## Discussion of Results

The agreement of the determinations of the amount of iodine liberated is more satisfactory than for the iodate and oxide formed in the residue. In the case of the iodate formed, the poorer agreement may be due to local overheating resulting in decomposition of the iodate into iodide and oxygen. We have no reliable information regarding the temperature at which lithium iodate begins to decompose. Lithium oxide is known to attack platinum and it is possible that this may account for the discrepancies in the determinations of the oxide. The striking feature is the large amount of iodate formed.

The equation $10LiI + 5O_2 \longrightarrow 2LiIO_3 + 4Li_2O + 4I_2$ seems to fit the facts most closely.

| | Iodine liberated, % | Iodate in residue, % | Oxide in residue, % |
|---|---|---|---|
| According to equation | 80.00 | 75.10 | 24.90 |
| Found | 80.22 | 71.25 | 23.97 |

## Summary

1. Heating anhydrous lithium iodide in a current of pure, dry oxygen to an elevated temperature results in an evolution of iodine and the formation of lithium iodate and oxide in the residue.

2. The reaction conforms closely to the equation $10LiI + 5O_2 \longrightarrow 2LiIO_3 + 4Li_2O + 4I_2$.

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# THE DECOMPOSITION AND OXIDATION OF DITHIONIC ACID

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## Introduction

The solutions of dithionic acid ($H_2S_2O_6$) and its salts are known[1] to be relatively unreactive towards strong oxidizing agents such as permanganate, dichromate, hypochlorous acid and bromine at ordinary temperatures. This is shown both by direct experiment and by the fact that dithionates are formed along with sulfates when the first two of these oxidizing agents react with sulfites. The only investigation that has been made is that of Muller,[2] who showed that iodine does not react directly with dithionic acid, but that the first step consists in the decomposition of the acid into sulfurous and sulfuric acid, and that this is followed by the reaction between iodine and sulfurous acid. The equations are

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[1] Gmelin-Kraut, "Handbuch der anorganischen Chemie," Carl Winter, Heidelberg, **1907**, vol. $1^1$, p. 593.

[2] Muller, *Bull. soc. chim.*, **9**, 183, 185 (1911).

$$S_2O_6^{=} + H_2O = SO_4^{=} + H_2SO_3 \qquad (1a)$$
$$\text{or} \quad S_2O_6^{=} = SO_4^{=} + SO_2 \qquad (1b)$$
$$H_2SO_3 + I_2 + H_2O = SO_4^{=} + 4H^+ + 2I^- \qquad (2)$$

In spite of the fact that Equation 1a seems not to require acid to make it take place, Muller's results showed that the rate of the decomposition is greatly increased by increasing the acid concentration. More will be said later about this effect.

It does not follow, however, that decomposition is the first step when oxidizing agents other than iodine are used. It was, therefore, one of the purposes of this investigation to establish the mechanisms of the oxidation reactions with other oxidizing agents. For this purpose dichromate, bromate and iodate in acid solution were used. It is also believed that the results may be of interest when the mechanisms of the oxidation of sulfites are more thoroughly studied.

It should be remarked that dithionic acid has been definitely proved to be dibasic[3] and highly ionized in solution. Moreover, the facts that the dithionates are formed only by the oxidation of sulfites and not by mixing sulfurous and sulfuric acid, and that like the nitrates, all the known salts are very soluble, seem to indicate that the two sulfur atoms are equivalent, rather than one being of sulfite and the other of sulfate character.

## Preparation of the Dithionic Acid and Analysis of the Solutions

A solution of manganous dithionate was prepared by treating a 1 *M* solution of sulfurous acid with manganese dioxide according to well-known procedures.[1] From this the pure barium salt was prepared, and by treating solutions of this with potassium sulfate or dil. sulfuric acid the potassium salt or acid was formed.

Iodimetric methods were used throughout to determine the concentration of the oxidizing agent, care being taken to adjust the acid concentrations so that the conditions of the methods of Bray and Miller[4] were fulfilled. In the oxidation experiments the samples were diluted to the proper volume and treated with potassium iodide, and the liberated iodine was then titrated with thiosulfate. We believe the results of the experiments to be free from any greater errors than are involved in any volumetric method of analysis.

## Rate of the Decomposition

Experiments on the rate of decomposition of dithionic acid in the presence of other acids were first made. Solutions of the desired concentrations in dithionic acid and added acid were prepared at room temperature; 25cc. portions were pipetted into test-tubes. These tubes were then sealed and placed in the thermostat. After measured intervals of time, a tube

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[3] Ostwald, *Z. physik. Chem.*, **1**, 106 (1887). Meyer, *Habilitationsschrift*, Breslau, 1903; *Ber.*, **34**, 3606 (1901).

[4] Bray and Miller, THIS JOURNAL, **46**, 2204 (1924).

was withdrawn and opened under a definite amount of standard iodine solution and the excess of iodine was then titrated with thiosulfate.

In Table I are given the detailed results of a typical experiment at 50°. The concentrations are expressed in equivalents per liter of solution and the time in hours. The rate constants *k* are those calculated from the integrated form of the differential equation for first-order reactions, using logarithms to the base *e*. It will be noted that the constancy of *k* is satisfactory.

TABLE I

TYPICAL EXPERIMENT ON THE RATE OF DECOMPOSITION

Experiment 4. Initial concentration of HCl, 1.2178 *N*.

| Hours | $H_2S_2O_6$, *N* | *k* |
|---|---|---|
| 0 | 0.0414 | ..... |
| 77.67 | .0262 | 0.00590 |
| 123.70 | .0197 | .00601 |
| 143.60 | .0173 | .00608 |
| 173.13 | .0144 | .00610 |
| | | Av. 0.00602 |

Table II gives a summary of the results of the experiments on the rate of decomposition at 50° and 80°. The units used are the same as those in Table I.

TABLE II

RATE OF DECOMPOSITION OF DITHIONIC ACID IN THE PRESENCE OF ACIDS

| Expt. | Temp., °C. | Initial normality of $H_2S_2O_6$ | Acid added | Normality of total acid ($\Sigma H$) | Rate constant *k* |
|---|---|---|---|---|---|
| 1 | 50 | 0.0379 | HCl | 3.582 | 0.0403 |
| 2 | 50 | .0329 | $HClO_4$ | 3.441 | .0352 |
| 3 | 50 | .0401 | HCl | 1.6628 | .0074 |
| 4 | 50 | .0414 | HCl | 1.2178 | .00602 |
| 5 | 50 | .0476 | HCl | 0.9536 | .00350 |
| 6 | 80 | .0252 | HCl | .9488 | .2291 |
| 7 | 80 | .0350 | HCl | .6058 | .0974 |
| 8 | 80 | .0319 | HCl | .2193 | .0355 |
| 9 | 80 | .0309 | HCl | .1187 | .0209 |

It will be seen that at the high acid concentrations which prevailed in the experiments at 50° the acid increases the rate much more than proportionally to its concentration. This is in accord with the great increase of activity which acids exhibit above 1 *N*. Table III, where the values of $k/(\Sigma H)$ are given, shows that in the experiments at low acid concentration at 80°, the rate is approximately proportional to the acid concentration.

TABLE III

RATE OF DECOMPOSITION IN RELATION TO THE ACID CONCENTRATION

| Expt. | 6 | 7 | 8 | 9 |
|---|---|---|---|---|
| Acid, concn. | 0.9488 | 0.6058 | 0.2193 | 0.1187 |
| *k* | .2291 | .0974 | .0355 | .0209 |
| $k/(\Sigma H)$ | .242 | .161 | .161 | .177 |

If the decomposition takes place according to Equation 1a, it could be regarded as a hydrolytic reaction, and its rate, as in the case of the inversion of sucrose, might be expected to be proportional to the concentration of $H^+$ or perhaps $H_3O^+$; or at higher acid concentrations approximately proportional to the activity of $H^+$. If, however, the reaction occurs according to Equation 1b, one would hardly expect it to be catalyzed by acid. It might be true that the ion $HS_2O_6^-$ decomposes more rapidly than the ion $S_2O_6^{=}$, in which case the law of mass action would require, since the proportion of $HS_2O_6^-$ is certainly small, approximate proportionality between the rate and the acid concentration. The fact that acid acts as it does makes it probable, however, that the process is one of hydrolysis. The fair agreement of the constants $k/(\Sigma H)$ of Table III would hardly be expected, in view of the anomalous behavior of strong electrolytes, if the rate were determined by the concentration of the $HS_2O_6^-$ ion produced as the result of a true mass-action effect.

It may finally be pointed out that from Expts. 5 and 6 of Table II, in which the total acid present was nearly the same but the temperatures were 50° and 80°, respectively, the average effect of temperature on the reaction rate, as computed by the equation $ln\ (k_2/k_1) = A(T_2 - T_1)/T_1T_2$, is found to correspond to a 4.0-fold increase of the constant $k$ for each 10° rise of temperature.

## Rate of Oxidation of Dithionic Acid

The results of the oxidation experiments with dichromate, bromate and iodate show conclusively that the rate of disappearance of dithionic acid is independent of the concentration of these oxidizing agents. This was established by comparing the results of experiments which differed only in the concentration of the oxidizing agent, and also by comparing the results graphically with those of the experiments on the decomposition; dithionic acid, therefore, shows the same behavior toward dichromate, bromate and iodate as it does towards iodine.[2]

Table IV contains the results of some of the oxidation experiments at 50°. All the concentrations here are expressed in equivalents per liter.

TABLE IV

RATE OF OXIDATION OF DITHIONIC ACID

| Oxidizing agent | Initial concn. of oxidizing agent | Initial concn. of $K_2S_2O_6$ | Acid | Av. concn. of acid | Rate constants $k$ | |
|---|---|---|---|---|---|---|
| | | | | | Obs. | Calcd. for $(\Sigma H) = 3.4N$ |
| Dichromate | 0.0307 | 0.0357 | HCl | 3.378 | 0.0304 | 0.0311 |
| Dichromate | .0548 | .0346 | HCl | 3.457 | .0267 | .0253 |
| Bromate | .0658 | .0592 | $HClO_4$ | 3.395 | .0366 | .0366 |
| Bromate | .0664 | .0618 | $HClO_4$ | 3.162 | .0279 | .0350 |
| Iodate | .0572 | .0486 | $HClO_4$ | 3.435 | .0352 | .0341 |

In these experiments, the acid concentration increases somewhat since the reactions occur according to the equations of the type $2BrO_3^- + 5S_2O_6^{=}$-

$+ 4H_2O = Br_2 + 10SO_4^{=} + 8H^+$. To correct for this, an average acid concentration was determined graphically. This is given in Col. 5 of Table IV. In the last column are given the values of the rate constant when calculated for a uniform acid concentration of 3.4 *N* by means of an empirically determined equation. These calculated values agree well with the value (0.0352) found for the rate of decomposition in Expt. 2 of Table II (at acid concentration 3.44 *N*). The deviations noted in the experiments with dichromate may well be due to activity effects of dichromate and chromic salts. The corrected results are also in agreement with that found by Muller[2] for the acid concentration in question when he used iodine as oxidizing agent.

These results show that the first step in the oxidation of dithionic acid is its decomposition into sulfurous and sulfuric acids.

This conclusion is confirmed by the fact that other strong oxidizing agents have no effect at ordinary temperatures; thus, even freshly prepared trivalent silver[5] has no effect, judging from qualitative experiments. It would nevertheless be of considerable interest to determine whether there is any oxidizing agent active enough to react directly with dithionic acid or its salts in solution. A study of the effect of fluorine would be of interest in this connection.

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## Summary

The rate of decomposition of dithionic acid into sulfurous and sulfuric acids has been measured at 50° and 80° and in the presence of various concentrations of hydrochloric or perchloric acid. The rate was found to be proportional to the concentration of the dithionate and to that of the total acid, provided its concentration does not exceed 0.6 *N*; but at higher acid concentrations the rate increases more rapidly. These facts indicate that the catalytic effect of the acid is probably one of hydrolysis.

The rate of oxidation of dithionic acid by dichromate, bromate and iodate has been found to be about the same for these three oxidizing agents, to be independent of their concentrations, and to be nearly identical with the rate of the decomposition of the acid into sulfurous and sulfuric acids. This clearly shows, as Muller concluded in the case of its oxidation by iodine, that the first step in the oxidation of dithionic acid is commonly, if not always, its hydrolysis, and that the sulfurous acid thereby produced is then oxidized.

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[5] Yost, THIS JOURNAL, **48**, 152 (1926).