1 hr. 40 min.	1	84.3	...	0.225
2 hrs. 52 min.	1	74.5	...	.415
3 hrs. 52 min.	1	63.8	(93.33)	.560
5 hrs.	1	..	...	.564

Temp., 6°. Normality of H<sub>2</sub>SO<sub>4</sub>, 10. Normality of CoSO<sub>4</sub>, 1.2. Volume of anode solution, 100 cc. Theoretical amount of electricity, 2 faradays.

The anode liquor was always kept free from soluble organic materials since they either retarded the rate of oxidation of the cobaltous salt or prevented its oxidation.

From the results of the experiments carried out it may be shown that satisfactory conditions for the preparation of cobaltic sulfate in the apparatus described are as follows.

The solution must not be allowed to rise in temperature above 10°. The normality of free sulfuric acid should be 10. The current density may vary roughly between 0.01–0.2 amp. per sq. cm.<sup>2</sup> Higher current densities cause the product to form in smaller crystals than in the case of lower current densities. Not more than a five-ampere current should be employed for 500 cc. of anolyte; otherwise the temperature cannot be controlled. The cobaltic sulfate precipitates out in the form of greenish-blue crystals on account of its insolubility in the strong sulfuric acid. The maximum yield will be obtained at the end of four hours.

**Oxidations with Cobaltic Sulfate.**—In order to estimate the strength of cobaltic sulfate as an oxidizing agent, it was tried with the following organic compounds of varied susceptibilities toward oxidation: amylene, benzene, ethyl alcohol and acetic acid.

It was thought that cobaltic sulfate might be used to best advantage as an analytical reagent to oxidize certain organic compounds to carbon dioxide quantitatively rather than as an oxidizing agent in preparations because too large quantities were necessary on account of its high molecular weight. With this idea in mind the following compounds were studied: acetone, glycerin, ethylene glycol, and formic, tartaric, citric and malic acids.

### Apparatus and Procedure

For the oxidations to test the oxidizing power of cobaltic sulfate a shaking machine was set up, holding an Erlenmeyer flask of 500-cc. capacity which could be surrounded by an ice-salt bath.

The organic compound to be oxidized was placed in the flask with the cobaltic sulfate suspension just as formed in the anode compartment of the cell. A rubber stopper was inserted containing a rubber tube leading to a gas-collecting bottle filled with water. The flask was surrounded by an ice-salt bath and was then shaken for two to three hours. At the end of that time it was found that oxidation had taken place

and the green suspension had turned to a pink solution. The gas was analyzed for carbon dioxide and the solution steam distilled after the removal of insoluble material.

The steam distillate was neutralized with standard sodium hydroxide, evaporated to dryness and the salt weighed. The salt was dissolved in water and less than the theoretical quantity of sulfuric acid was added to liberate any organic acid. Sufficient water was used to obtain a solution of 1 to 2% of free organic acid. This was distilled away from the sodium sulfate and a Duclaux<sup>4</sup> test run.

The procedure for the complete oxidations was not the same. In this case the apparatus and procedure of Franz and Lutze<sup>5</sup> was followed.

The organic compound to be oxidized was placed in a three-necked flask equipped with a stirrer. In one neck was placed a glass tube leading to the bottom of the flask and drawn out to a capillary. This was connected by rubber tubing to a soda lime tower. The tubing could be closed by a screw clamp. The soda lime tower was connected to the air line. The other neck of the flask was connected to a train consisting of a wash bottle containing water, a large calcium chloride tower, an anhydrone tower and an ascarite tube in the order named.

A weighed amount of the organic compound was placed in the flask with the cobaltic sulfate suspension. Liquids were washed in with a little water and the connection to the air line shut off. The stirrer was started and the oxidation was allowed to proceed for about an hour. The air line was then opened and a slow stream of air was allowed to bubble through the liquid in the flask for half an hour while the flask was heated by a water-bath. The ascarite tube was weighed and the percentage of carbon dioxide calculated.

In the preparations of cobaltic sulfate for these runs it was found that the yields were practically identical if the conditions were always the same. Therefore, no determination of the amount of cobaltic sulfate in the suspension was made. It was assumed that the same quantity was present in every run. The results of the investigation are given in Table IV.

TABLE IV  
RESULTS AND CONCLUSIONS

	CO <sub>2</sub> , %	Aldehydes	Acids	Moles of compound	Moles of Co <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
Amylene (mixture)	0	Trace	Formic and others	0.422	0.14
Benzene	0	Phenolic	Compounds	.5	.14
Acetic acid	0.2	.....	.....	.75	.14
Ethyl alcohol	4.08	Considerable	Considerable acetic	.0164	.14
Acetone	13	None	Considerable acetic	.0149	.14
Glycerine	0	None	Considerable formic	.0274	.14
Ethylene glycol	96.05	..	.....	.0099	.14
Formic acid	99.96	..	.....	.0205	.14
Tartaric acid	101.22	..	.....	.00099	.14
Citric acid	99.87	..	.....	.000745	.14
Malic acid	100.3	..	.....	.001368	.14
Malic acid	73.2	..	.....	.002543	.14

The amount of product from the oxidation of benzene was insufficient for purposes of identification. Phenolic compounds were shown to be present by their odor.

<sup>4</sup> Kamm, "Qualitative Organic Analysis," 1923, p. 139.

<sup>5</sup> Franz and Lutze, *Ber.*, 57B, 768 (1924).

The results of the oxidation of amylene, benzene, ethyl alcohol and acetic acid show that cobaltic sulfate behaves as a strong oxidizing agent and should be an excellent oxygen carrier for anodic oxidations in cases where no interference with its formation occurs.

It may seem strange that while formic acid is completely oxidized when no other compounds are present, it remains unoxidized in the presence of amylene and glycerin. This may be explained by the fact that formic acid might be more difficult to oxidize than the other two compounds in strong acid. Hatcher and West<sup>6</sup> found formic acid in the oxidation of malonic acid by acid permanganate. They showed that the rate of oxidation of formic acid was inversely proportional to the  $P_H$  of the solution. The Duclaux test was carried out with great care and it is not believed that the information from it is misleading.

The results of the experiments on complete oxidation indicate that cobaltic sulfate may be used in the same manner as persulfates for types of compounds which are easily oxidized to carbon dioxide.

In all cases where cobaltic sulfate is used as an oxidizing agent most of it decomposes to yield free oxygen. Rapid decomposition sets in even at low temperatures. The organic compound seems to catalyze this decomposition. Consequently for complete oxidations it is necessary to use very large quantities of cobaltic sulfate. It is used, therefore, to best advantage as an analytical reagent and not for the purpose of oxidizing large quantities of material.

### Summary

1. A study of the electrolytic preparation of cobaltic sulfate has been carried out.

2. The behavior of cobaltic sulfate as an oxidizing agent for organic compounds has been studied. It has been shown that cobaltic sulfate is a strong oxidizing agent. It may be used as an analytical reagent for oxidizing certain compounds quantitatively to carbon dioxide.

URBANA, ILLINOIS

---

<sup>6</sup> Hatcher and West, *Trans. Roy. Soc.*, 3, 21 [Sec. 3], 269 (1927).