here given show that at each temperature the yield of ether passes through a maximum as the time of contact is lengthened. The yield of ethylene, on the other hand, increases continuously. This is in agreement with the results of Pease and Yung[1] at 300°. The maximum yields of ether are, however, higher than those reported by Pease and Yung[1] and are as high as the best yields reported by Clark, Graham and Winters.[2] These maximum yields amount to 82.20% at 269°, 73.50% at 300° and 55.00% at 354°. Pease and Yung[1] report 62.00% at 275°; Clark, Graham and Winters[2] report 85.00% at 275°. The author obtained 82.20% at 269°. The indication is that the higher value is more nearly correct.

Summary

1. The dehydration of ethanol by alumina has been studied at 269, 300 and 354°, respectively, and the results are plotted.
2. Maxima in the ether yields have been obtained at 269, 300 and 354°.
3. The maximum yield of ether at 269 corresponds to 82.20%.
4. A reasonable explanation has been offered for the mechanism of the reactions taking place in the dehydration of ethanol by alumina at the temperatures studied.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORIES, UNIVERSITY OF THE PUNJAB]

ESTIMATION OF –SOOH (SULFINIC) GROUP AND FE^{+++}

BY S. KRISHNA AND HARNAM SINGH

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In a paper on the "Isolation of Sulphinic Acids," Thomas[1] has shown that sulfinic acids give a voluminous precipitate when treated with solutions of ferric salts in strongly acid solutions. These orange colored ferric salts on analysis are found to be of the general formula $(RSOO)_3Fe$, and are insoluble in water and in dilute mineral acids. They are, however, decomposed by alkalies, giving ferric hydroxide and salts of the corresponding sulfinic acids. Sulfinic acids, as a class, have thus been characterized by this property of yielding ferric sulfinates.

It was therefore found desirable to investigate the formation of such ferric salts on quantitative lines, and to employ this method for the estimation of –SOOH group in organic compounds. The importance of this is apparent when it is known that sulfinic acids, which are fairly strong acids, cannot be estimated by titration against standard alkalies when other negative groups (such as, COOH, SO_3H, etc.) are present in the molecule.

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[1] Thomas, *J. Chem. Soc.*, **95**, 342 (1909).

Experiments have shown that the formation of insoluble salts is confined to the sulfinic acid group alone; such other groups as mentioned above are not affected at all, though the compounds containing a carboxyl group give a buff colored precipitate with ferric chloride in neutral solutions, which, however, dissolves in dilute acids.

It has been found in the present work that the formation of ferric sulfinates is quantitative, and this suggested an interesting portion of the problem, the estimation of Fe^{+++} in soluble ferric salts. Another interesting fact which has been noticed is that the sulfinic acids form no such salts with Fe^{++} and this consequently gives us a method of separating Fe^{+++} from a mixture of Fe^{+++} and Fe^{++}. This process can also be employed for the quantitative estimation of Fe^{+++} and Fe^{++}, and thus simplifies the methods hitherto employed for their estimation in the presence of each other.

The formation of sulfinates has been studied with such metals as nickel and cobalt, which occur with iron in the periodic table, and chromium and aluminum, which are closely related to iron in qualitative analysis, and such sulfinates, if formed at all, are unstable under the conditions of the experiments. Therefore the method is applicable where it is desired to estimate or isolate Fe^{+++} in the presence of Ni, Co, Cu, Al, etc.

Experimental

Preparation of Standard Solutions

Ferric Chloride.—Ferric chloride solutions of the following eight concentrations were used in the experimental work: 1, 2, 3, 4, 5, 6, 9 and 15%. These were prepared by dissolving known amounts of ferric chloride in water for different concentrations and the amount of iron per liter was determined by the usual methods of reduction of ferric to ferrous and titration against a standard dichromate solution.

Sulfinic Acid Solutions.—These were prepared by dissolving known weights of sulfinic acid in boiling water. If the sulfinic acid is added to cold water and then warmed, it usually changes to an insoluble disulfoxide and disulfone:

$$\mathrm{RSOOH + HOSOR = RSO_2SOR + H_2O}$$
$$\mathrm{RSO_2SOR + O \longrightarrow RSO_2SO_2R}$$

Since the solubility of sulfinic acids is not great, only low concentrations were tried. An attempt was made to raise the concentrations by employing alcoholic solutions, but without success because the presence of alcohol interfered in the titrations against standard oxidizing agents. Therefore only about 1% solutions of the sulfinic acids have been used in these experiments.

Reducing Agents Employed.—Two reducing agents (stannous chloride in strong hydrochloric acid or zinc dust and sulfuric acid) have been used side by side for the reduction of ferric to ferrous, and both of these have been equally reliable for these experiments, the former being the more convenient.

Indicators Employed.—Two external indicators were employed in these experiments: a weak solution of potassium ferricyanide in the titration with potassium dichromate of ferrous chloride solution (to determine the complete oxidation of ferrous to ferric) and a dilute solution of potassium sulfocyanide in the titration of sulfinic acid solution and ferric chloride (to see whether or not the Fe^{+++} has been completely used up by sulfinic acid).

Sulfinic Acids.—These were prepared by the usual methods from the corresponding sulfonyl chlorides. As the literature on the subject does not give complete details for obtaining sulfinic acids in good yields, it is thought desirable to give an account of a typical reduction of the sulfonyl chloride to the corresponding sulfinic acid.

A mixture of 20 g. of the sulfonyl chloride, 50 g. of sodium sulfite ($Na_2SO_3 \cdot 9H_2O$) and 100 g. of crushed ice was shaken for three hours until the sulfonyl chloride had dissolved. The mixture was tested for alkalinity from time to time and dilute sodium hydroxide was added to prevent the formation of sulfur dioxide. The mixture was kept cold by further addition of ice, any undue increase of temperature being fatal to the success of the experiment on account of hydrolysis of the sulfonyl chloride. The mixture was filtered and acidified slowly with cold, concentrated hydrochloric acid, when sulfinic acids (usually crystalline) separated. The yield of sulfinic acid is in almost all cases about 80–90%. Recrystallized acids were dried thoroughly by keeping in a vacuum desiccator before using. These gave the usual test with phenetole and sulfinic acid (Smiles Test).

Estimation of –SOOH Group.—A known volume (10 cc.) of ferric chloride solution of a definite concentration was taken and acidified with dilute hydrochloric acid and to it was added a known volume (10 cc.) of the sulfinic acid solution. An orange colored precipitate of ferric sulfinate appeared. This was filtered, washed well with hot water and in the filtrate, which contained excess of ferric chloride, iron was determined by the method already mentioned. Knowing the amounts of iron in the ferric chloride solution before and after treatment with the sulfinic acid solutions, the strength of sulfinic acid was calculated according to the following equation

$$3RSOOH + FeCl_3 = (RSOO)_3Fe + 3HCl$$

In this way the experiments were performed with eight different concentrations of the ferric chloride solution, ranging between 2.01 g. and 28.95 g. of iron per liter. As the trend of error in all the eight experiments was similar, results obtained at extreme concentrations are recorded below.

TABLE I

RESULTS AT EXTREME CONCENTRATIONS

Weight of Sulfinic Acids = 0.1000 g.

Sulfinic acids	M. p., °C.	Method of preparation[a]	Wt. of Fe^{+++} = 0.0201 g. Wt. of acid found, g.	Error	Wt. of Fe^{+++} = 0.2895 g. Wt. of acid found, g.	Error
Benzene-	85	1	0.1001	+0.0001	0.0994	−0.0006
p-Toluene-	86–87	1	.1006	+ .0006	.1007	+ .0007
1,4-Dichlorobenzene-2-	180–182	2	.0999	− .0001	.1002	+ .0002
1-Chloro-4-nitrobenzene-2-	139	3	.1002	+ .0002	.0995	− .0005
m-Benzoic acid	197–198	1	.0995	− .0005	.1005	+ .0005
1,4-Dibromobenzene-2-	140		.1007	+ .0007	.1001	+ .0001
p-Chlorobenzene-	93–94	1	.0997	− .0003	.0999	− .0001
p-Anisyl-	97–98	1	.0998	− .0002	.0998	− .0002
p-Acetanilide-	160	2	.0999	− .0001	.1008	+ .0008
Salicylic acid-4-	159	2	.0999	− .0001	.0999	− .0001
m-Benzene-disulfinic	118–119	4	.0996	− .0004	.0994	− .0006
Cinnamic acid *p*-sulfinic	140–142	2	.1027	+ .0027	.1015	+ .0015

[a] Methods of preparation:

(1) Gattermann, *Ber.*, **32**, 1141 (1899); (2) Stewart, *J. Chem. Soc.*, **122**, 2557 (1922); (3) Krishna, *ibid.*, **123**, 157 (1923); (4) Autenrieth, *Ber.*, **36**, 189 (1903).

Estimation of Fe^{+++} in Ferric Chloride Solution by Means of Sulfinic Acids.—A known volume of ferric chloride solution was taken and titrated against a standard sulfinic acid solution in the presence of dilute hydrochloric acid (orange-yellow precipitate of ferric sulfinate settled down). A dilute solution of potassium sulfocyanide was used as an external indicator, the end-point being detected when a drop of the solution gave no red coloration with the sulfocyanide solution, the test being performed on a glazed tile. Knowing the volume of the sulfinic acid solution required for a given volume of ferric chloride solution, the amount of iron per liter can be calculated according to the equation given above. Similar results were obtained with all the sulfinic acids used in this work, and for the sake of brevity the results of only a few typical ones are recorded below. The error ranges from 0.0001 to 0.0004 g. of Fe^{+++}, with

TABLE II

TITRATION OF FERRIC CHLORIDE SOLUTIONS

Standard Sulfinic Acid Contained 10 g. of RSOOH per Liter

Fe^{+++} in 5 cc. of $FeCl_3$ soln., g.	0.0101	0.0202	0.0290	0.0402	0.0503	0.0606
Fe^{+++} found with benzene sulfinic acid, g.	0.0100	0.0201	0.0289	0.0401	0.0502	0.0605
Fe^{+++} found with *p*-toluene sulfinic acid, g.	0.0102	0.0203	0.0291	0.0404	0.0505	0.0609
Fe^{+++} found with *p*-dichlorosulfinic acid, g.	0.0102	0.0203	0.0292	0.0403	0.0504	0.0606
Fe^{+++} found with *p*-chloronitrobenzene sulfinic acid, g.	0.0106	0.0211	0.0306	0.0416	0.0500	0.0609

an abnormality of *p*-chloronitrobenzene sulfinic acid with 3% ferric chloride solution in which case the error is 0.0016 g.

Estimation of Fe^{++} in the Presence of Fe^{+++}.—A solution of ferrous chloride was prepared and the amount of iron per liter determined by titrating it against standard potassium dichromate solutions. Then a known volume of ferric chloride solution was added to a known volume of ferrous chloride solution. To this mixture excess of sulfinic acid solution was mixed so as to isolate ferric as orange-yellow ferric sulfinate. This was filtered, washed well and the filtrate titrated against standard potassium dichromate solution, and the amount of Fe^{++} thus determined was compared with the known ferrous chloride solution. The concentration of the ferrous chloride solution found agreed with the known value to within the accuracy of the measurement (about 0.1%) with all the sulfinic acids that were tried.

Estimation of Fe^{+++} in the Presence of Fe^{++}.—To a known volume of ferric chloride solution a definite volume of standard ferrous chloride solution was added. The mixture was then titrated against sulfinic acid solution of known strength, using potassium sulfocyanide as a side indicator. Results are tabulated below.

TABLE III

ESTIMATION OF FE^{+++} IN THE PRESENCE OF FE^{++}

RSOOH Contained 10 G. of RSOOH per Liter

Fe^{+++} in 5 cc. of $FeCl_3$ solution, g.	Titrated with benzene sulfinic acid, Fe^{+++} found, g.	Titrated with 1-chloro-4-nitrobenzene-2-sulfinic acid, Fe^{+++} found, g.
0.0101	0.0100	0.0106
.0202	.0201	.0211
.0290	.0289	.0299
.0402	.0401	.0404
.0503	.0502	.0500
.0606	.0605	.0609

The results obtained with other sulfinic acids were similar to those given here. The presence of Fe^{++} seems to have no influence on the quantitative precipitation of ferric sulfinates.

Estimation of Fe^{+++} in the Presence of Al, Cr, Ni and Co.—The solutions of the chlorides of these metals were used. The experiments were performed in exactly the same manner as given in the case of the estimations of Fe^{+++} in the presence of Fe^{++}. The results for Al alone are tabulated below since other results were exactly similar.

The results are in agreement with the theory. Again the presence of aluminum, chromium, nickel and cobalt have no effect on complete precipitation of ferric sulfinates.

Ferric Sulfinates.—Many of these sulfinates are not recorded in the literature and, therefore, warrant a short description here. The ferric

TABLE IV

RESULTS FOR ALUMINUM

RSOOH Contained 10 g. of RSOOH per Liter

Fe^{+++} in 5 cc. of $FeCl_3$ soln., g.	Titrated with *p*-toluene sulfinic acid, Fe^{+++} found, g.	Titrated with *p*-dichlorobenzene sulfinic acid, Fe^{+++} found, g.
0.0101	0.0102	0.0102
.0202	.0203	.0203
.0290	.0291	.0292
.0402	.0404	.0402
.0503	.0505	.0504
.0606	.0609	.0606

sulfinates prepared are found to be insoluble in all the usual organic solvents. The analysis was conducted by dissolving the ferric sulfinates in strong hydrochloric acid and precipitating ferric hydroxide from this by means of ammonia. The ferric hydroxide was ignited to Fe_2O_3 and from this the percentage of Fe was calculated as given in the table below.

TABLE V

ANALYTICAL DATA OF FERRIC SULFINATES

Ferric salt	Formula	Fe calcd., %	Fe found, %
Benzene sulfinate[1]	$C_{18}H_{15}O_6S_3Fe$	11.68	11.56
p-Toluene sulfinate[1]	$C_{21}H_{21}O_6S_3Fe$	10.74	10.94
p-Dichlorobenzene sulfinate	$C_{18}H_9Cl_6O_6S_3Fe$	8.16	8.24
Chloronitrobenzene sulfinate	$C_{18}H_9Cl_3N_3O_{12}S_3Fe$	7.83	7.93
m-Benzoic acid sulfinate	$C_{21}H_{15}O_{12}S_3Fe$	9.16	8.94
p-Dibromobenzene sulfinate	$C_{18}H_9Br_6O_6S_3Fe$	5.87	5.73
p-Chlorobenzene sulfinate	$C_{18}H_{12}Cl_3O_6S_3Fe$	9.61	9.48
p-Acetanilide sulfinate	$C_{24}H_{24}O_9N_3S_3Fe$	8.61	8.52
Salicylic acid sulfinate	$C_{21}H_{15}O_{15}S_3Fe$	8.49	8.40
m-Benzene disulfinate	$C_{18}H_{12}O_{12}S_6Fe_2$	15.46	15.78
p-Cinnamic acid sulfinate	$C_{27}H_{21}O_{12}S_3Fe$	8.13	8.01

Summary

Sulfinic acid (RSOOH) reacts with the ferric salt solutions to form orange-yellow ferric sulfinates of the general formula $(RSOO)_3Fe$.

The experiments have shown that the formation of such compounds is quantitative. Taking advantage of this property of the $-SOOH$ group, its method of estimation has been investigated on the lines mentioned in the experimental part.

The method employed gives satisfactory results and it is found that its application is possible even in the presence of other negative groups such as NO_2, OH and COOH in the molecule.

The method has been used in the isolation and estimation of ferric ions in the presence of ferrous ions and also in the presence of aluminum, chromium, nickel and cobalt, which share many of its properties with iron. This also simplifies the methods of estimation hitherto employed.

Different strengths of ferric chloride solutions seem to bring no difference in their behavior towards the sulfinic acid solutions.

LAHORE, INDIA

[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORIES, UNIVERSITY OF THE PUNJAB]

A QUICK METHOD FOR ESTIMATION OF HALOGENS IN CERTAIN ORGANIC COMPOUNDS

BY S. KRISHNA AND JOTI SWARUP

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Several methods are available for quantitative determination of halogens in organic compounds and these are employed when total halogen is to be estimated. But in compounds where two types of halogen atoms are present (as in chlorobenzene sulfonyl bromide) and the amount and proportion of each of these has to be determined some modification of the above methods has to be employed. When the two halogen atoms behave differently such quantitative determination becomes a comparatively easy matter. For example, in chlorobenzene sulfonyl bromide bromine is much more labile than chlorine and hence reacts differently with certain reagents. Based on this principle, Hirst and Macbeth[1] have developed a method of estimating labile halogen on reaction with hydrazine hydrate by measuring the volume of nitrogen evolved according to the equation

$$RSO_2NCl_2 + NH_2NH_2 \longrightarrow RSO_2NH_2 + N_2 + HCl$$

Sometimes an organic compound has to be prepared by a process that involves several stages of intermediate compounds and these intermediate compounds have to be analyzed in order to find their purity. The case in view is the preparation of chloronitrobenzene sulfinic acid ($Cl:NO_2:SO_2H$ 1:4:2) from the corresponding sulfonic acid by reduction of sulfonic chloride. The sulfonic chloride has to be analyzed every time it is prepared. The usual methods involve great length of time, and therefore need was felt for some rapid method of estimation of one of the elements in such compounds. The present communication describes a method of estimating quickly labile halogens in certain organic compounds.

Krishna and Das[2] have shown that Baumann and Kux's method[3] can be employed for the estimation of sulfinic group. It is assumed that sulfonic acids would also react in the same manner as sulfinic acids toward a mixture of potassium iodide and potassium iodate. Thus it becomes possible to estimate sulfonic chlorides, since these on hydrolysis give

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[1] Hirst and Macbeth, *J. Chem. Soc.*, **121**, 904 (1922).

[2] Krishna and Das, *J. Ind. C. S.*, **1927**, 367.

[3] Baumann and Kux, *Z. anal. Chem.*, **32**, 129 (1893).