

HYDROLYTIC REACTIONS OF ESTERS AND AMIDES OF THIOSULPHUROUS ACID IN A HOMOGENEOUS MEDIUM

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ABSTRACT

The hydrolytic reactions of esters and amides of thiosulphurous acid are investigated in a homogeneous medium. The esters are hydrolysed by alkali to give sulphide, sulphite and thiosulphate whereas the amides are resistant towards alkali. Both the esters and amides are hydrolysed by acids giving hydrogen sulphide, sulphur dioxide, polythionates and elemental sulphur. The hydrolysis of these esters and amides in presence of sulphurous acid and thiosulphuric acid gives tetrathionate and hexathionate, respectively.

THE formation of thiosulphurous acid has been postulated by the present authors during the alkaline hydrolysis of elemental sulphur in a homogeneous medium.¹ Further experimental support of the formation of thiosulphurous acid as a primary product has been obtained by studying the hydrolytic reactions, in homogeneous medium, of dimethyl thiosulphite, diethyl thiosulphite, tetraethyldithiodiamine and dithiopiperidine. The quantitative analytical results of the hydrolytic reactions of these compounds in alkaline and acid media as well as in the presence of sulphurous and thiosulphuric acids are described in the present communication.

EXPERIMENTAL

Reagents

Dimethyl and diethyl thiosulphites were prepared by reacting sodium methoxide and ethoxide, respectively, with disulphur dichloride.² These esters were purified by redistillation under reduced pressure. The boiling points and percentage purities (as determined by the total sulphur estimation by the Carius method) were as follows: Dimethyl thiosulphite, boiling point 39° C./18 mm., purity 99.21%. Diethyl thiosulphite, boiling point 64° C./16 mm., purity 98.91%.

Tetraethyldithiodiamine and dithiopiperidine were prepared by the method of Michaelis and Luxembourg³ employing the reaction between diethylamine and piperidine, respectively, with disulphur dichloride. The former was purified by redistillation under reduced pressure and the latter by recrystallisation from alcohol. Tetraethyl dithiodiamine, boiling point 110° C./12 mm., purity 99·38%: Dithiopiperidine, melting point 64° C., purity 99·65%.

These esters and amides were insoluble in water but soluble in benzene and carbon tetrachloride.

Aldehyde-free ethyl alcohol and pure dry benzene were prepared by standard methods.⁴ Sulphur-free carbon tetrachloride (Merck, extra pure) was dried and distilled over phosphorus pentoxide. Other chemicals used were of the AnalaR grade.

General Procedure

The hydrolytic reactions were carried out in a homogeneous medium as in the earlier studies.^{1, 10}

Five ml. of benzene or carbon tetrachloride were taken in a dry stoppered conical flask and a weighed amount of the ester or the amide was introduced and dissolved. Forty-five ml. of an aqueous solution of carbonate-free sodium hydroxide (or hydrochloric acid, sulphurous acid or thiosulphuric acid) were then added and the immiscible liquids were homogenized by the addition of 75 ml. of alcohol and the contents were thoroughly shaken.

The products of reaction were then analysed quantitatively by the analytical procedures of Kurtenacker and co-workers⁵ for a mixture of sulphide, sulphite, thiosulphate and polythionates, and of Goehring and co-workers⁶ for a mixture of polythionates. The total sulphur in solution was determined as barium sulphate after oxidation with bromine and nitric acid. The analytical results of alkaline and acid hydrolyses are presented in Tables I and II respectively. Tables III and IV present the analytical results of the hydrolytic reactions in presence of sulphurous and thiosulphuric acids, respectively.

RESULTS

Alkaline Hydrolysis

The products of hydrolysis of the esters by alkali in homogeneous medium were found to be sulphide, sulphite and thiosulphate. The hydrolysis was incomplete in $\frac{1}{2}$ hour at room temperature (25° C.) although 94% of the total sulphur could be accounted for in terms of the products. The

TABLE I
Alkaline hydrolysis of esters of thiosulphurous acid (over-all alkali normality = 0.50 N; Solvent: benzene)

Expt. No.	Substance	Amount of substance taken*	Temperature	Reaction time Hours	% Sulphide*	% Sulphite*	% Thio-sulphate*	Total % sulphur accounted*
1	S ₂ (OCH ₃) ₂	17.48	25°	½	23.63	19.73	50.58	93.9
2	do.	26.80	25°	24	25.90	24.05	47.10	97.1
3	do.	18.85	50°	½	23.44	21.16	52.19	96.8
4	S ₂ (OC ₂ H ₅) ₂	20.52	25°	24	30.84	21.78	46.05	98.7
5	do.	18.86	50°	½	25.58	27.54	45.24	98.4
6†	do.	18.21	50°	½	28.09	25.69	46.02	99.8
7‡	do.	23.34	50°	½	35.95	32.56	30.47	99.0

* Quantities of sulphur and sulphur compounds are all expressed in terms of gm. atoms of sulphur $\times 10^4$.

† The sulphide in this experiment was determined by oxidation with bromine and nitric acid and estimation as barium sulphate, instead of the iodometric estimation in the other experiments.

‡ A suspension of cadmium hydroxide was present at the commencement of the hydrolytic reaction in this experiment.

TABLE II
Acid hydrolysis of esters and amides of thiosulphurous acid (Solvent: benzene)

Expt. No.	Substance	Amount of substance taken*	Over-all acid strength	% Hydrogen sulphide*	% Sulphur dioxide*	% Penta-thionate*	% Tetra-thionate*	% Thio-sulphate*	% Elemental sulphur*
1	$S_2(OCH_3)_2$	37.74	0.20 N	18.24	16.90	28.76	..	1.35	34.75
2	do.	42.60	4 N	18.43	31.66	6.71	0.86	0.90	41.44
3	$S_2(OC_2H_5)_2$	21.92	0.20 N	16.14	14.41	25.09	..	2.91	41.45
4	do.	32.18	4 N	15.90	31.42	8.33	..	1.19	43.16
5	$S_2[N(C_2H_5)_2]_2$	15.69	0.20 N	12.48	13.69	23.58	0.66	3.25	46.34
6	do.	29.38	4 N	14.41	21.49	10.86	..	1.74	51.50
	$S_2(NC_5H_{10})_2$	16.62	0.20 N	11.40	11.32	24.57	1.84	3.07	47.80
8	do.	22.02	4 N	14.92	20.93	8.69	..	2.32	53.12

* Quantities of sulphur and sulphur compounds are all expressed in terms of gm. atoms of sulphur $\times 10^4$.

TABLE III
Reaction of esters and amides of thiosulphurous acid with sulphurous acid
 (Molar ratio of sulphurous acid/substance = 6)

Expt. No.	Substance	Amount of substance taken Moles $\times 10^4$	Solvent for substance	Tetra-thionate formed Moles $\times 10^4$	Tri-thionate formed Moles $\times 10^4$	Thio-sulphate formed Moles $\times 10^4$	Tetra-thionate formed (corrected) Moles 10×10^4	Tetra-thionate expected Moles $\times 10^4$	Tri-thionate expected Moles $\times 10^4$	Thio-sulphate expected Moles $\times 10^4$
1	$S_2(OCH_3)_2$	10.85	Carbon tetra-chloride	8.74	1.00	1.26	9.74	10.85
2	do.	10.70	Benzene	8.16	0.86	1.68	9.02	10.70
3	$S_2[N(C_2H_5)_2]_2$	11.73	do.	5.59	5.59	5.08	11.18	11.73
4	do.	11.87	do.	3.91	6.75	6.80	10.66	11.87
5	$S_2(OCH_3)_2$	14.34	Carbon tetra-chloride	..	13.66	14.00	14.34	14.34
6	$S_2(OC_2H_5)_2$	12.18	Benzene	..	11.75	12.19	12.18	12.18
7	$S_2[N(C_2H_5)_2]_2$	10.82	do.	..	10.85	11.03	10.82	10.82

Experiments 1-4 were carried out with 0.2 N HCl while for 5-7 the solution was neutral.

TABLE IV
 Reaction of esters and amides of thiosulphurous acid with thiosulphuric acid
 (over-all acidity = 0.7 N acetic acid)

Expt. No.	Substance	Amount of substance taken Moles $\times 10^4$	Molar ratio thio-sulphate substance	Solvent for substance	Hexa-thionate formed Moles $\times 10^4$	Penta-thionate formed Moles $\times 10^4$	Tetra-thionate formed Moles $\times 10^4$	Hexa-thionate formed (corrected) Moles $\times 10^4$	Hexa-thionate expected Moles $\times 10^4$
1	$S_2(OCH_3)_2$	6.21	8	Carbon tetrachloride	3.07	2.54	0.44	6.05	6.21
2	do.	7.04	2	do.	7.06	0.22	..	7.28	7.04
3	$S_2(OC_2H_5)_2$	11.29	2	Benzene	10.26	0.81	..	11.07	11.29
4	$S_2[N(C_2H_5)_2]_2$	7.83	2	do.	6.65	1.12	..	7.77	7.83
5	do.	10.87	2	do.	9.95	0.97	..	10.92	10.87

total sulphur content in terms of the products was found to be 98–99% when the hydrolytic reaction was allowed to take place over a period of 24 hours. However, the reaction could be hastened by carrying out the hydrolysis at 50° C. by immersing the reaction vessel in warm water. The percentage yields of sulphide and sulphite were nearly equal (each about 25%) and about 45–50% yield of thiosulphate was obtained. When the hydrolysis was carried out in presence of a suspension of cadmium hydroxide at the commencement itself, the sulphide and sulphite yields were increased to about 30–35% while the thiosulphate yield was decreased correspondingly.

The homogenized solution in alkaline hydrolysis was yellow, as with the alkaline hydrolysis of elemental sulphur in homogeneous medium¹ and has been attributed to the formation of a small amount of polysulphide. On the addition of cadmium hydroxide suspension to remove the sulphide from the reaction mixture, this polysulphide is decomposed into cadmium sulphide and sulphur.¹ The polysulphide sulphur will thus be unaccounted when the cadmium sulphide is estimated iodometrically. The fact that nearly 100% of the sulphur taken could be accounted for in the experiments where the cadmium sulphide precipitate is determined as barium sulphate after oxidation with bromine and nitric acid supports this view (Experiment No. 6 in Table I).

In contrast to the esters, the amides were found to be very resistant to alkali and could not be hydrolysed by alkali under the present experimental conditions.

Acid Hydrolysis

The hydrogen sulphide and sulphur dioxide produced by the acid hydrolysis of the esters and amides were rapidly swept off in a current of pure nitrogen and absorbed in sodium hydroxide solution containing cadmium hydroxide suspension; the sulphide and sulphite were then determined iodometrically.⁵

The main products of acid hydrolysis were pentathionate, sulphur dioxide, hydrogen sulphide and elemental sulphur. Increase in acidity led to higher yields of sulphur dioxide and lower yields of polythionates. In addition to these main products, traces of tetrathionate and thiosulphate were also produced.

Hydrolytic Reaction with Sulphurous Acid

It may be seen from Table III that both the esters and amides undergo hydrolysis and react with sulphurous acid (sodium sulphite in presence of acid)

to give almost quantitative yield of tetrathionate under optimum conditions (Experiments 1-4). Although only 2 moles of sulphurous acid per mole of ester (or amide) are theoretically needed, as explained later, it was found that the conversion to tetrathionate was not quantitative under these conditions. A sixfold molar concentration of sulphurous acid was hence employed. It has to be mentioned that there was some decomposition of the tetrathionate formed into trithionate and thiosulphate due to the sulphite degradation of tetrathionate, which takes place to a small extent in acid medium.



This was taken into account while calculating the corrected tetrathionate yields in Table III.

The sulphite degradation of higher polythionates into trithionate and thiosulphate is quantitative in a neutral or weakly alkaline medium, and therefore, it should be expected that, when the above reaction mixture is just neutralised by alkali to phenolphthalein endpoint and set aside for 10 minutes, all the tetrathionate would be degraded into trithionate and thiosulphate, by the sulphite present in excess, as per equation (1). This was found to be so and typical results of these experiments are included in Table III (Experiments 5-7). It will be noted that the trithionate and thiosulphate yields are almost quantitative.

Hydrolytic Reaction with Thiosulphuric Acid

When thiosulphuric acid is employed in place of sulphurous acid, the esters and amides undergo hydrolysis and react with thiosulphuric acid to give hexathionate (Table IV). It was found that the theoretically required amount, *viz.*, 2 moles of thiosulphuric acid per mole of ester (or amide), was quite adequate. It may be seen from Table IV that almost quantitative yields of hexathionate were obtained. There was slight decomposition of the hexathionate into pentathionate since the acidity employed was only 0.7 N acetic acid



For every mole of penta (or tetra) thionate similarly formed, one mole of hexathionate initially formed must have been decomposed. The corrected hexathionate yields in Table IV were calculated on this assumption.

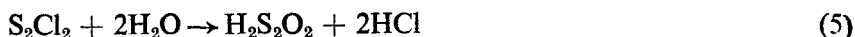
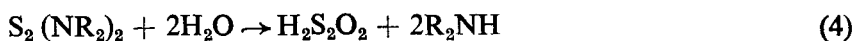
Alkaline and acid hydrolysis of these esters and amides have been quantitatively studied in detail in the present investigation. Meuwesen⁷ had observed that the reaction of potassium hydroxide in methyl alcohol with dimethyl

thiosulphite gave elemental sulphur and thiosulphate; he did not observe any sulphite or sulphide. Stamm and Wintzer⁸ observed the formation of polythionates during the acid hydrolysis of these esters; the quantitative analytical data were not reported. It is of interest to note that they observed that hydrogen sulphide was formed at the start of the reaction but they did not investigate this further. In their hydrolytic experiments, a petroleum ether solution of the esters was shaken with aqueous solutions of acids for long periods; it is therefore likely that any hydrogen sulphide initially formed might undergo secondary reactions. In the present investigation using a homogeneous medium, the reactions were carried out fast and the gaseous products could be rapidly swept off in a stream of nitrogen and analysed.

Two-phase hydrolytic studies, employing a petroleum ether solution of the esters or amides and aqueous solutions of sulphurous and thiosulphuric acids, were carried out by Goehring and Stamm,⁹ who observed the formation of tetrathionate with sulphurous acid and hexathionate with thiosulphuric acid. The present studies, where the technique was very much simplified by using a homogeneous medium, confirm the results of these earlier workers.

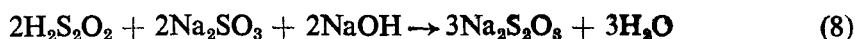
DISCUSSION

The results obtained in the present investigations show that the hydrolytic reactions of the esters and amides of thiosulphurous acid proceed in much the same way as those of disulphur dichloride.¹⁰ This is to be expected since thiosulphurous acid is the primary product in all these cases.



This highly reactive intermediate product, *viz.*, thiosulphurous acid [$S_2(OH)_2$] undergoes further secondary reactions in presence of alkali, acid, sulphurous acid and thiosulphuric acid.

It has been shown by B. S. Rao¹¹ that, in presence of alkali, thiosulphurous acid undergoes three simultaneous reactions.

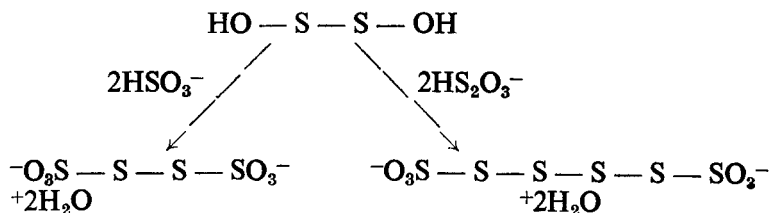


These three reactions explain the formation of sulphide, sulphite and thiosulphate during alkaline hydrolysis. In addition to these three reactions,

thiosulphate formation is facilitated by two other reactions which have been shown to take place readily in homogeneous medium, namely, the reaction of elemental sulphur with sulphite to form thiosulphate,¹² and the reaction of elemental sulphur with alkali to form mainly sulphide and thiosulphate.¹

During acid hydrolysis also, reaction (6) may be assumed to take place. However, the products, hydrogen sulphide and sulphur dioxide, are not fixed as salts in this case and are free to react with each other in the acid medium. The situation here is complicated and resembles the conditions for the formation of Wackenroder's solution. The formation of polythionates is thus only to be expected, and, just as in Wackenroder's solution, pentathionate is found to be the chief polythionate present. In the present homogeneous acid hydrolysis, a part of the hydrogen sulphide and sulphur dioxide could be expelled by rapidly bubbling nitrogen through the reaction mixture and could be estimated. This was possible due to the rapidity of hydrolysis in the homogeneous medium. Homogeneous acid hydrolysis thus gives direct evidence for the intermediate formation of thiosulphurous acid and its subsequent decomposition as per reaction (6).

Thiosulphurous acid is known to react with sulphurous acid to give tetrathionate and with thiosulphuric acid to give hexathionate. Polythionates have been shown to consist of unbranched chains of sulphur atoms,¹³ and hence, the formation of these polythionates may be represented schematically as:—



In conclusion, it may be mentioned that, although thiosulphurous acid itself has not so far been isolated either in the pure state or in solution, its anhydride, *viz.*, disulphur monoxide (S₂O) has been recently prepared in carbon tetrachloride solution.¹⁴ The technique of homogeneous hydrolysis is particularly convenient here since disulphur monoxide is a rather unstable compound and hydrolytic reactions have, of necessity, to be carried out rapidly.

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