STUDIES IN THE ORGANIC CHEMISTRY OF SULPHUR COMPOUNDS

THESIS

PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

by

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May 1934

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INTRODUCTION

The original problem was the investigation of the exchange reaction (vide (3)).

This thesis falls into three parts:-

(1) On Bisarylsulphonyl propanes.

(2) The Micro-estimation of Sulphur and Halogen in Organic Compounds.

(3) A Quantitative Investigation of the Exchange Reaction:-

$$RSO_2CH_2COCH_3 \xrightarrow{RSO_2SMe} RSO_2\underset{SMe}{CH}COCH_3 + RSO_2H$$

The sulphonyl propanes were investigated because more of them appeared toexist than could be accounted for on the usual theories of isomerism. It was thought that the anomaly might be explained on the basis of the mobility of the sulphonyl group. It is shown below that this is not the case. Their isomerism is to be traced to quite a different cause. (vide (1)).

Returning to the original problem of radical exchange it was evident that no quantitative idea of the exchange could be deduced from separating the products of the reaction as they were too similar in properties to be separated without serious loss. Accordingly it was decided to investigate the competition of two radicals containing such characteristic groups as could readily be estimated in the mixed final product. Thus if, in the above equation,

4-chlorophenylsulphonylacetone, ($ClC_6H_4SO_2CH_2COCH_3$) reacts with methyl p.toluenethiolsulphonate ($CH_3C_6H_4SO_2SMe$) the product will be either p.tolylsulphonylmethylthioacetone

$$CH_3C_6H_4SO_2\underset{SMe}{C}HCOCH_3$$

or 4-chlorophenylsulphonylmethylthioacetone

$$ClC_6H_4SO_2\underset{SMe}{C}HCOCH_3$$

or more probably a mixture of the two.

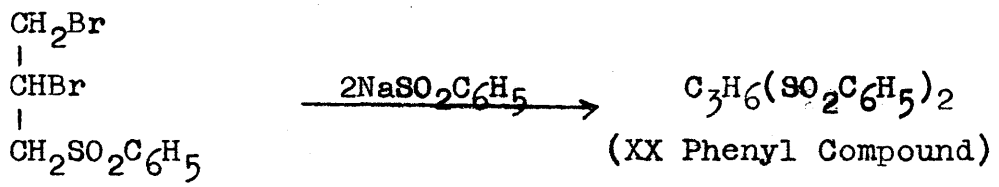
A reaction of the above type goes practically to completion so far as the substitution of the methylthio grouping is concerned and so it is evident that an estimation of the halogen content will indicate the percentage composition of the mixed product. Accordingly the development and detailed testing of a rapid and accurate micro method for the estimation of chlorine and sulphur had to be undertaken (vide (2)).

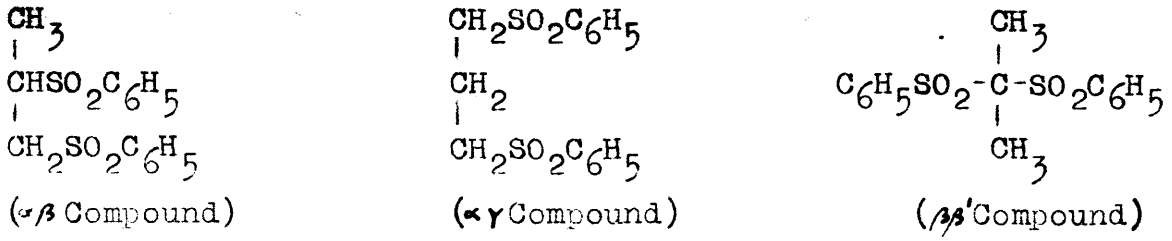
The application of this analytical procedure to the exchange reaction between 4-chlorophenylsulphonylacetone and methyl p.toluenethiolsulphonate has been worked out in detail (vide (3)).

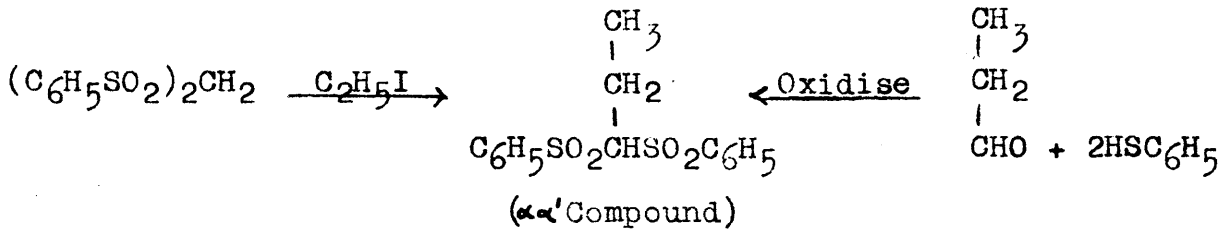
ON BISARYLSULPHONYLPROPANES

THEORETICAL

In attempting to prepare αβγ trisphenylsulphonyl propane from sodium benzene sulphinate and phenyl dibromopropyl sulphone, Otto (1) isolated a bisphenyl compound, m.p. 101°. That is :-







For the purpose of reference this compound is designated the "XX phenyl compound". As it was distinct from the known αβ and αγ bisphenylsulphonyl propanes, Otto tentatively suggested (2) that it might be a stereo-isomeric αβ form. He discovered a corresponding p-tolyl derivative also (XX tolyl) and Troeger and Artmann (3) who isolated a third "Bis-naphthylsulphonylpropane" (XX naphthyl) accepted his explan-

ation. As, however the mobility of the sulphonyl group (4) introduced new factors, the XX compounds were re-examined.

The first striking point was that Otto had only considered two structural possibilities for bisphenylsulphonylpropane : $\alpha\beta$ and $\alpha\gamma$: whereas, in fact there were four. The others are:-

$\beta\beta'$ bisphenylsulphonyl propane which was prepared by Shriner Struck and Jorison (5) and had a m.p. 181-182°

and

$\alpha\alpha'$ bisphenylsulphonyl propane, hitherto unknown which was prepared (a) by condensation of formaldehyde and phenyl mercaptan followed by oxidation and then ethylation and (b) by condensation of propionaldehyde and phenyl mercaptan (6) and subsequent oxidation. It was found that the compound had a m.p. 97-98° but it gave a distinct depression of melting point when mixed with the "XX phenyl compound".

The possibility that the compound was $\alpha\alpha'$ bisphenylsulphonyl ethane was then considered. This substance had a melting point of 101°. When mixed with the "XX phenyl compound" the melting point was distinctly depressed.

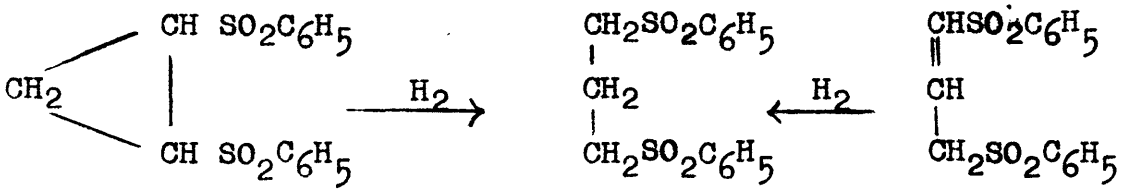
$$\begin{array}{l} CH_3 \\ | \\ CH\ (SO_2C_6H_5)_2 \end{array}$$

The next possibility to be considered was that the molecular weight of some one of these compounds was not simple, but direct determination showed this was not correct.

Now Stuffer showed (7) that while $\alpha\beta$ disulphones are readily hydrolysed $\alpha\gamma$ and $\alpha\alpha'$ are not. As the "XX phenyl com-

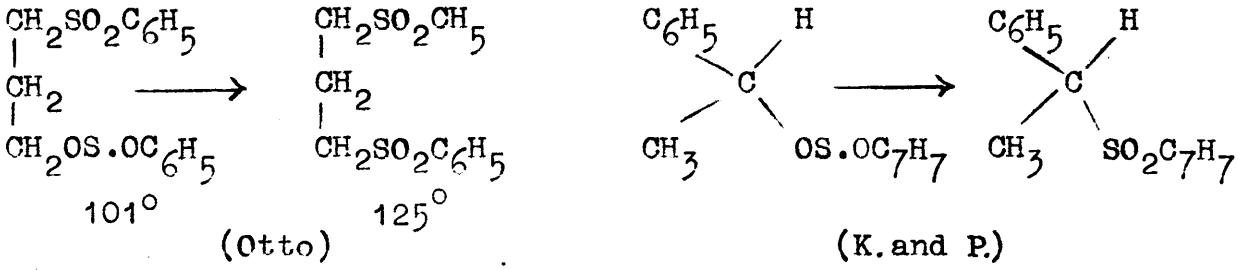
pound" was readily attacked by alkali this suggested that it might be a difficultly separable mixture of $\alpha\beta$ bisphenylsulphonylpropane with one or more other sulphones, but this suggestion must also be rejected for the "XX phenyl compound" was distinctly less volatile in a vacuum than $\alpha\beta$ bisphenylsulphonylpropane and was the only one of all these phenyl derivatives to be oxidised by cold permanganate. Moreover, an artificial mixture of the $\alpha\beta$ and $\alpha\gamma$ compounds was readily separated by crystallisation.

Meanwhile the melting point of a stoppered specimen of the "XX phenyl compound" was found to have risen from 101° to 123°, and was not depressed by admixture with the $\alpha\gamma$ disulphone. Such a change is by no means unknown in sulphur chemistry, examples being given in the work of Kenyon and Phillips (8), Fromm and Palma (9), and Hilditch (10). This observation incidentally eliminated any possibility of unsaturated or cyclo-propane sulphones because in comparison to bisulphonyl propanes, they are two hydrogen atoms short and whatever change occurred in the stoppered bottle absorption of hydrogen necessary to form the $\alpha\gamma$ bisphenylsulphonyl propane from the cyclo-propane sulphone can certainly be excluded.

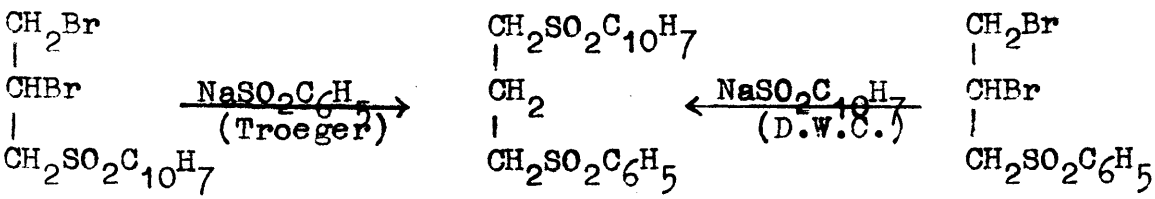


This melting point change phenomenon recalled that observed by Kenyon and Phillips of the spontaneous change of phenyl-

methylcarbinyl p-toluene sulphinate into the corresponding p-tolylsulphone, and supported the idea that Otto's compound is:-

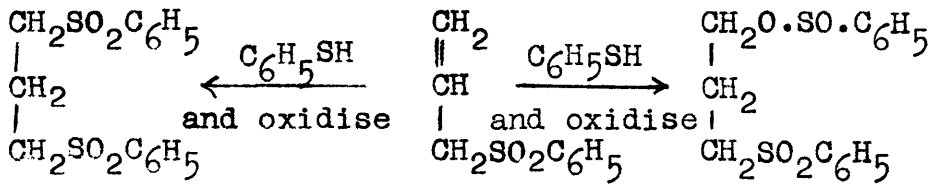


This was confirmed by an extension of Troeger's work. By the action of sodium benzene-sulphinate on α(β naphthylsulphonyl)βγ dibromopropane he obtained what he regarded as α(β naphthylsulphonyl)β phenylsulphonyl-propane, but as a compound, which had the same melting point (123°), and which gave no depression on mixing with Troeger's compound, was prepared from sodium β -naphthalene sulphinate and α phenylsulphonyl- βγ dibromopropane, there seems no doubt that the substituents must be in the terminal positions:-

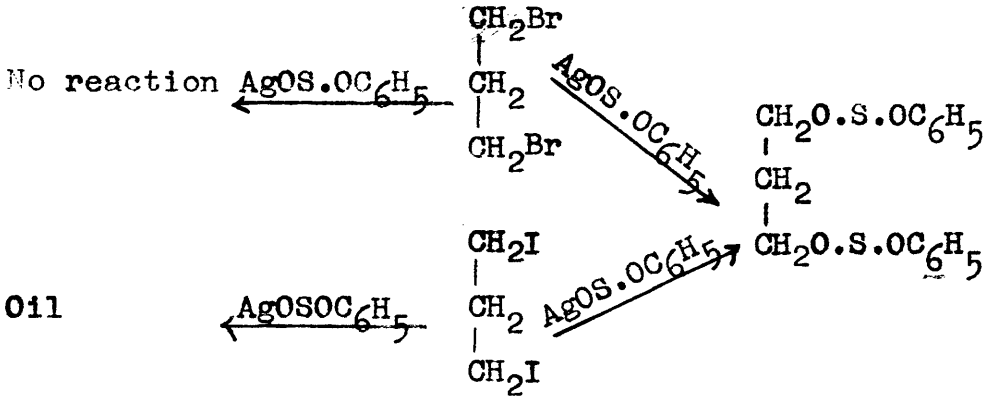


Attempts to prepare the "XX phenyl compound and the analogous p.tolyl and β naphthyl compounds in other ways gave entirely negative results. The following paragraphs indicate the various attempts and the actual products isolated. Those formulae printed in red show the reaction anticipated while those in blue show what was actually obtained.

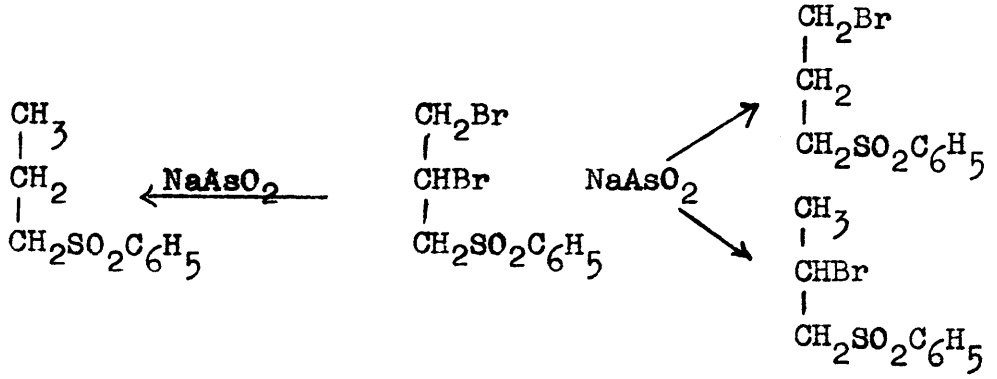
(1) The addition of mercaptan to an unsaturated compound (c.f. Posner (11): Ruhemann (12)). Allyl phenyl sulphone reacted directly with phenyl mercaptan to give on oxidation $\alpha\gamma$ bisphenylsulphonyl propane.



(2) Silver benzene sulphinate (instead of sodium benzene sulphinate) gave :-



It would have been interesting to have treated α bromo γ phenylsulphonyl propane with silver benzene sulphinate but attempts to prepare the former compound by reduction of the α phenylsulphonyl $\beta\gamma$ dibromo propane were unsatisfactory:-



(3) The addition of benzene sulphinyl chloride to trimethylene glycol :-

Compound M.P. 47° $\xleftarrow{C_6H_5SOCl}$ $CH_2OH.CH_2.CH_2OH$ $\xrightarrow{C_6H_5SOCl}$ $CH_2OSOC_6H_5.CH_2.CH_2OSOC_6H_5$

(4) The addition of benzene sulphinyl chloride to hydroxypropyl phenyl sulphone :-

$C_6H_5S.SC_6H_5$ $\xleftarrow{C_6H_5SOCl}$ $CH_2OH.CH_2.CH_2SO_2C_6H_5$ $\xrightarrow{C_6H_5SOCl}$ $CH_2OSOC_6H_5.CH_2.CH_2SO_2C_6H_5$

(5) The addition of benzene sulphonyl chloride to hydroxypropyl phenyl sulphone :-

Oil $\xleftarrow{C_6H_5SO_2Cl}$ $CH_2OH.CH_2.CH_2SO_2C_6H_5$ $\xrightarrow{C_6H_5SO_2Cl}$ $CH_2OSO_2C_6H_5.CH_2.CH_2SO_2C_6H_5$

(6) The addition of p.toluene sulphinic acid to allyl p.tolyl sulphone:-

$C_7H_7SO_2SC_7H_7$ $\xleftarrow{C_7H_7SO_2H}$ $CH_2{=}CH.CH_2SO_2C_7H_7$ $\xrightarrow{C_7H_7SO_2H}$ $CH_2OSOC_7H_7.CH_2.CH_2SO_2C_7H_7$

(7) Methyl β naphthyl sulphinate (MeO.SO.N) and trimethylene glycol:-

No reaction $\xleftarrow{\text{Ord. temp.}}$

$C_{10}H_7SO_2SC_{10}H_7$ $\xleftarrow{100^\circ C.}$

$CH_2OH.CH_2.CH_2OH$ $\xrightarrow{CH_3O.SOC_{10}H_7}$ $CH_2OSOC_{10}H_7.CH_2.CH_2OSOC_{10}H_7$

The p.tolyl and naphthyl "XX compounds" were more resistant to conversion into the corresponding trimethylene derivatives than the "XX phenyl compound." Pure "XX phenyl compound" was heated to 200° without conversion but the slighest trace of $\alpha\gamma$ bisphenyl-sulphonyl propane caused rapid conversion of the mass at 120°. All these compounds including the "(β naphthylsulphonyl) phenyl-sulphonylpropane" type were easily hydrolysed and oxidised with acid permanganate. Of the four normal types only the $\alpha\beta$ was hydrolysed and they were all unaffected by such oxidation conditions. This is in agreement with the statements of Otto and Damkohler (13) and Stuffer (see above).

Neither the compounds of the XX type nor any of the normal type gave a blue colouration on warming with anisole and sulphuric acid or a yellow colour with chloroform and tetra nitro methane. It would appear from this that a sulphinic grouping was not present but such negative tests could not be regarded as absolute. Furthermore the action of the solvent may have caused a temporary change in structure of the molecules of the XX compound.

MICRODETERMINATION OF SULPHUR AND HALOGEN IN ORGANIC COMPOUNDS

GENERAL

Two standard methods have been developed by Pregl for the microdetermination of sulphur and halogen in organic compounds. Substances containing carbon, hydrogen, and sulphur only, may be burned in a tube in a stream of oxygen. The acid vapours are collected in water and directly titrated against standard caustic soda. Compounds containing halogen are similarly combusted but the resultant vapours are collected in strongly alkaline sodium bisulphite solution. The halogen is extracted in the form of its silver salt, collected and weighed on a micro balance.

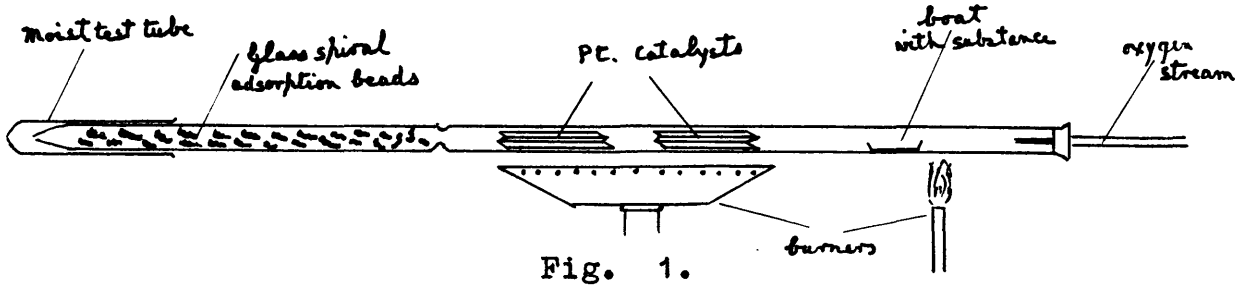


Fig. 1.

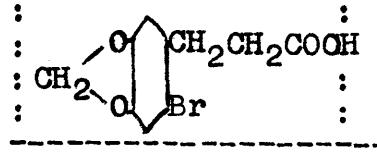
Figure 1 represents the Pregl apparatus. Since no Micro Balance was available for the work described below an assay balance capable of taking a maximum load of 2 gms and weighing to .01 mg. was used. It was therefore impossible to weigh precipitates and experiments were made with a view to a modifying Pregl's method for halogen so that the halide could be determined volumetrically.

These experiments are recorded in pages 34-37 and the results are summarised in the following table. The amount of material required is 5-7 mg and the time for combustion, 45 minutes. A complete estimation takes 1¼ hours.

TABLE I

(Halogen only)

Substance	Weight used	N/50 $AgNO_3$ titration	Percentage Halogen	
	m.gms.	c.c.	Found	Requires
$ClC_6H_4SO_2CH_2COCH_3$	5.11	1.09	15.1	15.3
	6.02	1.28	15.1	
	6.46	1.30	14.3	
$ClC_6H_4SO_2SC_6H_4Cl$	5.84	1.84	22.4	22.3
$(ClC_6H_4)_2SO_2$	4.91	1.69	24.5	24.7
	5.59	1.92	24.6	
$ClC_6H_4SO_2CH_2(SMe)$	6.18	1.30	14.9	15.0
o-ClC_6H_4CHNOH	5.85	1.89	23.0	22.8
p ClC_6H_4Cl	6.28	4.23	47.8	48.3
	4.73	3.22	48.3	
p BrC_6H_4CHNOH	6.22	1.56	40.2	40.0
$ClC_6H_4SSC_6H_4Cl$	4.35	1.51	24.6	24.7
	6.05	2.15	25.3	

Substance	Weight used	N/50 $AgNO_3$ titration	Percentage Halogen. Found	Requires
$Cl_2C_6H_3SO_2SC_6H_3Cl_2$	3.74	1.92	36.5	36.4
	6.17	3.15	36.2	
	7.97	1.43	28.7	29.3
	6.46	1.20	29.7	

This method of halogen estimation, while in itself satisfactory, was not adequate for the purpose of analysing the exchange reaction (see p. 19). A process which could also give the total acidity (that is, sulphur plus halogen) would be advantageous because it would to some extent check that one was dealing with a pure product of the type $R.SO_2\underset{SMe}{CH}\ COCH_3$ and not with a product contaminated with such substances as the starting materials ($RSO_2CH_2COCH_3$ and RSO_2SMe) which have considerably different sulphur values.

It is evident that any process which uses a relatively large quantity of sulphur in the absorbing medium cannot be extended to the estimation of sulphur in the products of combustion. On the other hand some reducing agent is necessary to ensure that all the halogen is in the form of halide before it is estimated by silver nitrate titration (Volhard(50)).

In the first experiments the total acidity(H_2SO_3, H_2SO_4, HCl, HClO) was estimated by collection of the gases in water and subsequently titrating with standard sodium carbonate solution. The neutralised liquid was then titrated with silver nitrate. It was hoped that the amount of sulphur -ous acid formed would serve to reduce the traces of hypo-chlorous acid and so give a correct halide determination. This was absolutely unsatisfactory.

Further experiments were made in which the gases were trapped in pure water as above and the total acidity determin -ed by titration. The neutralised liquid was then reduced with alkaline bisulphite and titrated with silver nitrate.

This was also shown to be unreliable even in complete absence of chlorine. In the procedure recommended (p.43) the gases were collected in excess standard sodium carbonate solution and the total acidity determined by back titration. with sulphuric acid. Any hypochlorite was reduced by the addition of hydrogen peroxide before titration (14).

$$Cl_2 + H_2O \longrightarrow HClO + H' + Cl'$$
$$HClO + H_2O_2 \longrightarrow H' + Cl' + H_2O + O_2$$
$$2ClO_2 + H_2O_2 \longrightarrow 2HClO_2 + O_2$$
$$HClO_2 + 2H_2O_2 \longrightarrow H' + Cl' + 2H_2O + 2O_2$$

The halide was determined by titration with N/71 silver nitrate solution according to the method of Volhard. Sulphur was thus obtained by difference.

4-7 mg of the substance were required and the analysis was completed in four hours. The average of 34 unselected

analyses (shown below) gave an error of 1 % for sulphur and 1 % for chlorine, the percentage error being calculated from the found value relative to the required value. The errors were random, being both positive and negative.

Analyses of bromine compounds gave similarly accurate results without any alteration to the factor of the standard silver nitrate solution.

TABLE II

SULPHUR AND CHLORINE

Substance	Weight used	N/71 $AgNO_3$ titration	N/50 Na_2CO_3 titration	% Chlorine		% Sulphur	
	m.gms.	c.c.	c.c.	Found	Requires	Found	Requires
Ethyl chlorocamphor-10-sulphonate	7.91	1.91	3.95	12.1	12.1	10.6	10.9
	7.09	1.70	3.54	12.0		10.6	
$Cl_2C_6H_3SO_2SC_6H_3Cl_2$	4.18	3.04	4.24	36.4	36.6	16.1	16.5
	4.19	3.06	4.26	36.5		16.1	
$ClC_6H_4SO_2SC_6H_4Cl$	7.53	3.26	6.91	21.7	22.3	19.6	20.1
	5.29	2.35	4.97	22.2		20.0	
	5.16	2.29	4.82	22.2		19.9	
$ClC_6H_4SO_2CH_2COCH_3$	6.65	2.05	4.29	15.4	15.3	13.7	13.8
	6.63	2.03	4.29	15.3		13.8	
$(ClC_6H_4)_2SO_2$	6.85	3.32	4.74	24.2	24.7	11.2	11.2
	4.23	2.09	2.91	24.7		10.9	

Substance	Weight used	$\frac{N}{71}$ $AgNO_3$ titration	$\frac{N}{50}$ Na_2CO_3 titration	% Chlorine		% Sulphur	
	m.gms.	c.c.	c.c.	Found	Requires	Found	Requires
* $(C_2H_5SO_2)_2CCl_2$	6.47	3.09	7.03	23.9	26.4	24.0	23.8
$ClC_6H_4SO_2CH_2COCH_3$	6.59	2.02	4.22	15.3	15.3	13.6	13.8
$(ClC_6H_4)_2SO_2$	6.45	3.19	4.47	24.7	24.7	11.0	11.2
$(C_2H_5SO_2)_2CCl_2$	7.21	3.84	8.08	26.6	26.4	23.9	23.8
	6.04	3.20	6.80	26.5		24.1	
$ClC_6H_4SO_2CH_3$	5.38	2.04	4.28	19.0	18.6	16.9	16.8
$ClC_6H_4SO_2CH_2COCH_3$	7.83	2.35	5.05	15.0	15.3	13.9	13.8
	6.99	2.10	4.49	15.0		13.8	
$Cl_2C_6H_3S.SC_6H_3Cl_2$	6.68	5.29	7.48	39.6	39.9	18.0	18.0
	7.04	5.58	7.84	39.6		17.8	
$(ClC_6H_4)_2SO_2$	5.69	2.83	4.02	24.9	24.7	11.4	11.2
	6.12	3.05	4.31	24.9		11.3	

* Compound subsequently found to be impure

Substance	Weight used	$\frac{N}{71}$ $AgNO_3$ titration	$\frac{N}{50}$ Na_2CO_3 titration	% Chlorine		% Sulphur	
	m.gms.	c.c	c.c.	Found	Requires	Found	Requires
$ClC_6H_4SO_2CH_3$	5.29	2.01	4.23	19.0	18.6	17.0	16.8
	7.10	2.68	5.67	18.9		17.0	
$(C_2H_5SO_2)_2CCl$	6.80	1.32	6.38	9.7	9.5	25.6	25.6
$(C_6H_5SO_2)$	6.45	1.23	6.02	9.5		25.6	
$CH_3C_6H_4SO_2Cl$	6.96	2.59	5.55	18.6	18.6	17.1	16.8
	7.15	2.69	5.70	18.8		17.1	
$Cl_2C_6H_3SO_2Cl$	5.77	5.00	5.90	43.3	43.4	13.2	13.0
	5.56	4.86	5.70	43.7		13.1	
$CH_3C_6H_3(OCH_3)SO_2Cl$	5.90	1.91	3.99	16.2	16.1	14.3	14.5
	7.21	2.34	4.95	16.2		14.6	
$C_{10}H_7SO_2Cl$	6.83	2.19	4.54	16.0	15.7	14.1	14.1
	6.99	2.22	4.62	15.9		14.0	

TABLE III

SULPHUR AND BROMINE

Substance	Weight used	$\frac{N}{71}$ $AgNO_3$ titration	$\frac{N}{50}$ Na_2CO_3 titration	% Bromine		% Sulphur	
	m.gms.	c.c.	c.c.	Found	Requires	Found	Requires
Methyl Bromo Camphor-10-sulphonate	6.59	1.44	3.03	24.6	24.6	9.8	9.8
	7.12	1.52	3.20	24.1		9.6	
$p.BrC_6H_4SO_2CH_3$	5.60	1.69	3.61	34.0	34.0	13.8	13.6
	6.54	1.94	4.09	33.5		13.3	

A QUANTITATIVE INVESTIGATION OF THE EXCHANGE REACTION

THEORETICAL.

It was originally observed by Gibson (4) that phenylsulphonylacetone (P) amd methyl p.toluenethiolsulphonate (T)yield a mixture of phenylsulphonyl-methylthioacetone and p.tolyl sulphonyl-methylthioacetone.

$$C_6H_5SO_2.CH_2COCH_3 + CH_3C_6H_4SO_2SMe \longrightarrow \begin{matrix} C_6H_5SO_2.\underset{SMe}{C}HCOCH_3 \\ \text{and} \\ CH_3C_6H_4SO_2.\underset{SMe}{C}HCOCH_3 \end{matrix}$$

(P) (T)

It was further noted that if P were in considerable excess the reaction product was substantially phenylsulphonyl-methyl thioacetone: on the other hand if T was in excess, the reaction product was substantially p.tolylsulphonyl-methylthioacetone.

The other product of the reaction was a mixture of benzene sulphinic acid and p.toluene sulphinic acid.

Now it was immediately evident that for any quantitative study, the properties of the phenyl derivatives were much too similar to those of the corresponding p.tolyl derivatives to permit any deduction of their relative proportions in a mixture of the two.

Accordingly other radicals were chosen

(a) p. tolyl, and

4-methoxytolyl-3-

Preliminary experiments showed that 4-methoxytolyl-3-sul-

phonamide could be separated from p. tolyl sulphonamide by fractional crystallisation. The intention was to convert the mixed sulphinic acids to sulphonamides and undertake a quantitative separation of these two derivatives.

Accordingly the reaction p.tolylsulphonylacetone with excess methyl 4-methoxytoluene-3-thiolsulphonate was examined and also the reaction of 4-methoxytolyl-3-sulphonylacetone with excess methyl p.toluene thiolsulphonate. In each case the resulting substituted product ($RSO_2CH(SMe)COCH_3$) corresponded with the radical which had been in excess.

It was to be expected that if either reaction were carried out with equimolecular proportions, a mixture of p.tolyl sulphinic acid and 4-methoxytolyl-3-sulphinic acid would be produced.

This, however, was never tested as more promise was offered by development of the reaction:-

(b) 4-chlorophenylsulphonylacetone, and
methyl p-toluenethiolsulphonate.

The idea with these latter compounds was to allow equimolecular proportions of p-chlorophenylsulphonylacetone and methyl p.toluenethiolsulphonate to react under the mildest conditions and investigate the percentage of sulphur and halogen in the reaction product.

$$ClC_6H_4SO_2CH_2COCH_3 + CH_3C_6H_4SO_2SCH_3 \longrightarrow \begin{matrix} ClC_6H_4SO_2\underset{SMe}{C}HCOCH_3 \quad \text{I} \\ (S = 27.1\% \quad Cl = 15.0\%) \\ \text{and} \\ CH_3C_6H_4SO_2\underset{SMe}{C}HCOCH_3 \quad \text{II} \\ (S = 29.6\% \quad Cl = 0\%) \end{matrix}$$

It is to be noted that the percentage of sulphur is much too similar to serve as more than a control.

The percentage of chlorine, on the other hand, gives a measure of the proportions of I and II in the mixture --- that is to say, of the relative success with which the p.tolylsulphonyl radical has competed with 4-chlorophenylsulphonyl. The results of these analyses indicate that with equimolecular proportions of 4-chlorophenylsulphonylacetone and methyl p.toluene thiolsulphonate equimolecular proportions of the substitution products I and II are formed.

Finally there are a number of experiments recorded in which evidence for exchange was sought.

$$RSO_2Na + RSO_2.\underset{SMe}{CH}COCH_3 \longrightarrow RSO_2\underset{SMe}{CH}COCH_3 \qquad III$$

Only in one case was any product or derivative of III encountered.

EXPERIMENTAL.

Methylene diphenyl disulphide $(C_6H_5S)_2CH_2$

Prepared by condensation of phenyl mercaptan and formaldehyde (Baumann (15)) in the presence of hydrochloric acid and zinc chloride. M.Pt. = 38°C. Yield 85%.

Oxidation of methylene diphenyl disulphide.

Otto & Troger (16) used chromic anhydride and glacial acetic for the oxidation and Baumann (17) used a 1% permanganate solution but in both instances the yield was very poor. An attempt was made to modify the method as follows:-

(1) To 2.5 per cent permanganate solution the equivalent quantity of sulphuric acid was added (3.5 cc per 1000 cc of solution). This was diluted with an equivalent volume of water and added to the methylene diphenyl disulphide in a winchester. It was found that the disulphide would absorb, at ordinary temperature, much more than theoretical permanganate so slight excess was added and the reaction stopped. A little sulphur dioxide was passed into the hot solution to clear the finer particles of manganese dioxide and the solution filtered at the pump. Yield-very poor.

(2) Oxidation was carried out in ice cold solution with permanganate as in experiment (1) but the yield was not any better.

(3) A small amount of methylene diphenyl disulphide was dissolved in acetic acid and a little acetic anhydride added. A 30% solution of hydrogen peroxide was added in slight excess.The

mixture was left standing for several days and then warmed for some hours. Poor results.

(4) 1.2 gm of methylene diphenyl disulphide was dissolved in glacial acetic acid and a large excess (10 gms) of H_2O_2 added. The solution was kept at 40° for 6 hours. It was then warmed to 65°, cooled, and the acetic acid etc. distilled off in vacuo.

Recrystallised from water. Yield theoretical. M.Pt = 120°. (Recorded by Otto (above) as 118°).

<u>$\alpha\alpha'$ Bisphenylsulphonyl propane</u>.

This was prepared by the monoethylation of methylene diphenyl disulphone on the same principle as the methylation by Shriner, Struck and Jorison (5) save that it was necessary to reflux longer (4 hours). Yield = 40% M.Pt. = 97°C. Failed to diethylate any appreciable quantity by this method.

Also prepared by condensation of phenyl mercaptan and propionaldehyde (Mol. Wt. Found = 247.5 Calc = 260), and subsequent oxidation with hydrogen peroxide. Five times theoretical hydrogen peroxide was used, and, owing to the difficulty of keeping the solution to small bulk with pure acetic acid, a little acetic anhydride was added. Yield (from alcohol) = 80 -90% M.Pt = 97½°. Mixed with the ethylation product above, gave no depression of melting point. Mol. Wt. Found = 325. Calc = 324.

<u>Attempted hydrolysis of $\alpha\alpha'$ bisphenylsulphonyl propane.</u>

Heated at 100° for 10 days with slight excess of strong caustic soda the whole of this compound was recovered unchanged.

Sodium benzene sulphinate

Prepared by reduction of benzene sulphonyl chloride with alkaline sulphite, it was purified by recrystallisation from alcohol.

Otto's "XX phenyl Compound". *

Prepared according to Otto (1), the final stage of the synthesis resulted in rather a poor yield, the following modifications were attempted.

(1) Magnesium carbonate was used instead of caustic soda and a slight excess of the carbonate was always allowed to remain. This prevented the solution becoming acid but at the same time introduced no appreciable alkalinity. This method was unsuccessful.

(2)Dibromo propyl phenyl sulphone was dissolved in alcohol and the appropriate quantities of sulphinate and caustic soda were mixed and added simultaneously over the space of three days. This gave a yield = 35% of the compound M.Pt = 101°C. and also a 12% yield of the trisphenylsulphonyl propane.

Hydrolysis of "XX phenyl Compound".

By heating at 100°C with slight excess of aqueous sodium hydroxide for 2 days decomposition was obtained. The portion insoluble in sodium hydroxide was extracted with ether and this extract was recrystallised from alcohol. The substance so obtained was only slightly soluble in ether, very soluble in alcohol and M.Pt = 160 - 170°C.

Oxidation of "XX phenyl Compound".

This compound was readily oxidised in sulphuric acid

solution by $\frac{N}{20}$ permanganate.

αβ Bisphenylsulphonylpropane. *

Prepared according to Otto(1). Crystallised from alcohol, m.p.=115°. Mixed m.p.with "XX phenyl compound"=84°. Unaffected by permanganate. Sublimes in vacuo without decomposition.

αγ Bisphenylsulphonylpropane *

Prepared according to Otto (above). Crystallised from alcohol, m.p. = 127-8°. Sublimes in vacuo at 200° without decomposition. For mixed m.p. with "XX phenyl compound"see below. Extremely slight reaction with $\frac{N}{20}$ permanganate.

ββ' Bisphenylsulphonylpropane.

Prepared according to Shriner, Struck and Jorison(5); and also by the condensation of acetone and phenyl mercaptan (Baumann(6)), and subsequent oxidation. M.Pt. = 181°. Mixed melting point with the "XX phenyl compound" =84°.

αα' Bisphenylsulphonylethane.

Acetaldehyde and phenyl mercaptan were condensed in the usual manner using hydrochloric acid and zinc chloride. Solid, m.p. = 34°. Baumann (above) gives it as an oil. Oxidised by hydrogen peroxide in glacial acetic acid with a little acetic anhydride. White crystalline solid, m.p. = 101-102°. Mixed with the "XX phenyl compound" gave m.p. = 83°.

The "XX phenyl compound"

On taking mixed m.pts. with the trimethylene and propylene compounds it was noticed that the m.pt. of the "XX phenyl com-

pound" had altered to 122-124°. Further while a mixed melting point with the propylene compound gave a depression to 93° C, with the trimethylene compound the mixed M.Pt was 125°(that is, the melting point was not depressed).

Addition of benzenesulphinyl chloride to trimethylene glycol (22) (page 7 reaction 3)

The benzene sulphinyl chloride, prepared according to Smiles etc. (23), was dissolved in ether and slightly less than the equivalent quantity of glycol in ether together with anhydrous potassium carbonate added. This was allowed to stand for several days (in dark). This was extracted with benzene and washed with water. A very small quantity of solid was obtained from an oil after it had been repeatedly washed with various solvents (ether, pet ether, benzene, alcohol, methyl alcohol and chloroform). It melted, impure at 47°C.

A second attempt was absolute failure. Oily residue set to crystallise in various solvents gave negative result.

Addition of sodium benzene sulphinate to dibromo propyl β naphthyl sulphone.

(1) Carried out according to the modified method of Otto (p.25) After separating with water the product was crystallised from methyl alcohol and purified with animal charcoal. M.Pt = 123° (corresponds with Tröger and Artmann (3)).

Hydrolysis with caustic soda was very rapid.

Addition of sodium β naphthalene sulphinate to dibromo propyl phenyl sulphone.

(2) Carried out as above. Product crystallised from methyl alcohol gave yield (from 2 gms dibromide and 2.5 gms sodium

above = 123°.

Hydrolysis with sodium hydroxide was very rapid.

Compound was readily oxidised by permanganate.

Addition of phenyl mercaptan to allyl phenyl sulphone. (p.7 reaction 1)

Equivalent quantities of the two liquids were left standing for 60 days, mixed together in a test tube. After some time 1 drop of piperidine was added. The product was oxidised with 1% neutral permanganate and the manganese dioxide destroyed with sulphur dioxide. It was then extracted with ether and the resultant residue gave a crystalline compound M.Pt = 126° which was identical with the trimethylene phenyl sulphone (M.Pt = 127-8°). Mixed M.Pt = 126°C.

Attempted partial reduction of dibromopropylsulphones to Monobromopropylsulphones.

$$\begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2SO_2R \end{array} \xrightarrow{NaAsO_2} \begin{array}{l} CH_2Br \\ | \\ CH_2 \\ | \\ CH_2SO_2R \end{array} \quad \text{or} \quad \begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CH_2SO_2R \end{array}$$

.4050 gm sodium arsenite was dissolved in minimum water and added to a solution of .3500 gm dibromo propyl phenyl sulphone in alcohol and refluxed for 6 hours. The organic product was then extracted with ether and the solution (2) aqueous (1) titrated against $\frac{N}{10}$ $AgNO_3$: -= 18.15 cc ≡ .15 gm Bromine. (by Volhard)

Calculated for one Br = .08 gms.
Calculated for two Br = .16 gms.

.4126 gms $NaAsO_2$ added to .3230 gms dibromopropyl tolyl sulphone.-

$\frac{N}{10}$ $AgNO_3$ = 16.45 cc = .1316 gms Bromine.

Calculated for one Br = .07 gms
Calculated for two Br = .15 gms

These experiments showed more than one bromine atom was eliminated.

Trimethylene bromhydrin.

This was carried out according to Fruhling (24) save that instead of heating with hydrobromic acid at 100° in a sealed tube the solution was heated to 100° and dry hydrobromic acid continually passed through the solution for four hours.

Trimethylene bromhydrin and sodium benzene sulphinate (page 8 reaction 4)

Trimethylene bromhydrin was refluxed, in alcoholic solution, with sodium benzene sulphinate for several days. It was then washed with water, extracted with ether, dried with anhydrous sodium sulphate and distilled up to 100°C in vacuo (water pump), Further attempts at distillation at .6 mm resulted in a little coming over at about 220° to give a crystalline solid. It was not considered expedient, for our purposes, to complete the distillation.

Benzene sulphinyl chloride and Trimethylene benzene sulphon hydrin (page 8 , reaction 4).

The above compounds were mixed in equimolecular quantities in ethereal solution. After standing some time the mixture was refluxed for several hours on a waterbath. Everything distillable below 100°C at the water-pump was then removed. The residual oil was dissolved in alcohol, Eventually some phenyl

disulphide, m.p. = 61°, crystallised out.

Benzene sulphonyl chloride and hydroxy propyl phenyl sulphone. (page 8, reaction 5.)

The benzene sulphonyl chloride was mixed with the hydrin and the mixture allowed to stand for several days. A concentrated aqueous solution of the theoretical amount of sodium hydroxide was then added. Much heat was evolved and the mixture solidified. This was added to water and extracted with ether. The oil obtained on evaporation of the ether extract was dissolved in alcohol but failed to crystallise.

Trimethylene dibromide and silver benzene sulphinate (page 7, reaction 2.)

Dry silver benzene sulphinate, prepared according to Kalle, Rosenheim and Singer (25) was refluxed in ethereal solution with the equivalent quantity of trimethylene bromide for ten days, the flask being exposed to the light as little as possible There was absolutely no reaction, the sulphinate being recovered unchanged.

This latter experiment was repeated using trimethylene iodide, instead of the bromide, and silver toluene sulphinate. An oil was obtained.

αγBistolylsulphonylpropane *

Otto (1). Yield = 90% of crystals, m.p. = 125-129°. It was not hydrolysed by caustic soda. The range 125-129° was very definite and attempts at fractional crystallisation failed to isolate any second compound. Some of the compound was exposed to light and another portion was heated for several days but in neither case was there any change of melting point.

α/β Bistolylsulphonylpropane. *

As reported by Otto (above) M.Pt 144 - 148°. Mixed M.Pt with "XX tolyl" = 125°

Otto's XX tolyl compound. *

M.Pt = 154°C. Molecular weight Found = 336, 331.5, 368.5 Calculated 352. Hydrolysed by sodium hydroxide, oxidised by acid permanganate and scarcely sublimes at 200° at .6 mm.

Toluene sulphinic acid.

This was prepared by extracting the precipitated acid from aqueous solution with ether, drying with sodium sulphate, and evaporating the solution to small bulk. Melting point, crystallised from water = 86 - 90°C. From ether = 92°C. (see Meyer (24) ( ).

Allyltolyl sulphone and toluene sulphinic acid (page 8 ,reaction 6)

These substances were dissolved in equimolecular proportions in ether and left for several days, but nothing happened. They were then warmed alone on the waterbath for about an hour when an oil resulted From this oil in alcoholic solution crystals were obtained M.Pt = 73 - 75°C. These proved to be the disulphoxide ($C_7H_7SO_2SC_7H_7$). M.Pt = 77°C.

Trimethylene iodide and silver benzene sulphinate.

Trimethylene iodide was prepared according to the method of Perkin (27).

The iodide was refluxed with silver benzene sulphinate in ethereal solution. The product was an oil. (cf. page 30)

α/γ Bis-naphthylsulphonylpropane. *

Prepared according to Tröger and Artmann (28) had M.Pt = 145°. Sodium hydroxide did not hydrolyse the substance. It was unaffected by permanganate.

α/β Bis-naphthylsulphonylpropane.

Yield 65% M.Pt = 125°. Readily hydrolysed but not oxidised.

XX naphthyl compound. *

Carried out in the usual modified method (page 25). Yield 40% M.Pt = 157°. Readily hydrolysed by alkali and oxidised by permanganate. Mixed melting points with either α/β or α/γ gave depressions of more than 20°.

Methyl ether of β naphthyl sulphinic acid.

This compound was prepared by the method of Otto and Rossing (29). Crystallises in large clusters of small crystals M.Pt = 44°. Yield 70%.

Methyl ether of β naphthyl sulphinic acid and trimethylene glycol. (page 8 reaction 7).

Equimolecular quantities were kept at about 50°C for some days without reaction, the products being recovered unchanged. On heating to 100°C there was obvious reaction with effervescence and an oil insoluble in water was obtained. This solidified on standing. The solid was proved to be β naphthalene disulphoxide ($C_{10}H_7SO_2SC_{10}H_7$). M.Pt = 106°

*

With sulphuric acid and Anisole.

The substances asterisked* in the preceding pages were tested with sulphuric acid and anisole, and also with tetra nitro methane.

This suggested that the "XX compounds" were converted by concentrated sulphuric acid into "$\alpha\gamma$ compounds". When the "XX naphthyl" compound was dissolved in concentrated sulphuric slightly warmed and reprecipitated by dilution with water, it was recovered unchanged.

ESTIMATION OF HALOGEN
(Pregl's procedure adapted to Volumetric)

(c.f. Theory p.10)

The combustion tube was thoroughly washed out with distilled water and part KU (see diagram on back cover) dried and the end UV again thoroughly washed with water. 2 cc of the sodium carbonate solution and 2 drops of bisulphite solution (prepared as above) were placed in a clean test tube. The nozzle of the combustion tube was placed in this solution and the solution drawn by controlled suction until the beads (U S) were thoroughly moistened.

The tube was placed on the stand, the platinum contacts entered and the combustion carried out according to Pregl. The optimum speed was about 18 bubbles (or 3.5 cc) per minute. A speed of 22 bubbles per minute would give perfectly satisfactory results, provided greater care was taken in the actual running of the combustion, but a slower speed was liable to result in the formation of moisture at the end (K)of the combustion tube The test tube which contained the remainder of the sodium carbonate-bisulphite solution which was used to moisten the beads was then emptied into a clean 50cc conical flask and the still moist test-tube placed as a final absorber over the end of the tube.

When the combustion was completed the tube was allowed to cool in the stream of oxygen. This took 10-15 minutes. It was then disconnected and the nozzle placed over the 50cc conical

flask which contained the surplus sodium carbonate solution. 10 cc of distilled water was quickly poured into the tube from a measuring cylinder and when this had drained it was further washed out with 3cc of water. The nozzle was also cleaned with a fine spray of water. After standing for 10 minutes 2 drops of perhydrol were added and the solution boiled to expel the excess hydrogen peroxide. The solution was then acidified with 2 cc of 8N nitric acid and slight excess of .0141N silver nitrate added. It is important that a large excess of silver nitrate should not be used as this invariably resulted in occlusion of silver nitrate solution and consequently high answers for halogen. Excess was avoided by adding .3cc of silver nitrate at a time and shaking vigorously. Coagulation occurred just before the end point so that when one obtained coagulation one added another drop of silver nitrate solution to see if there was any further precipitation. The chloride was then filtered off, 3 cc of ferric indicator added, and the solution titrated with .00705 N ammonium thiocyanate soltuion until a faint, permanent, brown colouration was produced.

EXPERIMENTAL NOTES

on the

ESTIMATION OF HALOGEN

Indication of end-point

(a) Without indicator

Attempts were made to determine the end point by observing the last trace of precipitation of silver halide. This did not allow accuracy for such small quantities as were involved in the above titrations.

(b) Potassium chromate as indicator

According to Fajans and Frankenburger (30) the results obtained by the method of Mohr (31) are usually high. On the contrary, results obtained by this method were low, probably due to the presence of oxyacids of chlorine. Reduction of these with magnesium gave seriously high results but this was traced to impurity in the magnesium. A sharp end-point could only be obtained in very concentrated solutions and the result was also very sensitive to pH fluctuations (limit 7-10.5) brought about by imperfect neutralisation before titration with silver nitrate.

(c) Ammonium thiocyanate and ferric alum as indicator.

This had the great advantage that the titration could be carried out in nitric acid solution. The end point at the

above dilution was perfectly definite provided that only a small excess of silver nitrate solution was used and that the silver chloride precipitate was filtered off (Rosanoff and Hill (32)) before back titration with thiocyanate.

PART II

Estimation of Halogen and Sulphur.

Recommended Procedure.

Description of Apparatus.

The above diagram (p.85) represents the apparatus as finally devised and used. It is constructed on a board, measuring 47½" x 4" x 5/8", made of cyprus wood. This type of wood eliminates the tendency that such a long and narrow strip would have to carp when subjected to heat. The marked sections A (22") and A^1 (12¾") on this board are coated with white rubber paint and B (12¾") with a black heat-resisting paint. This allows the apparatus to be washed and consequently kept absolutely clean.

Working from the right to the left of the diagram C is a piece of rubber tubing of 3/8" thickness and bore 3/16" which is connected to the fine adjustment valve of an oxygen cylinder. This tubing is broken at D to allow the insertion of a glass T piece and then continued on to the glass tube emerging from E. To the other arm of the T-piece a soft piece of rubber tubing is attached and is closed by means of a screw clip. Thus, by allowing a slight leak at D, an even finer adjustment of the oxygen stream can be obtained.

Into a sixteen ounce wide necked bottle (80 mm diameter) which is firmly attached to the base by inserting into a neat fitting ring, there is placed a tube of 34 m.m. bore. This is satisfactorily fixed into position by means of two strips of

cork (F) each equivalent to one third of the total circumference. A small tube (4 m.m. bore), through which the stream of oxygen passes, runs down the centre of this large tube. These two tubes are fixed in position with a glass seal at E so that the relative position of the tubes can not vary. Thus the pressure inside is at no time appreciably greater than atmospheric. The larger tube is equipped with an end, like the lip of a beaker (H), which greatly facilitates the escape of gas in the event of back pressure developing. Tap I may then be closed, the cause of such pressure removed, and the tap reopened without any greater pressure having accumulated in the part of the apparatus just described.

The tube emerging from tap I has still a bore of 4 m.m. but it is connected by a piece of rubber tubing to another tube ofsmaller bore (2m.m.) but having the same external diameter (6 m.m.). This latter tube is drawn into a thin straight point about half an inch in length and .75 m.m. in bore and on to it is fitted a cork 3/8" in thickness, so that the point of the tube protrudes by ½". When the cork is tightly fitted into the combustion tube at K it is half embedded (that is 3/16").

The combustion tube itself is as specified by Pregl. The space S-V is a modification of the tube as originally supplied It prevents a drop of water from the spiral being driven into the tip V and so creating back pressure.

Returning to the other end of the tube, it contains four removable objects. The first is a small tube (N) containing the substance to be burnt. This tube is made of hard glass

and measured ¾" x 3/16". It is placed 3½" from the end of the tube K. Further along are the platinum contacts or catalysts. The pieces marked Q, Q^1 are of pure platinum. They are constructed from platinum sheets of the dimensions 2" x ½" and 2½" x ½" the larger (Q^1) being placed nearest K and folded as described by Pregl. The introduction of R is novel and greatly increased the fool proof qualities of the method. R consists of a piece of silica tubing of slightly smaller dimensions than the bore of the combustion tube (5/8" x 7 m.m. with 2m.m. bore) This silica tube is wound with a piece of platinum wire which also passes through the centre of the tube. The net effect is that a rotary motion is set up on the gases coming in contact with R and thus they are forced to come completely into contact with the second piece of platinum. (Q).

Two pieces of wire gauze (M) are wrapped round the tube at the points which required to be heated. One piece 7" long, covers the catalysts which are heated by means of a straight burner placed ¼" below the tube. The small container is covered by a piece of gauze 2½" long and heated by an ordinary bunsen the mouth of which is placed 2½" below the tube. The bunsen is fitted with a draught shield (O)and travels on rails being slowly and evenly propelled along by the screw P. The combustion tube is supported by two angle brackets J. (1/8" thick, 3" broad, 9½" high). At the top a V section is cut out giving a minimum height of 7 7/8". The tube does not rest directly on these brackets but on strips of wire gauze (L) placed across the V. The heat transmitted from the bracket is

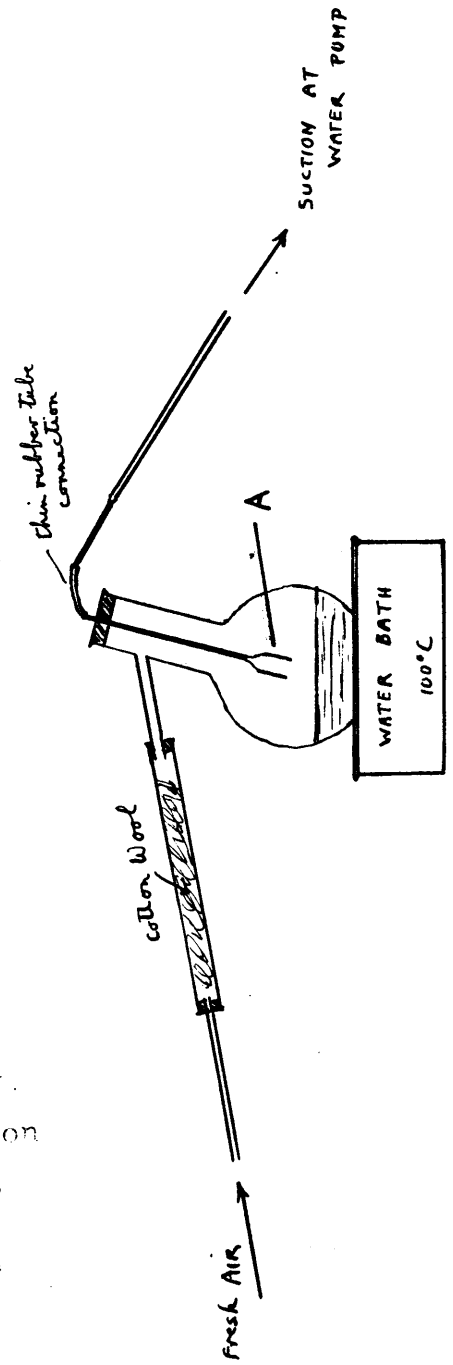
therefore lessened and at the same time distributed over a wider area.

On to the end of this tube is placed a bent glass tube of 9 m.m. bore. The last ½" at the end of this tube is tapered out to a maximum bore of 1.1 m.m. It thus fits securely on to the end of the combustion tube and the joint is completed, by the formation of a water seal (X). This tube extends for a further 3½" and it should be noted that it is not quite horizontal but on a slight slope. It then bends at an angle of 30° and continues for a further 6"into a flask. This latter portion is fitted for adsorption purposes with a glass spiral.

Z is an adjustable stand to support the flask. It consists of a block of wood (3" x 4")on the top of which is embedded the upturned glass stopper of a wide necked bottle . At the side is a piece of 3 ply wood 6½" in height which has a semicircle of 1" diameter cut out of the top.It is fastened by means of a bolt, driven through the block, which fits in to a slotted hole in the plywood and is secured by means of a brass wing nut. This permits the height of the plywood to be adjusted so that the desired slope may be attained on Y.

CONCENTRATION APPARATUS.

This consists of a 100 cc quartz distilling flask into which is fixed a narrow tube of small bore (1.5 mm internal, 3 mm external diameter) which widens at the end into a tube of 10 mm bore. (A) This tube is fixed in position by means of a rubber stopper. The solution to be concentrated is placed in the flask and heated on a waterbath and a current of air drawn over the surface by connecting the narrow tube (A) to a suction pump. It was found that the narrow tube produces more rapid concentration than is obtained by having a tube of large bore throughout. The air which enters the flask via the side arm is purified by previously being drawn through cotton wool. This apparatus is capable of reducing the volume of solution from 80 to 8 cc in 1½ hours with absolute safety.



SIMULTANEOUS ESTIMATION OF SULPHUR AND HALOGEN

For the purpose of this estimation the apparatus used is exactly as shown on the diagram.

The combustion tube is washed out with distilled water and the part KU is dried by attaching the tube to the waterpump at V and drawing the air through a piece of filter paper at K while the portion KU is heated by means of a non-luminous bunsen flame. After allowing to cool it is disconnected from the pump and the end US again thoroughly washed with water. The beads are then freshly moistened with distilled water by sucking some into the tube out of a test tube. Next the catalysts are washed, heated red hot and entered into position. Finally the weighed tube (N) containing about 4 mg of the substance to be analysed is placed in position.

The speed of the oxygen stream is then fixed at 18 bubbles per minute (3.5 cc) and the apparatus connected at K. As before the large burner is lit and the excess water removed from the nozzle of the combustion tube with filter paper.

Tube Y and the 100 cc distilling flask are washed out with distilled water and 5 cc of .0200 N sodium carbonate solution entered via. Y. This extension tube is then connected to the main combustion tube by means of a neat fitting glass joint which is completed with a water seal . The actual burn- is carried out exactly as described by Pregl.

When the combustion is completed, and the tube cool, tap I is closed and the extension tube disconnected. This tube is

washed clean with 20cc of distilled water from a very fine jet wash-bottle. The main combustion tube is then washed out with a further 15cc of distilled water.

One drop of perhydrol is added to the solution in the flask and this is allowed to stand for ten minutes. It is then boiled vigorously for two minutes, cooled, one drop (= .03cc) of methylene blue-methyl red indicator added and the solution titrated with .0100N sulphuric acid solution until the green colour disappears, The solution is again taken to boiling, cooled, and more standard acid added when the solution will swing from an intense green to a definite violet colour with one drop of .0100 acid. It is necessary to boil as the indicator is affected by the presence of carbonic acid, but for the actual end point a much sharper change-over is experienced in the cold solution.

Having thus obtained the total acidity due to the hydrochloric and sulphuric acids the solution is concentrated in the apparatus described, (see p. 42), down to 10 cc. ½ cc of 8N nitric acid and a slight excess of .0141N silver nitrate are added. A large excess of silver nitrate was found to lead to high results and so the end point was approximately determined by observing when the precipitates coagulated and if a further drop of the silver nitrate solution produced any opalescence. This could easily be determined in the concentrated solutions against a black background. The silver chloride precipitate is filtered off using No. 40 Whatman quantitative filter papers. 3 cc ferric indicator is then added to the clear solution which is titrated back with .00705N

ammonium thiocyanate solution until a clear permanent brown colour is obtained.

EXPERIMENTAL NOTES

On the

ESTIMATION OF HALOGEN AND SULPHUR

1. Absorbing gases in water only.

The following experiments indicated that absorption was incomplete, or that all the halogen was not present as acid (HCl, HClO, etc.,), or that the weaker halogen acids (HClO) did not allow a true end point.

$(ClC_6H_5)_2SO_2$

			Theoretical	
Weight of substance	= 8.43mgs	= 6.48mgs	= 7.19mgs	
Volume of .02N Na_2CO_3	= 5.26cc	= 4.12cc	= 4.44cc	
Volume of .02N $AgNO_3$	= 2.74cc	= 2.21cc	= 2.41cc	
% Chlorine	=23.1	=24.2	=23.8	= 24.7
% Sulphur	= 9.6	= 9.4	= 9.0	= 11.2

Ethyl chlorocamphor-10-sulphonate

Weight of substance=	= 8.23mgs	Theoretical
Volume of .02N Na_2CO_3	= 4.17cc	
Volume of .02N $AgNO_3$	= 1.42cc	
% Chlorine	= 12.3	= 12.1
% Sulphur	= 10.7	= 10.9

2. Methods of reducing acid products of combustion of halogen compounds.

The efficiency of the various proposed methods was tested on $\frac{N}{50}$ chlorine water:-

(a) Sulphite reduction.

Consistent results were obtained with the usual sodium carbonate and bisulphite reduction.

5cc Chlorine water = 4.64cc .02N $AgNO_3$ solution

(b) Palladium reduction.

Reduced with palladium foil saturated with hydrogen by immersion in zinc and sulphuric acid:-

(1) Standing 10 minutes.

5cc Chlorine water = 3.85cc .02N $AgNO_3$ solution

(2) Standing overnight.

5cc Chlorine water = 4.25cc .02N $AgNO_3$ solution

Reduced with untreated, clean, palladium foil:-

Standing 1 hour.

5cc Chlorine water = 4.20cc .02N $AgNO_3$ solution

Hydrogen was passed over palladium foil which had been previously washed in nitric acid and heated in a bunsen. The chlorine water was then added in an atmosphere of hydrogen:-

(1) Standing 1 hour.

5cc Chlorine water = 4.22cc .02N $AgNO_3$ solution

(2) Standing 24 hours.

5cc Chlorine water = 4.19cc .02N $AgNO_3$ solution

(c) Perhydrol reduction.

Direct attempts to neutralise chlorine water failed owing to the methylene indicator being destroyed. Two drops of perhydrol were added to the solution and it was found that a definite and consistent end point could be obtained after ten

minutes but that after five minutes it was still unsatisfactory:-

5cc Chlorine water = 4.64cc .02N Na_2CO_3

The above factor also agreed with that obtained by sulphite reduction. The acidity originally present in the hydrogen peroxide was taken into account. (see page).

3. Absorbing the gases in peroxide solution.

For simplicity a compound containing no sulphur was used.

(a) Dilute peroxide (1:20)

Chlorocamphor

	1.	2.	3.	4.
Weight of substance	= 6.85mgs	= 6.51mgs	= 6.20mgs	= 6.72mgs
Volume of .02N Na_2CO_3	= 1.85cc	= 1.68cc	= 1.59cc	= 1.66cc
% Chlorine	=19.2	=18.3	=18.2	=17.5
Volume of .02N $AgNO_3$	= 1.75cc	= 1.67cc	= 1.64cc	= 1.77cc
% Chlorine	=18.1	=18.2	=18.8	=18.7

Theoretical % Chlorine = 19.0

Dibromocamphor.

	5.	6.	Theoretical
Weight of substance	= 9.27mgs	= 6.18mgs	
Volume of .02N Na_2CO_3	= 1.23cc	= .78cc	
% Bromine	=21.2	=20.2	
Volume of .02N $AgNO_3$	= 1.28cc	= .81cc	
% Bromine	=22.1	=21.0	= 51.6

If (1) which suggested a practical error be excluded, then four out of the remaining five showed the acidity to be lower than the halogen accounted for would warrant (i.e. by silver nitrate titration). Therefore it was likely that some halogen might be present in some other form,due to incomplete combustion,

which does not affect methylene blue.

(b) 10% Hydrogen peroxide solution.

Chlorocamphor.

	7.	8.	Theoretical
Weight of substance =	6.69mgs	= 7.80mgs	
Volume .02N Na_2CO_3 =	1.61cc	= 1.86cc	
% Chlorine =	17.1	= 16.9	
Volume .02N $AgNO_3$ =	1.70cc	= 1.89cc	
% Chlorine =	18.0	= 17.2	= 19.0

These results only served to show that chlorocamphor was somewhat difficult to burn and so ethyl chlorocamphor 10 sulphonate was tried as being more easily combusted:-

	9.	10.	11.	Theoretical
Weight of substance =	7.54mgs	= 5.92mgs	= 6.90mgs	
Volume .02N Na_2CO_3 =	3.89cc	= 3.07cc	= 3.56cc	
Volume .02N $AgNO_3$ =	1.32cc	= 1.07cc	= 1.24cc	
% Chlorine	=12.4	=12.8	=12.8	= 12.1
% Sulphur	=10.9	=10.8	=10.8	= 10.9

(c) Absorbing gases in water and subsequently treating with alkaline peroxide

Several experiments were carried out with absorption by beads moistened with distilled water. The combustion products were washed into excess standard ($\frac{N}{50}$)alkali. Four drops of perhydrolwere added and the solution allowed to stand for 10 minutes. It was then boiled, cooled, and titrated back with

$\frac{N}{100}$ sulphuric acid. $\frac{1}{2}$cc ofsaturated sodium carbonate solution and 6 drops of $NaHSO_3$ solution were added and, after standing for an hour, the solution was again treated with 6 drops of perhydrol, boiled, cooled, acidified with 2cc of HNO_3, excess $AgNO_3$ and 2cc of ferric indicator added, and the whole warmed until the precipitate formed coagulated. The precipitate was filtered off from the cold solution through a barium sulphate filter paper and back titrated with $\frac{N}{50}$ ammonium thiocyanate solution.

Ethyl chlorocamphor-10-sulphonate

Weight of substance	= 6.17mgs	= 8.43mgs	= 5.22mgs	= 6.35mgs
Volume of .0196N Na_2CO_3	= 3.26cc	= 4.34cc	= 2.69cc	= 3.31cc
Total acidity (as % S)	=16.6	=16.1	=16.1	=16.3
Volume of .0193N $AgNO_3$	= 1.20cc	= 1.56cc	= .96cc	= 1.18cc
% Chlorine	=13.3	=12.7	=12.6	=12.7

Theoretical % Chlorine = 12.1

4. The necessity of adding as small an excess of silver nitrate as possible

It can be seen from the above results that the total acidity (theoretical = 16.3)was satisfactory but that the silver nitrate titration was inconsistently high.The only explanation which could be offered was that some silver nitrate was being adsorbed in the silver chloride precipitate. This could to a large extent be avoided if only a small excess of silver nitrate was used, and the following results were obtained with that modification:-

Ethyl chlorocamphor-10-sulphonate

Weight of substance	= 8.27mgs	= 7.36mgs	Theoretical
Volume of .0196N Na_2CO_3	= 4.25cc	= 3.77cc	
Volume of .0193N $AgNO_3$	= 1.44cc	= 1.30cc	
% Chlorine	= 11.9	=12.1	= 12.1
% Sulphur	= 10.7	=10.6	= 10.9

These results,under the experimental conditions noted above, must be regarded as fairly satisfactory.

5. The elimination of bisulphite.

In order to simplify the method as much as possible it was resolved to eliminate the bisulphite. This, according to Viebock (33) should be quite effective. It was found however that the elimination of this process prevented the acidity indicator (methylene blue and methyl red) from being destroyed and so in subsequent experiments (2 and3) this was achieved by the addition of two further drops of perhydrol to the just alkaline solution and boiling. Only half a cc. of nitric acid solution was then required before adding excess silver nitrate.

Ethyl chlorocamphor-10-sulphonate.

	1.	2.	3.	Theoretical
Weight of substance	= 7.80mgs	= 8.02mgs	= 6.71mgs	
Volume of .0196N Na_2CO_3	= 3.91cc	= 4.10cc	= 3.42cc	
Volume of .0193N $AgNO_3$	= 1.35cc	= 1.38cc	= 1.19cc	
% Chlorine	=11.8	=11.8	=12.2	= 12.1
% Sulphur	=10.4	=10.7	=10.5	= 10.9

6. Guard tube to retain traces of halogen.

The previous method gave low results when used with 2 : 5 dichlorophenyl-2':5' -dichlorobenzenethiolsulphonate which is rich in chlorine and sulphur:-

$Cl_2C_6H_3SO_2SC_6H_3Cl_2$			Theoretical
Weight of Substance	= 4.37 mgms	= 5.88 mgms	
Volume .0196N Na_2CO_3	= 4.55 cc	= 5.88 cc	
Volume .0193N $AgNO_3$	= 2.28 cc	= 2.86 cc	
% Chlorine	= 35.7	= 33.3	= 36.6
% Sulphur	= 16.5	= 16.3	= 16.5

These results suggested that the compound was not undergoing complete decomposition. To combat this the hydrogen stream was run slower (20 bubbles to the minute) by means of a "leak" and a baffle of palladium foil was introduced. The idea was the palladium might also be an effective catalyst but unfortunately it was definitely attacked. The palladium washed, before entering, was washed and dried by placing in a quarty tube and heating over a bunsen.

$Cl_2C_6H_3SO_2SC_6H_3Cl_2$

	1.	2.	Theoretical
Weight of Substance	= 5.04 mgms	= 6.76 mgms	
Volume .0196N Na_2CO_3	= 5.28 cc	= 6.39 cc	
Volume .0193N $AgNO_3$	= 2.64 cc	=	
% Chlorine	= 35.9	=	= 36.6
% Sulphur	= 16.7	=	= 16.5

In case (1) a piece of palladium was placed only between the palladium contacts and it remained a blue- black. In the second case a piece was also put in front of the contacts.This became practically brown and had a corroded appearance. Thus it was decided to try a small piece of silica tube covered with platinum wire as a baffle.

$Cl_2C_6H_3SO_2SC_6H_3Cl_2$

			Theoretical
Weight of Substance	= 7.31 mgms	= 6.14 mgms	
Volume .0196N Na_2CO_3	= 7.29 cc	= 6.03 cc	
Volume .0193N $AgNO_3$	= 3.51 cc	= 2.83 cc	
% Chlorine	= 32.9	= 31.6	= 36.6
% Sulphur	= 16.4	= 16.5	= 16.5

These results indicate that while sulphur was consistently satisfactory halogen was inconsistently low and so it was sugg-ested that some of the latter must be escaping. In order to test this a further tube filled with glass-wool was attached to the combustion tube by means of a water seal. The tube contained a solution ≡ .001 cc N/50 sodium carbonate with indicator:-

Weight of Substance above = 5.78 mgms

	(a)	(b)	Theoretical
Volume .0196N Na_2CO_3	= 5.66 cc	= .52 cc	
Volume .0193N $AgNO_3$	= 2.63 cc	= .39 cc	
∴ % Chlorine	= 31.2	=35.8	=36.6
∴ % Sulphur	= 16.7		=16.5

(a) was the normal combustion and (b) the additional absorp-tion in the glass wool tube. During the actual combustion which took 2 hours the colour of the indicator did not change but on standing (with the addition of 2 drops perhydrol) the solution became decidedly acid. The acidity of the perhydrol was, of course, taken into account. It was made alkaline and boiled with a further 2 drops of perhydrol and titrated to neutrality. The equivalent halogen titration was much lower than the alkali titration indicated and this might to attributed to slow oxidation of alcohol in the indicator solution to acetic acid. As this tube was now definitely proved necessary it was decided to abandon the use of indicator and wash the guard tube with excess of standard N/50 alkali.

$CL_2C_6H_3SO_2SC_6H_3Cl_2$

			Theoretical
Weight of Substance	= 5.43 mgms	= 4.90 mgms	
Volume .0196N Na_2CO_3	= 5.74 cc	= 5.15 cc	
Volume .0193N $AgNO_3$	= 2.88 cc	= 2.60 cc	
∴ % Chlorine	= 36.4	= 36.4	= 36.6
∴ % Sulphur	= 16.8	= 16.6	= 16.5

These results seemed quite satisfactory and a further substance was proceded with.

$(ClC_6H_4)_2SO_2$

Weight of Substance	= 8.43	Theoretical
Volume .0196N Na_2CO_3	= 6.30	
Volume .0193N $AgNO_3$	= 3.07	
% Chlorine	= 24.9	= 24.7
% Sulphur	= 12.2	= 11.2

The fact that this result was not satisfactiry may be due to mechanical error. It was difficult to wash the glass wool tube satisfactorily. This was therefore replaced by a tube containing a glass spiral and the angle of the bend was also lessened. Some difficulty was experienced in being confident that the tube was thoroughly washed with a small fixed amount of water. This was overcome by using a small wash bottle with a fine and long jet in which a regulation 20cc of water was placed.

7. Concentration (prior to titration with silver nitrate)

The end point in halogen titrations by this method caused some concern. Any one consistently working with these would soon be capable of accurately determining the end poimt. Various references were consulted (34) but these did not produce a satisfactory solution. Tests were carried out to see if the colour was affected by the presence of the destroyed indicator. This did not appear to be the case. It was found that a satisfactory end point could be obtained by concentrating the solution in the apparatus previously described (page 42).

8. Test experiments

This method was tested out on compounds containing halogen but no sulphur and proved absolutely satisfactory as the following table of consecutive results illustrates:-

TABLE IV.

(Chlorine in Sulphur-free compounds)

Substance	Weight used	$\frac{N}{50}$ Na_2CO_3 titration	% Chlorine	$\frac{N}{71}$ $AgNO_3$ titration	% Chlorine	Requires
chlorocamphor	7.18	1.92	19.0	2.73	19.0	19.0
	6.92	1.85	19.0	2.64	19.1	
p.dichlorobenzene	6.39	4.32	48.0	6.11	47.8	48.3
	6.38	4.30	47.8	6.13	48.0	
	6.46	4.35	47.8	6.15	47.9	

Appendix on methods considered but not exhaustively tested.

Barium Method.

Another method of analysis which received consideration was that of precipitating the sulphate present as the barium salt and volumetrically estimating the amount of barium left in solution by means of the method of Küster (35). This involved neutralising, in the usual manner, the acids formed by the combustion and so obtaining a total acidity factor. The solution was then treated with a standard solution of a soluble barium salt (barium chloride) and then with standard sodium carbonate solution when the position was as indicated by the following equations:-

$$H_2SO_4 + HCl \xrightarrow{Na_2CO_3} Na_2SO_4 + NaCl$$

$$\xrightarrow{BaCl_2} BaSO_4 + NaCl + BaCl_2$$

$$\xrightarrow{Na_2CO_3} BaSO_4 + NaCl + BaCO_3 + Na_2CO_3$$

The excess sodium carbonate could then be titrated to the bicarbonate stage without any interference from the barium carbonate. This method is however open to many objections when used on the micro scale. The numerous titrations involve many slight errors which are liable to accumulate. The sodium carbonate must be exceptionally pure and especially free from bicarbonate and finally it is difficult to obtain a satisfactory indicator. According to Kolthoff (34) phenol phthalein is only accurate when titrated from red to a rose colour which must be compared with a standard reference solution. Kuster represses the hydrolysis of the bicarbonate by working at $0^{\circ}C$

in the presence of excess sodium chloride, and the addition of glycerin has also been found to improve matters. Simpson (37) suggested that a mixture of six parts thymol blue to one part cresol red is fairly satisfactory for N/10 solutions. There is also the method of Giblin (38) for the determination of Barium and of sulphates using the sodium salt of rhodizonic acid. This gives a red colouration in the presence of Barium ion but the method does not allow of great accuracy and the use of external indicators is objectionable. Further, the author does not claim any sharpness of end point below $\frac{N}{10}$. It was decided after a thorough examination of the various points that it would not be any improvement on the existing silver nitrate method.

Friedrich's Method.

Pregl's method for sulphur analysis in halogen and nitrogen free substances has been adapted by Friedrich (39) for compounds containing these elements. The apparatus is precisely the same as that used by Pregl for a sulphur combustion in halogen and nitrogen free substances. When a compound containing these substances is combusted all the sulphur is retained in the form of sulphuric acid. A small amount of halogen is also trapped in the absorption tube. This mixture of acids is washed out and titrated to neutrality using standard sodium carbonate solution. An amount of standard sulphuric acid equivalent to the carbonate titration is then added. This means that there has been added, to the original solution of the combustion acids, neutral sodium sulphate solution

which is in slight excess of that quantity required to form sodium bisulphate with the sulphuric acid present in the original solution. The solution will thus contain, sodium sulphate, sodium bisulphate and hydrochloric acid. It is now taken to dryness on the waterbath when the hydrochloric acid is expelled. The residue consisting of sodium sulphate and sodium bisulphate (or in other words neutral sodium sulphate and the sulphuric acid formed in the combustion) is redissolved in water and titrated to neutrality with standard sodium carbonate solution. This final titration is therefore equivalent to the sulphuric acid content of the original solution.

The first attempts to carry out this method proved rather futile owing probably to "creeping" in the evaporating basin. This was prevented by the introduction of an atmosphere of steam produced by covering the basin with an inverted larger basin under which a suction tube was led. Numerous experiments using artificial mixtures of hydrochloric and sulphuric acids showed that under these conditions it was possible to obtain satisfactory results.

An improvement in the method of concentration was devised by the introduction of apparatus such as described on page 12. The method by which the air enters definitely diminishes any slight tendency there may be to creeping.

This method had the great disadvantage that one had no guide to show when all the hydrochloric acid had been driven off. The only method which could be adopted was to neutralise, slightly acidify with sulphuric acid and take to dryness

a second time. One fact which is worth mentioning is that experiments showed that only silica vessels may be used for the concentration when one has to determine the acidity or alkalinity of the final solution.

Adsorption Indicators.

Adsorption indicators (Fajans (40)) suggested an attractive method of obtaining a satisfactory end point in the silver nitrate - halide titration. It was found however that these indicators are very sensitive to slight fluctuations in pH values, and the presence of electrolytes, and often fail completely in dilute solution.

With fluorescein the colour changes from yellow to pink could be destroyed by mineral acid present to the extent of 1 part in 10,000. Further the "changing over" is not sufficiently sharp requiring about .1 cc $\frac{N}{50}$ Silver nitrate.

Dichlorofluorescein gives fairly satisfactory results if the end point is approximately known and the indicator added just prior to the end point (Kolthoff, Lauer & Sunde (41)). Such an end point cannot be accepted for these analyses.

Tartrazene, which will work in $\frac{N}{2}$ nitric acid solution, gives unfortunately the rather indefinite end point of yellow-green.

Ink blue, which should work in a nitric acid medium was found under the required conditions to be most unreliable and spasmodic.

APPENDIX.

Check Combustions.

The following substances were analysed according to the standard method of Pregl:-

TABLE V.
(Sulphur only)

Substance	Weight Used	$\frac{N}{50}$ Na_2CO_3 Titration	Percentage Sulphur Found	Requires
$CamSO_2 \diagdown CH_2$ $CH_3SO_2 \diagup$	6.90	4.42	20.5	20.8
	7.03	4.48	20.4	
$(C_6H_5CH_2)_2S$	7.45	3.47	14.9	15.0
	6.80	3.12	14.7	
$CH_3SO_2CH_2SO_2C_2H_5$	6.58	7.01	34.1	34.4
$CH_3SO_2CH(SC_6H_4CH_3)COCH_3$	8.72	6.73	24.7	24.8
$CH_3SO_2 \diagdown CHSO_2C_6H_4CH_3$ $C_6H_5SO_2 \diagup$	4.98	3.81	24.5	24.8
$C_6H_5SO_2 \diagdown CHCOC_6H_5$ $CH_3SO_2 \diagup$	5.28	3.03	18.4	18.9
$C_6H_5CH_2SO_2 \diagdown CH_2$ $CH_3SO_2 \diagup$	8.45	6.91	26.2	25.8
	6.63	5.44	26.3	
$CH_3S \diagdown CH_2$ $C_6H_5CH_2SO_2 \diagup$	5.26	4.91	29.9	29.6
	4.85	4.56	30.1	
	4.73	4.39	29.7	

Substance	Weight used	$\frac{N}{50}$ Na_2CO_3 titration	Percentage Sulphur Found	Requires
$CamSO_2 \diagdown CHCOCH_3$ / $CH_3SO_2 \diagup$	4.04	2.34	18.5	18.3
	7.32	4.21	18.4	

The standard acid and alkali were used to check some equivalents:-

TABLE VI.

Substance	Weight used	$\frac{N}{50}$ Na_2CO_3 titration	Equivalent Found	Requires
$CH_3SO_2 \diagdown CHSO_2C_6H_4CH_3$ / $C_6H_5SO_2 \diagup$	7.11	.94	378	388
$CamSO_2 \diagdown CHCOCH_3$ / $CH_3SO_2 \diagup$	3.53	.50	353	350
	7.67	1.13	339	
$(C_2H_5SO_2)_2CHSO_2Cam$	6.84	.83	412	414
$C_6H_5SO_2 \diagdown CHCOC_6H_5$ / $CH_3SO_2 \diagup$	7.16	1.02	351	338

Cam = Camphor radical, $C_{10}H_{15}O$

STANDARD REAGENTS.

Water.

The word water invariably means, in the accounts below, pure freshly distilled, halogen free (tested) water.

Nitric Acid Solution.

Halogen free concentrated nitric acid was diluted with an equal volume of distilled water and boiled vigorously for five minutes in order to expel any oxides of nitrogen. The strength of this solution is approximately 8 Normal.

Ferric Indicator Solution.

5 grams of iron alum was dissolved in 50 cc of concentrated nitric acid (free from halogen), and the solution vigorously boiled to expel oxides of nitrogen.

Standard Silver Nitrate Solution.

It is recommended that .0141 N silver nitrate solution (thus 1 cc of solution is equivalent to .5 m.gm of chlorine) be used. The solution was prepared with a slightly greater normality and diluted down to the required strength. Analytical reagent was used and no acid was added. The solution, if kept in a clean dark bottle, was perfectly stable and it had the advantage of being unaffected when passed over any traces of precipitated silver which had inadvertantly formed on the mouth of the bottle.

Standard Ammonium Thiocyanate Solution.

This solution was made from A.R. materials and had a normality of .00705 which is exactly half of that of the silver nitrate solution.

Standard Sodium Carbonate Solution.

The normality of this solution was .0200. Unfortunately this solution is not very stable, readily attacking the glass of an ordinary winchester. The solution should be restandardised every fortnight and renewed every month for the first six months. Thereafter the normality factor can be depended upon to remain constant for four months. This procedure can be satisfactorily avoided by coating the bottle with wax.

Standard Sulphuric Acid Solution.

This solution was .0100 Normal.

Weighing.

All weighings were carried out on a Sartorius assay balance using a .5 milligram rider. This permitted, using the dial scale for the last figure, a reading in milligrams to the second decimal place with an error of ± .01. The substances were weighed out in a small tube (N) which was counterpoised with a similar tube, and additional weights added, if necessary in order to bring the reading on the rider scale to near zero.

Titration.

Micro burettes of 5 cc. capacity were used. Readings were taken to the nearest .005 cc. After a titration one minute per cubic centimetre of solution used was allowed to elapse before the final reading was taken.

Standardisation of Reagents.

Fresh solutions were prepared and standardised as below. It was found that the $\frac{N}{50}$ Sodium Carbonate solution had slightly attacked the glass of the winchester which contained it and thus weakened the strength of the solution.

The methylene blue - methyl red indicator was still used for acid and alkali but whereas formerly the end point had been decided by the first trace of green on the addition of alkali, it was now decided by the first disappearance of green colour on the addition of acid.

As usual the silver nitrate titration was determined by the first tinge of colour produced with ferric indicator. Cross checking of results showed these end points from the inorganic point of view to be concordant.

An important alteration on obtaining the end point accurately was devised here. Until now the actual end point in the titration had been calculated by the varying depth of colour produced on adding one whole drop to the solution which required less. This method was open to serious objection in that it brought in the personal element. Now, by making one solution $\frac{N}{50}$ and one $\frac{N}{100}$, the actual end point to within .01 cc $\frac{N}{50}$ may be obtained without splitting drops.

One drop is equivalent to .04 cc. Therefore on addition of the $\frac{N}{50}$ solution the results cannot be more than .03cc $\frac{N}{50}$ out with the last drop. Now if .04cc (one drop) $\frac{N}{100}$ solution is added the difference from the actual end point cannot exceed .01 cc $\frac{N}{50}$

$AgNO_3$ against NH_4CNS

Using 2 cc nitric acid solution and 2 cc indicator

Volume .0200 N $AgNO_3$ - 2.04 cc - 2.88 cc

Volume NH_4CNS - 1.93 cc - 2.74 cc

$\therefore \frac{NH_4CNS}{AgNO_3}$ - .947 - .951 - .95

Blank on $AgNO_3$ Reagents.

Using 6 drops of bisulphite, ½ cc sodium carbonate solution 12 drops hydrogen peroxide, 2cc nitric acid solution, 2cc ferric indicator, 1 drop Methylene blue.

Volume $AgNO_3$ - 2.04 cc - 2.02 cc

Volume NH_4CNS - 1.91 cc - 1.91 cc

$\therefore$ effect of these reagents may be neglected.

Standardisation of $AgNO_3$

Using 2 cc nitric acid solution and 2 cc ferric indicator only in (1) and (2) and also including sodium carbonate bisulphite and hydrogen peroxide solutions in (3)

	(1)	(2)	(3)
Volume $AgNO_3$ -	2.27 cc	- 4.01 cc	- 4.21 cc
Volume .0220 HCl -	1.98 cc	- 3.52 cc	- 3.72 cc
$\therefore$ N.F. $AgNO_3$ -	.0192	- .0191	- .0194

Using a weighed quantity of dried sodium chloride with nitric acid solution and ferric indicator only:-

Weight of NaCl	- 5.34 m.gms	- 5.19 m.gms
Volume $AgNO_3$	- 4.77 cc	- 4.59 cc
$\therefore$ N.F. $AgNO_3$	- .0191	- .0193

Standardisation of HCl.

Weight of Na_2CO_3	- 6.85 m.gms	- 5.18 m.gms	- 5.20 m.gms
Volume HCl	- 5.07	- 4.44	- 4.46
$\therefore$ N.F. HCl	- .0218	- .0220	- .0220

Standardisation of Na_2CO_3.

Volume .0220 HCl	- 3.9 cc	- 3.91 cc
Volume Na_2CO_3	- 4.46 cc	- 4.42 cc
$\therefore$ N.F. Na_2CO_3	- .0196	- .0195

Effect of boiling N_2O_2 with Na_2CO_3.

(1) was boiled with $\frac{1}{2}$ cc H_2O_2 and (2) contained none at all

	(1)	(2)
Volume Na_2CO_3	- 2.20 cc	- 1.36
Volume H_2SO_4	- 2.19 cc	- 1.46
$\therefore \frac{Na_2CO_3}{H_2SO_4}$	- 1.005	- .932

$\therefore$ The acid effect of hydrogen peroxide is equivalent to a strength of $\frac{N}{150}$ and must be taken into consideration.

Standardisation of H_2SO_4.

Volume .0196N Na_2CO_3	= 4.96 cc	=	4.21 cc
Volume H_2SO_4	= 9.62 cc	=	8.15 cc
$\therefore$ N.F. H_2SO_4	= .0101	=	.0101

EXPERIMENTAL
(Preparation of Materials)

4-METHOXYTOLYL-3-SULPHONYL CHLORIDE.

This was first prepared (Stewart (42)) by slowly adding one volume of p.tolyl methyl ether to five volumes of chlorsul-phonic acid at 0° and pouring the solution over crushed ice.

Experiments were carried out to determine whether it was essential to have such a large excess of chlorsulphonic acid present. It was found that four volumes did not appreciably diminish the yield if the mixture was allowed to stand for one hour before adding to the ice. A quantity containing three volumes of acid was left standing for forty hours but the yield was not so good. M.Pt = 84°.

SODIUM 4-METHOXYTOLUENE-3-SULPHINATE

This was prepared by reduction of the sulphonyl chloride with alkaline sodium sulphite solution.

4-METHOXYTOLYL-3-SULPHONACETONE.

This was prepared by the method of Gibson and Smiles (51). Colourless needles M.Pt = 79°C.

SODIUM 4-METHOXYTOLUENE-3-THIOLSULPHONATE.

(1)According to Hilditch (43)). 10 gms of sodium sulphide crystals ($Na_2S, 9H_2O$) were placed in 20 cc. alcohol. To this, a solution of the sulphonyl chloride (10 gms) was added gradually. It was found necessary to add an equal volume of water. No fresh addition of the sulphonyl chloride was made until all the precipitated sulphur was reabsorbed. The

solution was then boiled, to remove most of the alcohol, filtered and poured into water. (The oily residue obtained here proved to be sulphur m.p. = 116°). After removing this by extraction with ether the aqueous layer was evaporated to dryness. Methylation of this product gave an extremely poor yield of methyl 4-methoxytoluene-3-thiolsulphonate. (1.6gms).

(2) 10gms of sodium 4-methoxytoluene-3-sulphinate were refluxed for several days in a 50% alcohol-water solution with the equivalent amount of sulphur. The alcohol was then evaporated off and the solution filtered free from sulphur. Yield = 76% theoretical.

METHYL 4-METHOXYTOLUENE-3-THIOLSULPHONATE

The equivalent amount of neutralised methyl sulphate was added to an aqueous solution of the sodium salt and the whole shaken for about 2 hours. Care was taken to see that the solution was kept just alkaline. The solid mass was filtered off and pressed free from any adhering methyl sulphate. It was recrystallised from alcohol m.p. = 77°. Yield = 70% of theoretical.

ANALYSIS

Weight of substance	Titration $\frac{N}{50}$ Na_2CO_3	Percentage sulphur Found	Requires
8.20mgs	7.06cc	27.55	27.59
5.02mgs	4.29cc	27.35	

4.METHOXYTOLYL-3-SULPHONYLMETHYLTHIOACETONE.

4-methoxytolyl-3-sulphonylacetone (1 mol.) and methyl 4-methoxyltolyl-3-thiolsulphonate (1.1 mol.) were dissolved in alcohol and sodium carbonate ($\frac{1}{2}$ mol.) added. This mixture was refluxed on the waterbath until the sodium carbonate had dissolved. The alcohol was then distilled off and the residue cooled in ice. Ice was then added to the residue and also the theoretical quantity of caustic soda necessary to dissolve the product. This solution was washed with ether to remove any hydrolysed product etc.,and the final product precipitated with acetic acid and extracted with ether. Recrystallised from alcohol M.Pt. = 114½°C. Yield = 70% of theoretical.

ANALYSIS.

Weight of Substance	Titration $\frac{N}{50}$ Na_2CO_3	Percentage Found	Sulphur Theoretical
4.00 m.gms.	2.79 cc	22.32	22.22
5.21 m.gms.	3.58 cc	21.99	

4-METHOXYTOLYL-3-SULPHONYLMETHYLTHIOMETHANE.

4-methoxytolyl-3-sulphonylmethylthioacetone was warmed for 20 minutes on the water bath in sodium carbonate solution and the resultant product recrystallised from water M.Pt. = 88°C. The yield was theoretical.

ANALYSIS

Weight of Substance	Titration $\frac{N}{50}$ Na_2CO_3	Percentage Found	Sulphur Requires
4.98	4.08	26.22	26.02
4.74	3.84	25.91	

4-METHOXYTOLYL-3-SULPHONAMIDE (44).

p.TOLYL SULPHONAMIDE (45).

p.TOLYLSULPHONYL ACETONE (46).

p.TOLYLSULPHONYLMETHYLTHIOACETONE (47).

p.TOLYLSULPHONYLMETHYLTHIOMETHANE (48)

The above compounds were prepared according to the references and found to agree.

It was found relatively easy to separate pure 4-methoxytolyl-3-sulphonamide (least soluble portion) from a mixture of the methoxytolyl and p.tolyl sulphonamides but it was extremely difficult to extract pure tolyl from an aqueous solution.

Alcoholic solution proved an unsatisfactory medium for either separation.For the purpose of estimation (page79) water was used as solvent.

p.TOLYLSULPHONYLACETONE WITH EXCESS METHYL 4-METHOXYTOLUENE-3-THIOLSULPHONATE.

1 gm of p.tolylsulphonylacetone and 4.4 gms of the methyl 4-methoxytoluene-3-thiolsulphonate compound were dissolved in alcohol and refluxed for 2 - 3 hours with .25 gms of sodium carbonate. The alcohol was then distilled off and the residue was treated with ice water and 1.5 cc 10N. Sodium hydroxide,and the whole shaken with ether (ether = alkali insoluble fraction) The aqueous layer was then acidified with 30% acetic acid and again extracted with ether (alkali soluble fraction).

Alkali insoluble fraction consisted mainly of the excess

methyl-4methoxytoluene-3-thiolsulphonate.

Alkali soluble fraction. The ether was evaporated off and the residue dissolved in alcohol. Crystals, M.Pt =114°C were obtained. Mixed M.Pt. with 4-methoxytolyl-3-sulphonyl-methylthioacetone = 114°C. Yield = .45 gm.

4-METHOXYTOLYL-3-SULPHONYLACETONE WITH EXCESS METHYL p.TOLUENE THIOLSULPHONATE.

(1) 6 to 1 with 1 mol. Sodium Carbonate.

1 gm of the 4-methoxytolyl-3-sulphonylacetone compound and 5 gms of the methyl p.toluene thiolsulphonate were dissolved in alcohol and .438 gm of carbonate added. This was refluxed for 2 hours on the waterbath and then distilled at 100°C until nothing further came over. The residue in the flask was cooled and, after the addition of ice water, treated with 5 cc of 10N caustic soda and ether (Fraction 1). Carbon dioxide was then passed in to drive out the dissolved ether and the product was precipitated in ice cold solution with the calculated quantity of acetic acid. The precipitate tended to be oily and was separated by means of extraction with ether (Fraction 2).

Fraction 1 contained a little of the hydrolysed p.tolyl-sulphonylmethylthioacetone and excess thiolsulphonate.

Fraction 2 gave just over 40% yield of p.tolylsulphonyl-methylthioacetone M.P.t. = 82.°

See tabled results (page 79)

2. 5 to 1 with ½ mol. Sodium Carbonate.

This experiment was repeated exactly as above with the

quantity differences noted in the sub-heading. The tolyl exchange product was obtained in 60% yield.

4-CHLOROPHENYLSULPHONYLACETONE AND METHYL 4-METHOXYTOLUENE-3-THIOLSULPHONATE.

Attempts to carry out analyses with equimolecular proportions of methyl-4-methoxytoluene-3-thiolsulphonate and 4-chlorophenylsulphonylacetone on the same basis were unsatisfactory owing to the fact that 4-methoxytolyl-3-sulphonylacetone was soluble in sodium carbonate solution and therefore contaminated the exchange products. Consequently the product isolated was an oil and analysis would be of little value.

4-CHLOROPHENYLSULPHONYLACETONE AND METHYL p.TOLUENE-THIOLSULPHONATE.

EXPERIMENT 1.

.23 gms of 4-chlorophenylsulphonylacetone were refluxed in 20 cc alcohol with .20 gms methyl p.toluenethiolsulphonate and .053 gms sodium carbonate for one hour. The alcohol was then evaporated off and the residue extracted with ether and water. These fractions were thoroughly washed with small quantities of water and ether respectively.

Aqueous solution. This was warmed and a little air drawn through the hot solution in order to remove the last traces of ether. It was then titrated, in the cold, in a weak sulphuric acid solution, with $\frac{N}{10}$ permanganate. Required 15.75 cc $\frac{N}{10}$: Theoretical, assuming the reaction gave pure sodium sulphinate, = 20 cc. $\frac{N}{10}$.

Ethereal solution. This fraction was dried with sodium

sulphate, evaporated to dryness, and finally heated in vacuum (water pump) at 50°C for about 4 hours: before being analysed. On combustion the product left a slight residue equivalent to >1% by weight.

ANALYSIS.

Weight of substance	$\frac{N}{71}$ $AgNO_3$ titration	$\frac{N}{50}$ Na_2CO_3 titration	% Chlorine Found	% Sulphur Found
7.08mgms	1.35 cc	5.75 cc	9.5	21.7
7.21mgms	1.38 cc	5.78 cc	9.6	21.3

Nothing could be derived from these results because of the number of variable possibilities in the analysed residue. eg. sulphinic acid, 4-chlorophenylsulphonylacetone and the hydrolysed and unhydrolysed substitution products. It was proposed to eliminate hydrolysis as far as possible by substituting potassium acetate for sodium carbonate and reducing heating to a minimum.

EXPERIMENT 2.

Equimolecular quantities of 4-chlorophenylsulphonylacetone (.23 gm), methyl p.toluenethiolsulphonate and potassium acetate were dissolved in cold alcohol, the total bulk of solution being 40 cc. This was allowed to stand overnight at ordinary temperatures. Portions were then tested, to see if the thiolsulphonate had been exhausted, by dissolving as much as possible in sodium hydroxide solution. It was found necessary to heat the solution to boiling before proceeding with the evaporation of the alcohol. The following method was employed using 3/5

of the original solution. After the alcohol had been removed at the pump the residue was dissolved in 5 cc N. sodium hydroxide solution filtered and the filtrate run directly into a solution of acetic acid exactly equivalent to the amount of sodium hydroxide added. This was then extracted with ether and the process finished as in experiment 1.

Aqueous solution. The amount of $\frac{N}{10}$ $KMnO_4$ required = 18 cc while for 3/5 solution, theoretical = 12 cc.

Ethereal Solution.

ANALYSIS.

Weight of substance	$\frac{N}{71}$ $AgNO_3$ Titration	$\frac{N}{50}$ Na_2CO_3 Titration	% Chlorine Found	% Sulphur Found
5.94mgms	2.01 cc	4.58 cc	16.9	17.0
7.56mgms	2.60 cc	5.94 cc	17.2	17.3

The excessive permanganate titration might be accounted for by the fact that the sulphinic acid was for some reason incapable of liberating sufficient acetic acid from the potassium acetate to liberate all the substitution product. Some of the latter was thus retained in the aqueous solution.

EXPERIMENT 3.

This time the mixture, dissolved in about 20 cc of cold alcohol, was allowed to stand for 4 days before the alcohol was taken off below 30°C at the water pump. The residue was then treated with a standard quantity of sodium carbonate solution and extracted with ether. The substitution product dissolved in the aqueous carbonate solution but the hydrolysed

and unchanged products remained in the ethereal solution. The ether was extracted with caustic soda which took out the unchanged 4-chlorophenyl product and this was precipitated by carbon dioxide. The substitution product was hydrolysed, before analysis, by boiling with sodium carbonate on the waterbath for 30 minutes, cooling, filtering off as much as possible and extracting the remainder with ether.

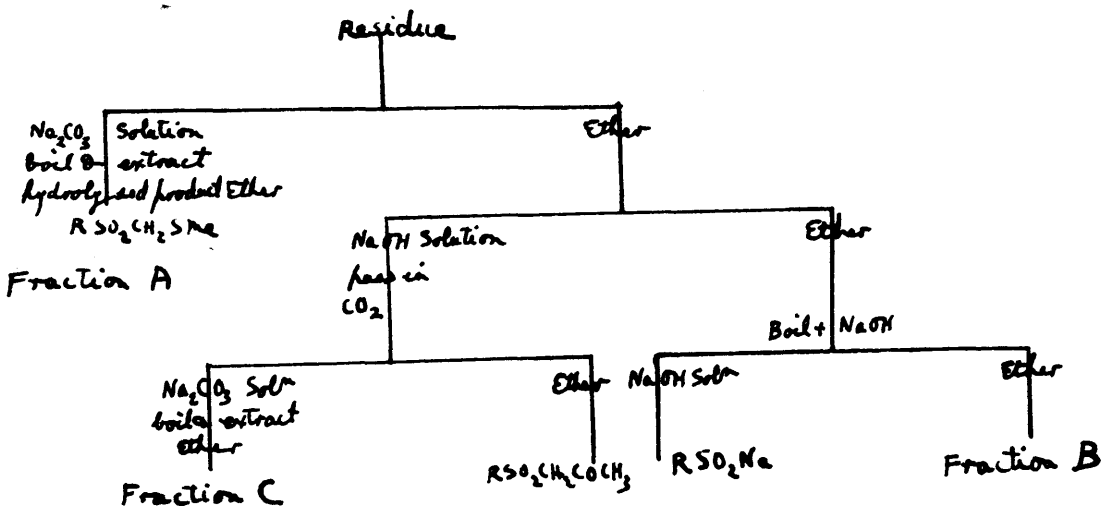
Hydrolysed product = .11 gm.

EXPERIMENT 4.

This represented the most complete method of separation. In view of the fact that the total yield was not satisfactory on previous occasions the bulk of the original solution was reduced to 7 cc and kept proportionately small throughout.

The distillate was collected in an ice cooled receiver. This proved to contain practically pure alcohol with only the very slightest trace of methyl mercaptan.

The separation can best be illustrated by the following diagram:-



The above experiment was repeated twice. On each of the three occasions .15 gm of hydrolysed product was accounted for This meant an approximate yield of 70% of theoretical.

ANALYSES.

Substance	Weight used	Titration $\frac{N}{71}$ $AgNO_3$	Percentage Chlorine Found
Experiment 1.			
Product A	6.71	.95	7.1
Product B	7.21	1.01	7.0
Product C	5.80	1.00	8.6
Experiment 2.			
Product A	6.12	.87	7.1
Product B	6.96	.96	6.9
Product C	5.68	.94	8.3
Experiment 3.			
Combined Products A, B & C	6.14 6.21	.86 .87	7.0 7.0

4-METHOXYTOLYL-3-SULPHONYLACETONE WITH EXCESS METHYL p.TOLUENE THIOLSULPHONATE.

ETHER EXTRACT

May contain:- RSO_2CH_2

Excess TSO_2SMe

Any impurities eg. TSO_2Me

Fractionally crystallise from aqueous alcohol:-

Least sol.

Yellow oil which solidifies. Warmed on water bath with Na_2CO_3 and extracted with ether.

Ether

Dissolved in alcohol and crystallised. M.Pt. = 79° Mixed with TSO_2CH_2SMe = 80° Weight = .05

Aqueous

Ether evap. off and solution made slightly acid. $FeCl_3$ added. Precipitate washed with alcohol and ether. Weight = .41

Middle

White crystalline solid. M.Pt. (crude) = 53° Mixed with TSO_2SMe = 49° Weight = .25

Most Sol.

Precipitated by $FeCl_3$ in slightly acid solution. Weight = .09

$(RSO_2)_3Fe$ (49)

ALKALI EXTRACT

May contain:- $RSO_2CH_2COCH_3$ (SMe) and RSO_2Na

CO_2 passed in to drive out dissolved ether Precipitate with calculated minimum acetic acid (ppt. would dissolve in excess). Cool and stir when the precipitated oil solidifies. Filter and extracted with ether.

Precipitate

$RSO_2CHCOCH_3$ (SMe)

Dissolved in minimum aqueous alcohol (60-70°) and set to crystallise. M.Pt. = 78-82° Gave no depression with $TSO_2CHCOCH_3$ (SMe)

Weight = .45

Solution

RSO_2Na

Solution made alkaline with 5 cc 10N NaOH Treated with Bromine in KBr, filter. Weight = 4.2 gms. Add to strong NH_3

Weight = .3 gm.

$CMeSO_2NH_2$, M.Pt.= 183°

Attempts to realise

$$RSO_2\underset{SMe}{CH}COCH_3 + RSO_2Na \qquad RSO_2\underset{SMe}{CH}COCH_3$$

The following table summarises several experiments which were carried out on the above lines. Only in the case marked with an asterisk was the slightest trace of conversion observed.

Methylthioacetone used	Sulphinate used	Solvent used	Conditions of reaction	Added substances	Result
p tolylsulphonyl (1 mol.)	p dichlorobenzene (4 mol)	acetone	Reflux 10 hours	Nil	100% tolyl compound recovered unchanged
4 methoxytolyl-3-sulphonyl (1 mol)	p toluene (1 mol)	Methyl alcohol	Reflux 8 hours	Sodium carbonate ($\frac{1}{2}$ mol)	hydrolysed methoxy-tolyl compound recovered
p tolylsulphonyl (1 mol)	4 methoxyltoluene 3	methyl alcohol	Reflux 2 hours	Sodium carbonate	hydrolysed tolyl compound recovered
p tolylsulphonyl (1 mol)	p chlorobenzene (4 mols)	ethyl alcohol	Reflux 10 hours	Sodium carbonate ($\frac{1}{2}$ mol)	hydrolysed tolyl compound 85% yield
p tolylsulphonyl (1 mol)	p chlorobenzene (4 mols)	ethyl alcohol	Reflux 3 hours	Sodium carbonate (1 mol)	hydrolysed tolyl poor yield

Methylthioacetone used	Sulphinate used	Solvent used	Conditions of reaction	Added substances	Result
*p tolylsulphonyl (1 mol)	p chlorobenzene (4 mols)	ethyl alcohol	Reflux 6 hours	Sodium bicarbonate ($\frac{1}{2}$ mol)	hydrolysed tolyl & trace 4-chlorophenyl. separated by crystallisation
p tolylsulphonyl (1 mol)	p chlorobenzene (4 mols)	ethyl alcohol	ordinary temperature 4 days	Sodium bicarbonate ($\frac{1}{2}$ mol)	mostly unchanged tolyl (70%) some hydrolysed
p tolylsulphonyl (1 mol)	p chlorobenzene (4 mols)	water	stand overnight	NaOH ($\frac{1}{2}$ mol)	No exchange
p tolylsulphonyl (1 mol)	p chlorobenzene (4 mols)	water	ordinary temperature 3 days	$NaHCO_3$ (1 mol) Na_2CO_3 ($\frac{1}{2}$ mol)	No exchange

Two similar attempts were made to obtain exchange of the radicals using the sulphinic acid instead of the sodium salt of p.chlorobenzene with p.tolylsulphonyl methylthioacetone. They were carried out at ordinary temperatures in alcohol and acetic solutions respectively. No exchange was detected.

In conclusion may I take this opportunity of conveying my sincerest thanks and deepest appreciation to my chief, Prof. G. G. Henderson F.R.S. and to my supervisor Dr. D. T. Gibson for their encouragement and many helpful suggestions.

I desire also to express my thanks to the Robert Donaldson Trustees to whom I am indebted for a Scholarship (1932-33).

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Literature.

1. Otto Annalen 1894 , 283, 183.
2. Otto Annalen 1894, 283, footnote 199, 201.
3. Troeger & Artmann J. pr Chem. 1896, 53, 493.
4. Gibson J.C.S. 1931, 2641
5. Shriner, Struck & Jorison J.A.C.S. 1930, 52, 2060.
6. Baumann Ber 1885, 18, 883.
7. Stuffer Ber 1890, 23, 1411, 3226.
8. Kenyon & Phillips J.C.S. 1930, 1677.
9. Fromm & Palma Ber 1906, 39, 3308.
10. Hilditch J.C.S. 1910, 97, 2580.
11. Posner Ber 1905, 38, 646.
12. Ruhemann J.C.S. 1905, 87, 18,
13 Otto & Damkohler J.fur Pharm. Chem. 1884, 30, 171, 321.
14 Viebock Ber 1932, 65, 586.
15. Baumann Ber 1886, 19, 2804.
16. Otto & Troger Ber 1892, 25, 3429.
17. Reference 15 page 2806.
22. Phillips J.C.S. 1925, 127, 2569.
23. Hilditch & Smiles Ber 1908, 41, 4114.
    Hilditch J.C.S. 1910, 97, 2585
    Otto J.pr. Chem. 1884, (2) 30, 177.
    Braun & Kaiser Ber 1923, 56, 553.
    Whalen & Jones J.A.C.S. 1925, 1355.
24. Fruhling, Monatshefte 3, 697.
25. Kalle Annalen 119, 162
    Rosenheim & Singer Ber 1904, 37, 2154.

26. Meyer J.pr. Chem. 1901, (2) 63, 170.

27. Perkin J.C.S. 1887, 51, 13.

29. Otto & Rossing J.pr. Chem. 1893, (2) 47, 165.
J.pr. Chem. 1898, (2) 58, 189.

30. Fajans & Frankenburger Z. physik Chem. 1923, 105, 225.

31. Mohr Annalen 1856, 97, 335.

32. Resanoff & Hill J.A.C.S. 29, 269.
Drechsel Z. anal. Chem. 1877, 16, 351.

33. Viebock Ber 1932, 65, 497.

34. Fajans & Hassel Z.Elektrochem. 1 923, 29, 495.
Fajans & Wolf Z anorg. allgem. Chem. 1924, 137, 221.

35. Kuster Z. anorg. Chem. 1897, 13, 134.

36. Kolthoff Z. anorg. allgem. Chem. 1921, 100, 156.

37. Simpson Ind. Eng. Chem. 1924, 16, 709.

38. Giblin Analyst 1933, 58, 752.

39. Friedrich Mikrochemie Pregl - Festschrift p.91-102, 1929.

40. Fajans & Hassel Z.Electrochem. 1923, 29, 495.
Pieters Chem. Weekblad 1929, 26, 6.
Berry & Durrant Analyst 1930, 55, 613.

41. Kolthoff, Laner & Sande J.A.C.S. 1929, 51, 3273.

42. Stewart J.C.S. 1922, 121, 2558.

43. Hilditch J.C.S. 1910, 97, 1098.

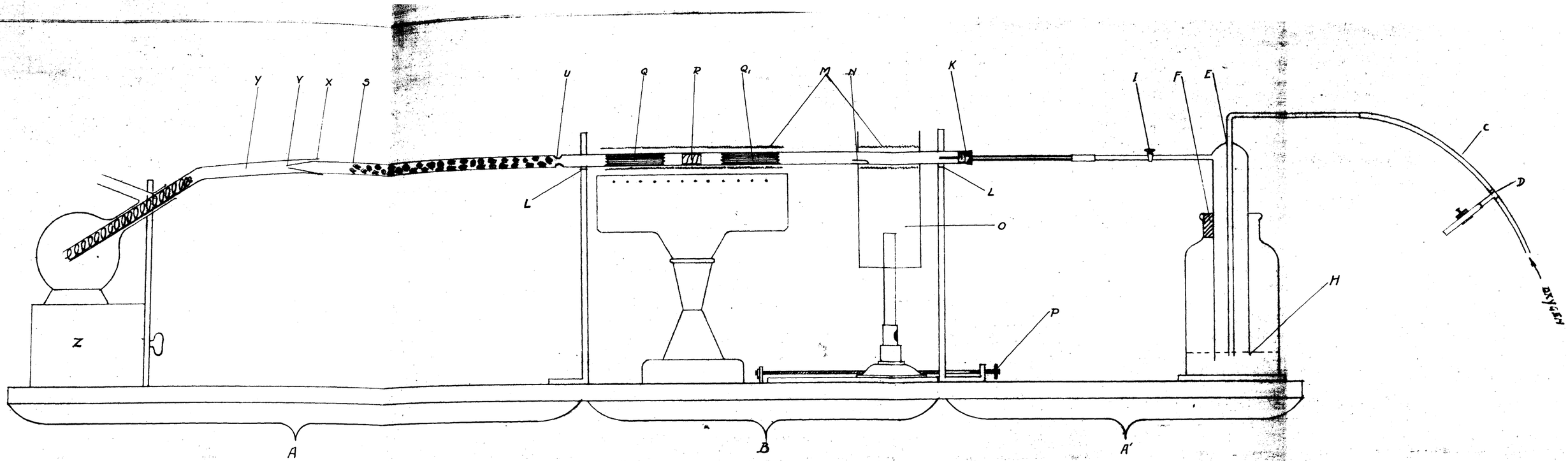
44 & 45 Otto Annalen 1867, 141, 373.

46, 47, & 48. Gibson J.C.S. 1932, 1819.

49. Thomas J.C.S. 1909, 95, 342.

50 Volhard Annalen 1878, 24, 190

51 Gibson & Smiles J.C.S. 1923, 123, 2390.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