

THE CATALYTIC EFFECT OF OSMIUM TETROXIDE
ON THE
OXIDATION OF HYDRAZINE BY POTASSIUM CHLORATE

Thesis

by

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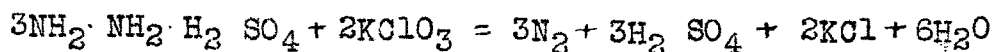
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Introduction

It is well known that neutral or weakly acid solutions of alkali chlorates show no appreciable oxidizing power. However, it has been observed by K. A. Hofmann (Ber. 45,3329, 1912; 46,1567,1913) that, in the presence of very minute amounts of osmium tetroxide, the oxygen becomes readily available. Chlorate solutions activated in this way will, for example, oxidize hydrazine to free nitrogen, potassium iodide to iodine, and arsenic to arsenious acid.

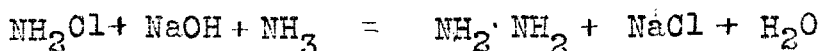
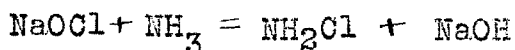
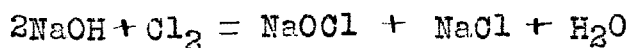
Hofmann found that, in the oxidation of hydrazine sulfate, nitrogen is liberated quantitatively according to the equation



The investigation of the mechanism of this reaction has been taken as the subject of this thesis.

Experimental Work

Hydrazine sulfate was prepared by the method of Conant (Organic Syntheses, V.2, P.31). The reactions involved are:



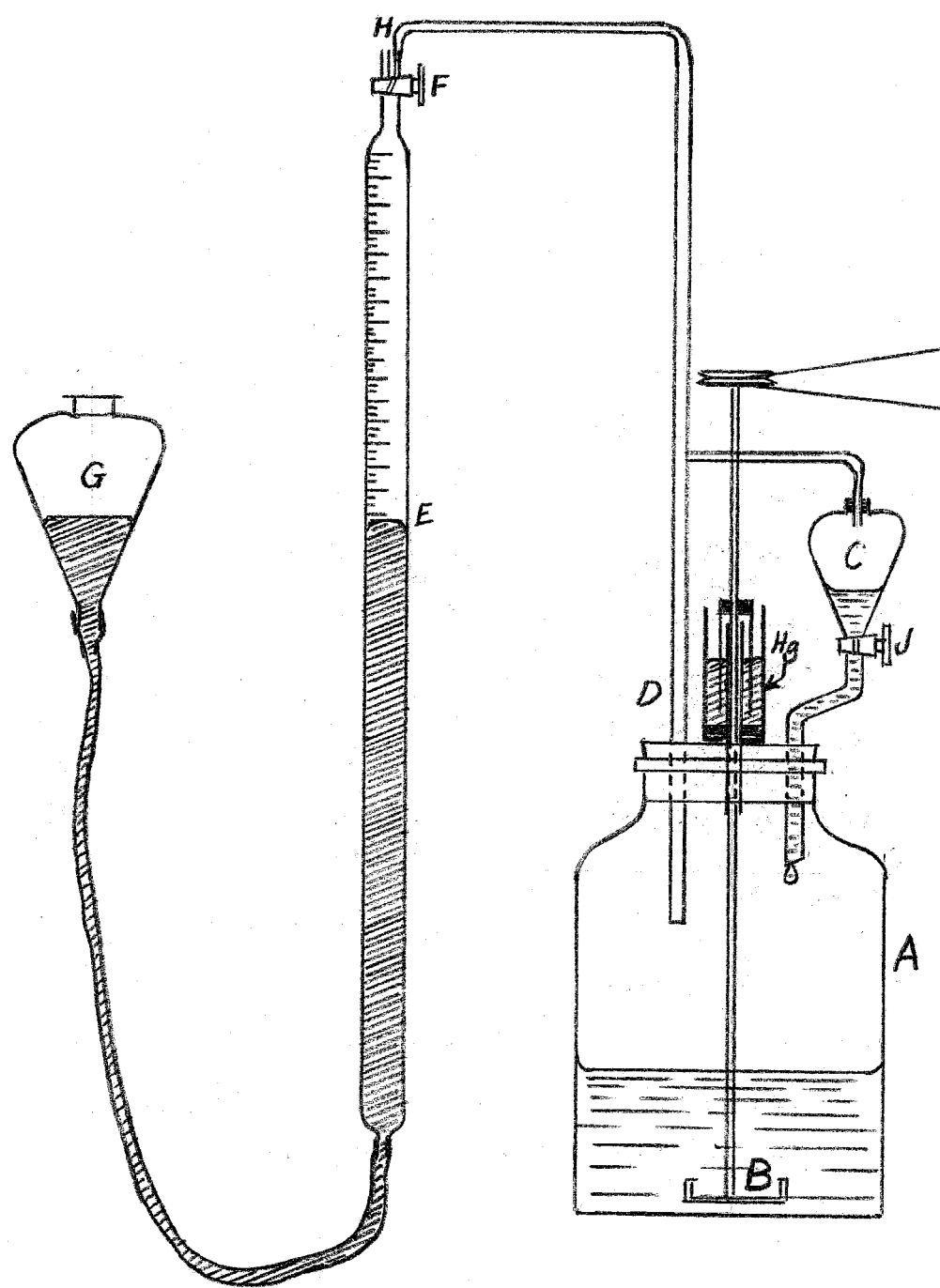
The sodium hypochlorite solution was prepared by passing chlorine into a 6l. flask containing 480 gm. of sodium hydroxide,

2400 gm. of water, and 3400 gm. of cracked ice until the flask had gained 340 gm. in weight. During the addition, the flask was kept thoroughly cooled in order to avoid the formation of chlorates.

To each of four 1200 cc. batches of the sodium hypochlorite solution was added 1500 cc. of concentrated ammonia water, 900cc. of water, and 375 cc. of a 10% gelatine solution. These mixtures were evaporated as rapidly as possible to about one-third the original volume. The residual solutions were cooled with ice and filtered; then cooled again with ice and salt. When the temperature reached 0° , an excess of concentrated sulfuric acid was slowly added with constant stirring. When the hydrazine sulfate had completely precipitated it was filtered off and washed with cold alcohol.

About 220 grams of hydrazine sulfate were obtained, corresponding to a yield of 35% on the basis of ammonia used. One re-crystallization yielded a product which was almost entirely free from chloride.

The first experimental work done was an attempt to follow the rate of the reaction by measuring the liberated nitrogen. For this purpose the apparatus sketched on p. 3 was constructed. It consists essentially of a reaction flask (A) equipped with a mercury seal stirrer (B), a dropping funnel (C), connected at the top to the delivery tube (D), which, in turn, is connected to the gas burette (E), through the two-way stop-cock (F). A water reservoir (G), is connected at the bottom of the burette to equalize pressures when making readings.



GASOMETRIC APPARATUS
For measuring rate of
evolution of Nitrogen.

In operating this apparatus, the reaction flask, containing the potassium chlorate and osmium tetroxide solution, was immersed in a thermostat. The hydrazine sulfate solution was put in the dropping funnel, and all connections were thoroughly coated with paraffin. Then the stirrer was started and the water level in the burette brought to the zero point, pressures in both the burette and the reaction flask being adjusted to atmospheric by opening the air vent (H). The stop-cock (F) was then turned to shut off the air vent and ^{to} connect the burette with the delivery tube. Then the stop-cock (H) on the dropping funnel was opened and the hydrazine sulfate solution was allowed to enter the reaction flask. The volume of nitrogen evolved at successive time intervals was read from the burette, pressures being equalized by bringing the water in the reservoir to the level of that in the burette.

A great many trials were made in an effort to get consistent results with this apparatus. One of the chief difficulties was the impossibility of maintaining a uniform rate of stirring, because of continual voltage fluctuations in the power supply. Since the relative heights of the mercury columns in the stirrer are dependent on the velocity of revolution, variations in speed caused marked discrepancies in the burette readings. Furthermore, it was found that, in order to avoid large errors due to supersaturation of the solution with nitrogen, a very high stirring velocity (1000 to 1500 r.p.m.) was necessary. Repeated attempts to construct a stirrer that would run at this rate for a sufficient length of time were unsuccessful. These difficul-

ties finally made it necessary to abandon the gasometric method.

Various methods of analyzing the solution for chloride and hydrozine were tried. The oxidizing action of the chlorate and osmium tetroxide prevented the use of the ordinary iodimetric methods for hydrozine; and the silver-chromate determination of chloride was useless because of the reducing action of the hydrozine. It was found, however, that silver chloride could be precipitated without appreciable reduction, provided the solution was one-tenth normal or stronger in nitric acid. On this basis the following procedure was adopted:

Stock solutions of hydrozine sulfate, .15 molal; potassium chlorate, .20 molal; and osmium tetroxide, 1 mg. per cc., were made up. These were kept in the thermostat and portions pipetted into reaction flasks to give solutions of the concentrations noted below for the rate experiments. For each analysis 25 cc. was pipetted from the reaction flask to a beaker containing 10 cc. of tenth normal silver nitrate solution, 3 cc. of 6N nitric acid, and 100 cc. of water. After a minute or two of stirring, the precipitate coagulated^{and} it was filtered through a weighed Gooch crucible, washed, dried and weighed.

The results of experiments performed are given below:

Run No. 1

Concentrations: KClO_3 , .08 molal; $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$, .06 molal; OsO_4 , .04 mg. per cc.

Time in Hours	Grams of AgCl
1	.0017
2	.0037

Time in Hours	Grams of AgCl
3	.0054
4	.0070
5	.0088
6	.0101
7	.0115
8	.0130
10	.0154
24	.0335

Run No. II

Concentrations: KClO_3 , .08 molal; $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$, .06 molal;
 OsO_4 , .08 mg. per cc.

Time in Hours	Grams of AgCl
1	.0043
2	.0078
3	.0113
4	.0143
5	.0168
7	.0226
9	.0287
11	.0347
23	.0695
28	.0967
33	.1330
$46\frac{1}{2}$.1335

Run No. III

Concentrations: KClO_3 , .08 molal; $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$, .015 molal;
 OsO_4 , .08 mg. per cc.

Time in Hours	Grams AgCl
4	.0337
8	.0339
13.2	.0338
21	.0344

Run No. IV

Concentrations: KClO_3 , .02 molal; $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$, .06 molal;
 OsO_4 , .08 mg. per cc.

Time in Hours	Grams AgCl
4	.0031
8	.0048
13	.0054
23	.0080

Run No. V

Concentrations: KClO_3 , .08 molal; $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$, .03 molal;
 OsO_4 , .08 mg. per cc.

Time in Hours	Grams AgCl
1	.0063
2	.0166
3	.0643
4.25	.0665

Time in Hours	Grams AgCl
5	.0668
6.2	.0667
8	.0683
18	.0684

Run No. VI

Concentrations: KClO_3 , .04 molal; $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$, .06 molal
 OsO_4 , .08 Mg. per cc.

Time in Hours	Grams AgCl
1	.0023
2	.0041
3	.0048
5	.0061
8	.0084
18	.0114

The above data are plotted on Page 9.

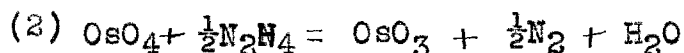
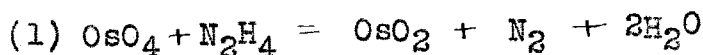
Discussion of Results

A comparison of curves IV and VI shows that each ordinate on VI is approximately twice the corresponding ordinate on IV, indicating that the rate of formation of KCl is directly proportional to the chlorate concentration. (Curve II shows this same relation for the first 3 or 4 hours, but later, as the hydrozine concentration decreases, it becomes proportionately faster.) Similarly, curves I and II indicate that the rate is directly proportional to the OsO_4 concentration. But a com-

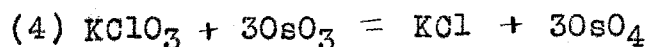
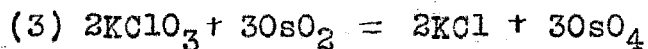
parison of curves II, III, and V shows that the rate is much greater with a lower hydrozine concentration.

This effect is also indicated by the shape of curves I, II and V.

The effect of catalysts in promoting oxidation-reduction reaction generally consists in the catalyst being alternately oxidized and reduced. It is highly probable that the first reaction which takes place in our case is the reduction of the osmium tetroxide to a lower oxide. In view of the effect of hydrozine on the reaction rate, it seems probable that more than one lower oxide of osmium is formed. We shall assume for the moment that the reduction takes place according to the following equations:



The corresponding oxidation equations are:



The ratio of the rates, V_1 and V_2 , of reactions (1) and (2) respectively is:

$$\frac{V_1}{V_2} = \frac{k_1 (\text{N}_2\text{H}_4) (\text{OsO}_4)}{k_2 \sqrt{\text{N}_2\text{H}_4} (\text{OsO}_4)} = K \sqrt{\text{N}_2\text{H}_4}$$

It is evident, then, that increasing the hydrozine concentration increases the rate of reaction (1) more than that of reaction (2), thereby increasing the OsO_2 concentration and diminishing the OsO_3 concentration. Now, if reaction (3) is slow as compared to reaction (4), the net result of increasing

the hydrozine concentration is to slow up the reaction as a whole.

The presence of osmium dioxide may be recognized by the fact that it appears as a dark colored colloidal solution. In the foregoing experiments it was noticeable that the solutions with the higher concentrations of hydrozine were distinctly darker in color.

This investigation was carried out at the suggestion and under the direction of Dr. Don M. Yost.

Summary

The rate of reaction of potassium chlorate with hydrozine sulfate in the presence of osmium tetroxide has been determined for various concentrations of the reacting substances. It was found that the rate varies directly with the concentration of chlorate and of osmium tetroxide, but inversely as a function of the hydrozine concentration. A reaction mechanism which is in accordance with these observations has been proposed.