[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AMHERST COLLEGE]

COPPER SULFATE AS THE DEACON CHLORINE CATALYST?[1]

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Introduction

If we may judge from the literature, there is considerable doubt concerning the role of cupric sulfate when employed in the catalytic process of Deacon for the direct oxidation of gaseous hydrogen chloride. In the First Report of the Committee on Contact Catalysis,[2] following a discussion of a possible mechanism for cupric chloride catalyst, we find the statement, "when we start with copper sulfate as the catalytic agent, which may be done, the whole thing becomes hopelessly complicated." Levi and Bettoni[3] suggest an intermediate hydrate formation

$$CuSO_4 + 2HCl + {}^1/_2O_2 = CuSO_4{\cdot}H_2O + Cl_2$$
$$CuSO_4{\cdot}H_2O = CuSO_4 + H_2O$$

Now Hensgen[4] and others have shown that many of the metal sulfates are attacked by dry hydrogen chloride gas to form the corresponding chlorides and liberate sulfuric acid. This work suggests the possibility of the conversion of cupric sulfate according to the following equation

$$CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$$

If this be true, then it is probable, if we start with copper sulfate in the Deacon Process, that the copper chloride formed is the catalyst, and the mechanism is the same as if copper chloride had been used initially.

The available data for the action of hydrogen chloride on copper sulfate are rather controversial and indefinite as regards experimental conditions, especially temperature. Hensgen finds an addition compound of $CuSO_4{\cdot}2HCl$ (approximately) by the action of dry hydrogen chloride on anhydrous copper sulfate at room temperature. He suggests that this compound, $CuSO_4{\cdot}2HCl$, plays an important role in the Deacon reaction. In a later article,[5] Hensgen shows that 2.18 moles of hydrogen chloride are absorbed per mole of pentahydrated copper sulfate, giving this observation to support the following equation

$$CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$$

Other writers[6,7] find addition compounds or partial conversion to copper chloride. With the exception of one experiment by Hensgen, all these

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[1] This paper is the report of work previously cited in the Fourth Report of the Committee on Contact Catalysis, Taylor, *J. Phys. Chem.*, **30**, 145 (1926).

[2] Bancroft, *J. Ind. Eng. Chem.*, **14**, 328 (1922).

[3] Levi and Bettoni, *Gazz. chim. ital.*, **35** (I), 320 (1905).

[4] Hensgen, *Ber.*, **9**, 1675 (1876).

[5] Hensgen, *Ber.*, **10**, 259 (1877).

[6] Latchinoff, *J. Russ. Phys.-Chem. Soc.*, **20**, 585 (1888).

[7] Colson, *Compt. rend.*, **124**, 82 (1897).

reactions were run at temperatures well below that used in the Deacon Process.

To clear up any doubt, it seemed desirable to determine whether hydrogen chloride gas alone, or admixed with oxygen, does indeed quantitatively liberate sulfuric acid from copper sulfate with the concomitant formation of a chloride or oxychloride of copper, this test to be made at about 450°, the temperature used in the Deacon Process.

Preparation of Materials

The hydrogen chloride gas was prepared by dropping concentrated sulfuric acid on a solution of C. P. concentrated hydrogen chloride. The gas bubbled through two wash bottles containing concentrated hydrogen chloride solution, and thence passed through calcium chloride towers. The train of wash bottles and towers served effectively to remove any mechanically carried sulfuric acid. By counting the bubbles in the wash bottles it was possible to estimate rate of flow.

The oxygen was supplied from a commercial tank, passed through a bubbler containing paraffin oil to estimate rate of flow and thence through calcium chloride.

The copper sulfate was prepared by heating C. P. pentahydrated copper sulfate to about 450° in a stream of dry air. Analysis for copper and sulfate showed the product to have the composition of anhydrous cupric sulfate.

Procedure

In his experiments, Hensgen tested the reaction, $CuSO_4 + HCl$, by determining the composition of the residual copper salt. At the temperature employed by us cupric chloride is partially dissociated into cuprous chloride and chlorine. Moreover, in the experiments where oxygen was mixed with the hydrogen chloride, some oxychloride was probably formed. The residual copper salt would be a mixture of cupric and cuprous chloride and, in some experiments, probably oxychloride of copper $CuO \cdot CuCl_2$. Hence it was thought better to test the completeness of the reaction, $CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$, by determining the sulfuric acid evolved.[8]

Hydrogen chloride alone, or hydrogen chloride mixed with oxygen, was passed over a weighed sample of anhydrous copper sulfate contained in a hard glass tube which was electrically heated to about 450° as measured by a nitrogen filled mercury thermometer. When hydrogen chloride alone was used, the rate of gas flow was estimated at 12 liters per hour; when the mixture was used, the rate was 15 liters per hour. In these experiments on the liberation of sulfuric acid from the sulfate, a

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[8] At 450°, the sulfuric acid is, of course, largely dissociated into sulfur trioxide and water.

variation of 20° was found to have no effect on the total amount of sulfuric acid liberated; hence it was considered safe to keep the temperature between 440 and 460°. Preliminary to a run, the tube was swept out with dry hydrogen chloride and was brought to the desired temperature. The tube was then opened at the end where the gases were admitted, the sample of copper sulfate contained in a porcelain boat was quickly inserted and the tube was closed. The sulfuric acid in the effluent gas was absorbed in a train of four spiral wash bottles filled with concentrated hydrogen chloride solution. Concentrated hydrogen chloride was here preferred to water because its use eliminated the danger that the solution might suck back due to the too rapid solution of hydrogen chloride gas. The long train was found necessary to effect the complete absorption of the sulfuric acid. After action was complete, the liquid contained in the wash bottles was boiled down to a small volume to expel most of the hydrogen chloride. The residual liquid was neutralized by ammonia, then made slightly acid by hydrogen chloride, diluted and analyzed for sulfate content by precipitation of barium sulfate.

Results

Action of Hydrogen Chloride Alone.—The white color of the anhydrous copper sulfate gradually changed to a dirt-brown, resembling that of anhydrous cupric chloride. After five to six hours the mass began to liquefy and sublimed cuprous chloride was apparent on the cooler portions of the tube. At this stage, and not before, evolution of sulfuric acid was found to be complete.

Table I gives a comparison between the weight of barium sulfate calculated according to the equation, and the actual weight found by analysis.

TABLE I

ACTION OF HYDROGEN CHLORIDE ON COPPER SULFATE AT 450° (APPROX.)

Sample	$CuSO_4$ taken, g.	$BaSO_4$ calcd., g.	$BaSO_4$ found, g.	Yield of H_2SO_4, %
1	0.3609	0.5377	0.5401	100.4
2	.2166	.3167	.3188	100.6
3	.3046	.4454	.4484	100.6

Action of Hydrogen Chloride—Oxygen Mixture.—In order to duplicate the conditions of the Deacon Process, a test was made of the action of a mixture of hydrogen chloride and oxygen in approximate ratio, by

TABLE II

ACTION OF HYDROGEN CHLORIDE MIXTURE ON COPPER SULFATE AT 450° (APPROX.)

Sample	$CuSO_4$ taken, g.	$BaSO_4$ calcd., g.	$BaSO_4$ found, g.	Yield of H_2SO_4, %
1[a]	0.2501	0.3657	0.3622	99.3
2	.2280	.3334	.3342	100.2
3	.3200	.4689	.4681	99.8

[a] Crucible cracked—possibly slight loss.

volume, of 4:1. The observations concerning color change, time for completion, etc., were not sensibly different from those when hydrogen chloride alone was used. The results are tabulated in Table II.

Rate of Evolution of Sulfuric Acid.—In order to get an estimate of the course of the reaction with time, the absorption train was replaced at various time intervals by a duplicate and the amount of sulfuric acid evolved during the various intervals was determined by separate barium sulfate precipitations. The anhydrous copper sulfate used here weighed 0.2707 g.; the yield of barium sulfate should, therefore, have been 0.3960 g. when conversion was complete. The sum of the weights in Col. 2 of Table III is 0.3985 g. Col. 3 lists the percentages of sulfuric acid evolved in the various time intervals and Col. 4, the total percentage at the end of each interval.

TABLE III

RATE OF EVOLUTION OF SULFURIC ACID

Time interval, minutes	$BaSO_4$ found, g.	H_2SO_4 for interval, %	Total H_2SO_4, %
0–22	0.0347	8.77	8.77
22–60	.0809	20.22	28.99
60–100	.0460	11.62	40.61
100–140	.0450	11.37	51.98
140–230	.1527	38.75	90.73
230–380	.0392	9.88	100.61

It will be observed that the copper sulfate was not immediately decomposed. After 140 minutes only 52% had yielded up its sulfate, and 9.3% remained unchanged even after 230 minutes or almost four hours. The action was complete, however, at the end of six hours. This rate of evolution of sulfuric acid should be taken only as a roughly quantitative statement. Obviously the rate would be influenced by many factors such as amount of surface of copper sulfate exposed, size and shape of containing tube and variations in temperature.

The foregoing data prove definitely that a quantitative yield of sulfuric acid is obtained by heating copper sulfate to 450° in a stream of hydrogen chloride or hydrogen chloride-oxygen mixture. After six hours' time no sulfate is left in the catalyst mass. Hence, if we start with copper sulfate in the Deacon Process, the catalyst, after six hours' time, must be copper chloride and cannot be copper sulfate.

In one experiment the following test was made on the effluent gas produced when hydrogen chloride—oxygen mixture passed over copper sulfate. The gas stream was divided in two parts. One part bubbled through barium chloride solution to test for sulfate, the other through potassium iodide to test for chlorine. As nearly as could be determined, the evolution of sulfuric acid and the production of chlorine began almost simultaneously at the end of about five minutes from the time the catalyst was inserted. This time was doubtless needed to bring the catalyst to the temperature of the furnace. Since chlorine was not produced before the sulfuric acid began to come off, it is needless to assume that copper sulfate acted as catalyst even at the very start of the action; because as soon as a very small amount of copper sulfate was converted into chloride, the latter could function as the catalyst.

Summary

1. At 450°, sulfuric acid is quantitatively displaced from copper sulfate by the action of dry hydrogen chloride gas alone, or admixed with oxygen. We may assume that the residual salt is entirely in the form of copper chloride or oxychloride.
2. Hence the mechanism of the Deacon Process when copper sulfate is used as the initial form of the catalyst is no more complicated than it is when cupric chloride is used initially.

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VAPOR PRESSURE DATA FOR ISOPROPYL ALCOHOL AND TERTIARY BUTYL ALCOHOL

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The literature apparently contains no data for the vapor pressures of *iso*propyl alcohol and tertiary butyl alcohol over a range of temperatures. In view of the increasing importance of these substances, the present investigation was undertaken to remedy the deficiency.

Experimental Part

Two methods for measuring the vapor pressures of the liquids were employed. From 20 to 90° the static method of Smith and Menzies[1] was utilized. The isoteniscope was of the U type and was immersed in a small hand-regulated thermostat. The temperatures were measured to 0.01° by a thermometer which had been calibrated against a similar thermometer standardized by the United States Bureau of Standards. The manometer was U-shaped, with the evacuated side permanently connected to a high-vacuum pump consisting of a bulb of activated charcoal immersed in liquid air.

A second static method, developed in this Laboratory, was employed in measurements on *iso*propyl alcohol from 0 to 30° and on undercooled *tert.*-butyl alcohol at 20 and 25°. In this case our apparatus was essentially similar in principle to that described by Johnston,[2] although at the

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[1] Smith and Menzies, THIS JOURNAL, **32**, 1419 (1910).

[2] Johnston, *Z. physik. Chem.*, **62**, 333 (1908).