

**THE FORMATION AND
DECOMPOSITION OF
DITHIONATES:
DISSERTATION**

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649259045

The Formation and Decomposition of Dithionates: dissertation by Jacob Cornog

Except for use in any review, the reproduction or utilisation of this work in whole or in part in any form by any electronic, mechanical or other means, now known or hereafter invented, including xerography, photocopying and recording, or in any information storage or retrieval system, is forbidden without the permission of the publisher, Trieste Publishing Pty Ltd, PO Box 1576 Collingwood, Victoria 3066 Australia.

All rights reserved.

Edited by Trieste Publishing Pty Ltd.
Cover @ 2017

This book is sold subject to the condition that it shall not, by way of trade or otherwise, be lent, re-sold, hired out, or otherwise circulated without the publisher's prior consent in any form or binding or cover other than that in which it is published and without a similar condition including this condition being imposed on the subsequent purchaser.

www.triestepublishing.com

JACOB CORNOG

**THE FORMATION AND
DECOMPOSITION OF
DITHIONATES:
DISSERTATION**

**THE FORMATION AND
DECOMPOSITION OF DITHIONATES**

UNIV. OF
CALIFORNIA

DISSERTATION

**PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE
SCHOOL OF THE OHIO STATE UNIVERSITY**

**BY
JACOB CORNOG**

**The Ohio State University
1921**

I. THE POLYTHIONATES

Dithionic acid, $H_2S_2O_6$, the first member of this remarkable group of acids, was discovered in 1913 by Welter and Gay-Lussac¹; trithionic acid, $H_2S_3O_6$, in 1842, by Langlois²; tetrathionic acid, $H_2S_4O_6$, in 1843, by Fordos and Gelis³; pentathionic acid, $H_2S_5O_6$, in 1845, by Wackenroder⁴; finally potassium hexathionate, $K_2S_6O_6$, was discovered in 1888 by Debus⁵ as a part of his classic investigation of Wackenroder's solution. Dithionic acid was originally called hyposulfuric acid (*unterschwefelsauer* in the German). The present nomenclature was suggested by Fordos and Gelis³ in 1847 to simplify the naming of the increasing number of polythionic acids which were being discovered about that time. However the name hyposulfuric persists occasionally as late as 1880.

The obviously outstanding feature of these acids is the "piling up" of sulfur atoms in the molecule, increasing in number one atom at a time, from dithionic acid with two to potassium hexathionate with six sulfur atoms to the molecule. This is a promising field for investigation of valence and molecular structure. Indeed the molecular structure of the polythionates has already been the aim of much investigation, but apparently, thus far, results are more speculative than real. Without attempting a complete discussion of the results already attained in this field, the following facts and observations are mentioned.

Debus⁵ experimentally found that all the polythionates, save dithionate, are intermediate products between hydrogen sulfide and sulfur dioxide, on the one hand, and free sulfur and water on the other, as represented by the equation



The sulfur in the sulfur dioxide represents a higher state of oxidation than does the sulfur in any of the polythionates save the dithionate. So apparently the whole series of polythionates occurring between the first and last products of the above equation represents a "running down process" in the degree of oxidation of the sulfur. This opinion is in harmony with the findings of Thomsen¹ in the matter of heats of formation. He found for

the whole series of polythionates, that the heats of formation vary uniformly and inversely as the number of sulfur atoms in the respective molecules. From the decreasing heats of formation with increasing number of sulfur atoms in the molecule it would seem that there is an upper limit to the number of sulfur atoms that may occur in a single molecule, and further that the processes of formation and decomposition are not spontaneously reversible.

A further characteristic action of the polythionates occurs on their spontaneous decomposition in water solution under the influence of heat. Although in none of them is the sulfur found in a state of oxidation corresponding to that of sulfates, yet all of them on spontaneous decomposition in water solution yield sulfates as one of the chief products, along with sulfur dioxide and in some cases sulfur. This phenomenon in which a polythionate breaks down into products representing both a higher and a lower state of oxidation of the sulfur than is found in the parent substance is alluded to in the present work as "autoxidation". Such in brief, in the opinion of the author, are one or two of the more salient aspects of the general subject of polythionates. Since the formation of one or more of the polythionates is a very frequent factor in actions involving sulfur dioxide and in view of the wide importance of sulfur dioxide, it was thought desirable on the part of this laboratory to attempt a series of studies of this very interesting and important family of compounds in the hope of amplifying present knowledge of the subject and perhaps ultimately formulating a rational theory of molecular structure. In pursuit of this aim the following studies have been completed.

The Action of Sulfurous Acid on the Sulfides of Iron, Zinc, and Manganese.

Henderson and Weiser. *Journal of the American Chemical Society*. 35, 239.

Preparation and Decomposition of Some Thiosulfates.

Henderson and Hummel. (In Preparation.)

Preparation and Decomposition of Tetrathionates.

Henderson and Scott. (In Preparation.)

The present work contemplates a study of "the dithionates along lines indicated in the title. It is hoped that other papers will be forthcoming.

II. A REVIEW OF THE LITERATURE PERTINENT TO THE FORMATION AND DECOMPOSITION OF DITHIONATES.

A survey of the literature shows that the preparation, analysis, crystallography, and determination of chemical and physical properties have been rather thoroughly though by no means exhaustively studied. Salts of nearly all the common and many of the rare metals have been prepared. Many double salts are known though, singularly, no acid salts have been observed. In the resume of the literature which follows, there are included, as being pertinent to the present work, only those citations which bear on the formation or decomposition of dithionates. An extensive bibliography covering the entire field of dithionates is to be found in the files of the Chemistry Department of Ohio State University. The reason for this exclusion is that the bibliography is large and much of it without significance in the present work. Reference works such as Gmelin-Kraut or Abegg's "Handbuch" or Hoffman's "Lexikon" contain rather complete records of papers published on dithionic acid and its various salts.

The partly accidental discovery of dithionic acid was recorded by Welter and Gay-Lussac¹ as occurring in the following manner. M. Welter, a manufacturer of bleach, in attempting to recover the manganese dioxide that had been used in making chlorine, treated the spent material with sulfur dioxide. As a result he obtained a "neutral bisulfite" which he believed "to be at the base of manganese dioxide." At this point Welter consulted Gay-Lussac, with the ultimate result that dithionic acid and the manganese, barium, calcium, strontium, and potassium salts were prepared and described. The mode of preparation, more fully discussed later, was by the passage of a stream of sulfur dioxide through a water suspension of manganese dioxide, whereby manganese dithionate, along with manganese sulfate, was formed. Barium dithionate was prepared by double decomposition between barium hydroxide and manganese dithionate. Dithionic acid was prepared by treating barium dithionate with an equivalent of sulfuric acid. After removal of the resulting barium sulfate by filtration, the remaining water solution of dithionic acid was concentrated by evaporation under reduced pressure to a density of 1.375. Attempts at further concentration resulted in the decomposition of dithionic acid into sulfuric acid and sulfur dioxide.

In 1826, Heeren⁸ published the results of a rather extensive work on dithionates. He found that high yields of manganese dithionate were promoted by the fineness of the manganese dioxide used in the suspension, the purity of the manganese dioxide used, and by the maintenance of a low temperature during the time in which the action occurred. Heeren prepared some twenty salts, giving much attention to crystalline structure. He observed that dithionic acid and many of its salts in water solution spontaneously decompose into sulfur dioxide and the corresponding sulfate.

Jacquelain⁹ learned that a water solution of sulfur dioxide in a tightly stoppered bottle after standing two years at room temperature contained sulfurous, sulfuric, and dithionic acids. Pean de Saint Gilles¹⁰ found that dithionates in small quantities were formed by the action of permanganate on sulfur dioxide, also that dithionates are not oxidized by permanganate. Hauer¹¹ prepared sodium dithionate by neutralizing a solution of sulfurous acid with sodium carbonate. After this the solution was heated with finely divided manganese dioxide. When the excess manganese dioxide had been removed, crystals of sodium dithionate were obtained by concentrating the solution. Gelis¹² first completely described the action of sulfur dioxide on ferric hydroxide as a general method for preparation of dithionates. This is one of the best methods for preparation on a laboratory scale. Rathke and Zschiesche¹³ prepared sodium dithionate according to the equation $2\text{Na}_2\text{SO}_3 + \text{Se} = \text{Na}_2\text{Se} + \text{Na}_2\text{S}_2\text{O}_6$. Sokolow and Multschewski¹⁴ show that under proper conditions the following action occurs. $2\text{NaHSO}_3 + \text{I}_2 = 2\text{NaI} + \text{H}_2\text{S}_2\text{O}_6$.

Kluss¹⁵ studied the salts of metals having more than one valence and of metals just above and below hydrogen in the electrochemical series. Except in the matter of the composition of the salts prepared he records no experimental data. As bearing on the present work it may be gathered from the work of Kluss that:

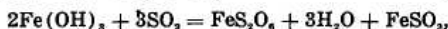
1. Heating solutions of dithionic salts, except those of the alkali and alkaline earth metals, causes spontaneous decomposition into sulfur dioxide and the corresponding sulfate.
2. The temperature at which decomposition begins varies in a general way with the position of the metal in the electrochemical series, *i. e.* the higher the position in the series the higher the temperature at which decomposition occurs.

3. Dithionates of the alkali and alkaline earth metals can be boiled in saturated solutions without decomposition.

4. Of metals having more than one valence, the "ous" salt decomposes as already outlined, while the "ic" salt decomposes with the formation of both "ous" and "ic" sulfates along with liberation of sulfur dioxide, and where possible a basic salt may be formed. The sequence of these actions is not to be deduced from the article.

Berthelot¹⁸ found that bromine water decomposes all the polythionates into sulfates. Antony and Lucchesi¹⁷ found that ruthenium dithionate is formed when sulfur dioxide is led through a solution of ruthenium sulfate. They say that the resulting ruthenium dithionate is decomposed by potassium permanganate into sulfate. No other workers have observed the decomposition of dithionates by this reagent. Nabl¹⁹ obtained barium dithionate in small quantity by treating barium sulfite with sulfur dioxide.

The careful work of Carpenter¹⁹ shows that cobaltic hydroxide as well as manganic and ferric hydroxides can be used with sulfur dioxide to form dithionates. He prepared ferrous dithionate in quantities as required by the equation



obtaining 96% of theoretical yield along with a small quantity of sulfate. With manganic hydroxide he obtained 75% and with cobaltic hydroxide 35% of theoretical yield as required by equations corresponding to the one just set forth for iron hydroxide. The sulfur not found in the dithionate was recovered as sulfate. No dithionate was obtained with a similar action between nickelic hydroxide and sulfur dioxide. Carpenter points out that the yields of dithionate with these metallic hydroxides varies directly as the heat absorbed in their reduction from the "ic" to "ous" hydroxide. For this reduction ferric hydroxide absorbs 546 calories, manganic hydroxide 448 calories, cobaltic hydroxide 225 calories, while nickelic hydroxide *gives off* 13 calories in this process.

Foerster and Friessner²⁰ and Friessner²¹ prepared sodium dithionate by the electrolysis of sodium sulfite. Baubigny²² describes the formation of dithionates by boiling silver sodium sulfite and the same author²³ prepared dithionate by the action of sodium sulfite on copper sulfate.

Numerous theories have been advanced during the past century seeking to explain the mechanics of the action of sulfur dioxide on manganese dioxide to form both dithionate and sulfate concurrently. Only a few of the more recent ones are mentioned. J. Meyer²⁵, from an investigation somewhat similar to that of Carpenter, formulated a theory that required that a molecule of sulfate be formed for each molecule of dithionate. Marino²⁶ demonstrated that the proportion of sulfate to dithionate varies with temperature, thus rendering the theory of J. Meyer untenable. Marino thinks the chief reaction is $\text{MnO}_2 + 2\text{SO}_2 = \text{MnS}_2\text{O}_8$, and that the sulfates always found are to be accounted for by the secondary action $\text{MnS}_2\text{O}_8 + \text{MnO}_2 = 2\text{MnSO}_4$. In Abegg's "Handbuch"²⁷, the chemical induction theory of Luther and Schilow²⁸ and Schilow²⁹ is applied to the action in question. The "chemical induction" theory supposes that two substances *A* (the actor) and *B* (the acceptor), which under ordinary conditions reacts very slowly, may be caused to react rapidly when a third substance *C* (the inductor), which reacts readily with *A*, is placed in the system along with *A* and *B*. That is, the actor *A* and the acceptor *B*, which ordinarily do not react, may be caused to react by the presence of the inductor *C*, which itself readily and simultaneously acts on *A*. Abegg points out that this theory fits the case of manganese dioxide and sulfur dioxide very nicely. "The actor is the oxidizing agent manganese dioxide, the inductor is sulfur dioxide, and the acceptor the manganese dithionate." The increasing amounts of manganese sulfate formed with rising temperature are explained by saying that heat accelerates the induced action. While the foregoing theory is in harmony with experimental facts, yet it seems to the author that a simpler explanation, which fits the facts equally well, may be formulated. Such an explanation will be attempted later when the experimental facts of the present work have been set forth.

III. SCOPE AND AIMS OF THE PRESENT WORK

The general aim of this work is to attempt a contribution to existing knowledge of polythionates, as a part of the general program of studies in this field being conducted in this laboratory. The specific aim is to study the formation and decomposition of the dithionates with the hope that such knowledge may lead to fuller understanding of their molecular structure and