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SYSTEMATIC ANALYSIS OF COMPOUNDS CONTAINING SULPHUR
BY REACTION GAS CHROMATOGRAPHY

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SUMMARY

A systematic analysis was developed for compounds containing sulphur, based on two basic principles: reaction gas chromatography and detection on chromatographic paper. The procedure involves combustion of the compound in air and oxygen, catalytic hydrogenation, decomposition on Raney nickel, fusion with sodium hydroxide and decomposition with boron trifluoride. Decomposition products resulting from these reactions are detected by using gas chromatography. The detection on chromatographic paper involves reactions with fuming nitric acid, pinacryptol yellow and copper(I) chloride. Positive and negative reactions of different types of sulphur bonds are presented in a table.

INTRODUCTION

In an earlier paper¹, the present authors dealt with the systematic analysis of compounds containing nitrogen. It was of great advantage to use reaction gas chromatography (GC) combined with a variety of suitable decomposition reactions. This allowed different types of chemical bonds of nitrogen in molecules to be distinguished.

The great importance of sulphur-containing compounds, for example in the petroleum industry, suggested that it would be useful to study different kinds of cleavage reactions of these compounds and to identify the products formed by using GC.

Previously, only a few other authors had used GC for studying compounds containing sulphur. THOMPSON and coworkers²⁻⁵ carried out a catalytic desulphurization process and identified the hydrocarbon residue by means of a GC method used for identifying certain sulphur-containing compounds in naphthalene. Another paper concerns sulphides⁶.

In the present paper, several reaction GC methods combined with various types of paper chromatographic detection are described.

COMBUSTION OF COMPOUNDS IN OXYGEN OR AIR

The method is based on the known reaction of sulphur-containing compounds

with oxygen to give sulphur dioxide, the formation of which is followed by using GC.

The combustion of compounds to be studied is carried out in a special 150-ml flask (Fig. 1). Filter paper is wrapped round a 0.3–0.5-g sample (the paper may be impregnated with the sample), and the paper is ignited, placed on a platinum wire and inserted into the flask. The flask is previously filled with oxygen or air when combustion in oxygen or air, respectively, is required. After completing the combustion process, a portion (about 10 cm³) of the gas in the flask is withdrawn with a syringe attached to the flask and is directly charged into a gas chromatograph.

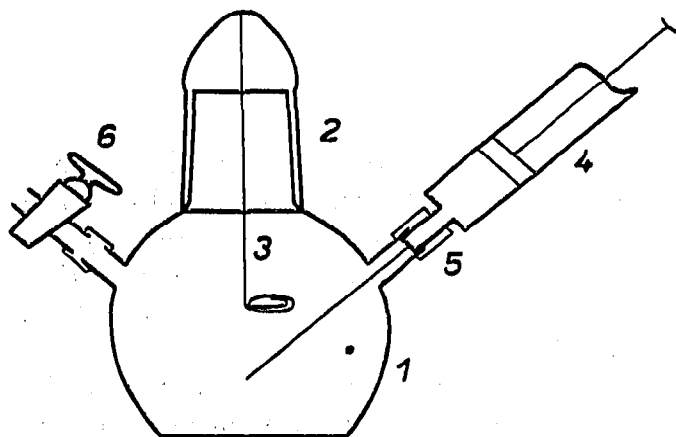


Fig. 1. Combustion flask. 1 = Glass flask; 2 = ground joint; 3 = platinum wire with a spire; 4 = syringe; 5 = silicone rubber tube; 6 = tap.

The GC procedure is carried out on silica gel previously activated at 250° for 8 h. Nitrogen is used as a carrier gas at a flow-rate of 3 l/h. The occurrence of sulphur dioxide is investigated.

Each experiment is performed twice. First the sample is burnt in oxygen, and then combustion in air is performed.

The results obtained with certain standard compounds are given in Table I. It can be seen from the results that the sulphur dioxide is formed during the combustion in oxygen of any compound containing sulphur. On the other hand, when these compounds are burnt in air, sulphur dioxide is formed (except in a few cases) only from compounds that have the =C=S bond, from compounds where the sulphur atom is a member of a heterocyclic ring, and from sulphoxides with the =SO group (in contrast to sulphones with the =SO₂ group).

CATALYTIC HYDROGENATION

In certain cases, hydrogen sulphide and sometimes also carbonyl sulphide and carbon disulphide, can be obtained from a catalytic hydrogenation process. Common catalysts cannot be used as sulphur is a catalyst poison; in addition to this, even the catalyst used here should often be renewed. The Leuna-Werke WK 9063 catalyst was found to be satisfactory.

The hydrogenation process was carried out in a quartz tube, which was situated

upstream from a chromatographic column and connected according to the scheme shown in Fig. 2.

First, the compound of interest (about 0.5 g) is dissolved in a solvent (ethyl alcohol, water, etc.) and then the catalyst is impregnated with the solution. After evaporating the solvent, the impregnated catalyst is put into a quartz reaction tube (8×0.5 cm) which is attached to the chromatographic column. Hydrogen is allowed to pass through the reaction tube for 5 min and after that tap K_1 is turned to introduce the hydrogen directly into the chromatographic column. The connection with the reaction tube is closed by tap K_2 . The reaction tube, which is equipped with a heating resistance wire, is heated to 620° in 3 min and held at this temperature for 2 min. Retention of the hydrogen sulphide formed occurs if the sample is heated for a longer period.

After 2 min, the hydrogen stream is introduced into the reaction tube by turning tap K_1 , and tap K_2 is opened so that the reaction products are carried directly into the chromatographic column.

The GC is performed under identical conditions as described above. The occurrence of hydrogen sulphide, carbonyl sulphide and carbon disulphide is examined. Only hydrogen sulphide is of interest for the purposes of this study.

As mentioned above, the formation of only hydrogen sulphide is followed

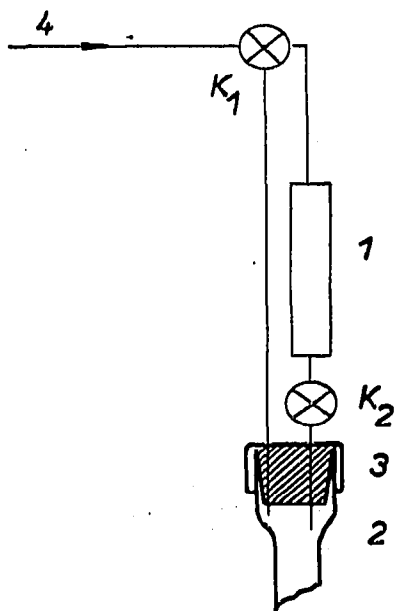


Fig. 2. Apparatus for catalytic hydrogenation. 1 = Catalytic tube; 2 = chromatographic column; 3 = cap at the top of the chromatographic column; K_1 , K_2 = taps.

during the catalytic hydrogenation, since carbonyl sulphide and carbon disulphide are actually the products of the pyrolysis that occurs together with the hydrogenation and cannot be avoided. As far as different types of sulphur bonds are concerned, the following groups show a positive reaction, *i.e.*, give hydrogen sulphide: $=SO$, $=C=S$, $-SCN$. In the case of $-SH$ and $-S$ -bonds, it was impossible to check whether or not the reaction was positive because of the volatility of the available standard compounds that resulted in their evaporation prior to the time when hydrogenation could occur.

TABLE I

SYSTEMATIC ANALYSIS OF SULPHUR-CONTAINING COMPOUNDS

+ = Positive reaction; · = traces; — = negative reaction. Coloration of spots: y = yellow; br = brown; v = violet; o = orange; bl = blue; g = grey; b = black.

Compound	Type of bond	Combustion in		Catalytic hydrogenation	Splitting on Raney nickel	Fusion with NaOH	Detection	
		Oxygen	Air				Pinacryptol yellow	Copper (I) chloride
1,2,4,5-Tetramethyl-3-benzenesulphonic acid	-SO ₃ H	+	·	—	—	—	y br	—
1,2,3-Trimethyl-4-benzenesulphonic acid	-SO ₃ H	+	·	—	—	—	y br	—
1,2,3,4-Tetramethyl-5-benzenesulphonic acid	-SO ₃ H	+	·	—	—	—	y br	—
2,5-Phenanthrenedisulphonic acid	-SO ₃ H	+	·	—	—	—	v	—
Sulphanilic acid	-SO ₃ H	+	·	—	—	—	br	—
Sodium <i>p</i> -toluenesulphonate	-SO ₃ Na	+	·	—	—	—	o	—
Methyl <i>p</i> -toluenesulphonate	-SO ₃ CH ₃	+	·	—	—	—	o	—
Sodium benzenesulphonate	-SO ₃ Na	+	—	—	—	—	o	—
Benzenesulphamide	-SO ₂ NH ₂	+	·	—	—	—	v	—
<i>o</i> -Toluenesulphamide	-SO ₂ NH ₂	+	·	—	—	—	v	—
Sulphanilacetamide	-SO ₂ NH-	+	·	—	—	—	br	—
<i>p</i> -Acetaminobenzenesulphamide	-SO ₂ NH ₂	+	·	—	—	—	br	—
<i>p</i> -Toluenesulphonic <i>N</i> -benzoyl-amide	-SO ₂ NH-	+	·	—	—	—	br	—
Dibenzyl disulphone	-SO ₂ -SO ₂ -	+	·	—	—	—	—	—
Dimethyl sulphone	=SO ₂	+	·	—	—	—	v	—
<i>n</i> -Propylbenzyl sulphone	=SO ₂	+	—	—	—	—	y	—

[illegible]

DECOMPOSITION ON RANEY NICKEL

The decomposition on Raney nickel is performed in such a way as to generate hydrogen sulphide during the reaction, which is again followed by a GC method. The reaction is performed in a glass reactor described previously¹, but with a larger volume.

The compound to be tested (0.5 g) is placed in the reactor and 1.5 ml of solution containing Raney nickel (10 g of Raney nickel in ethanol, water or *n*-butanol) is added. The reactor is heated at 100° for 15 min. Concentrated hydrochloric acid (2 ml) is added with a syringe through the rubber stopper of the reactor and gaseous products are sampled with a 10-ml syringe. These products are then charged into a gas chromatograph.

The presence of hydrogen sulphide is followed under the same chromatographic conditions as described above.

The decomposition process on Raney nickel is performed in such a manner as to obtain hydrogen sulphide as the final product. In addition to this, certain amounts of less volatile compounds occurred: this component was not identified since it was of no importance in the present study. The reaction was shown to be positive in the case of the following bonds: $=C=S$, $-S-$ (heterocyclic) and $-CSN$. Only a slightly positive reaction was found with sulphides.

ALKALI FUSION

The alkali fusion was also intended to give a sulphide whose acidification yields hydrogen sulphide, the formation of which is followed. About four pellets of potassium hydroxide are melted in a nickel crucible, and about 0.5 g of the compound to be tested is added (when it exists in the solid state). The melt is heated until it becomes dark (for about 3 min) and, after cooling, it is dissolved in 2 ml of water. The solution is transferred into a rubber-stoppered test tube. Concentrated hydrochloric acid (1 ml) is added with a syringe through the stopper. Hydrogen sulphide, when formed, is sampled with a 10-ml syringe and identified on the basis of a GC method. The GC procedure is performed in the manner described above.

Only certain types of bonds are able to react with potassium hydroxide during the alkali fusion to form potassium sulphide, *viz.*, $=C=S$ and $-SCN$ groups. It was not possible to decide which reactions of $-SH$ and $=S$ groups occurred owing to the high volatility of the standards available.

DECOMPOSITION WITH BORON TRIFLUORIDE

The decomposition of sulphur-containing compounds with boron fluoride shows a surprising behaviour. The sulphur dioxide is formed even in the presence of air and in certain cases, even other products such as carbonyl sulphide, hydrogen sulphide and carbon disulphide are formed.

The method for decomposition of the compounds by the action of the boron trifluoride is identical to that described earlier for decomposing organometallic com-

pounds^{7,8}. A small glass reactor is used for the decomposition process, and is described in detail in the earlier papers. The procedure is also the same except that the temperature to which the reactor is heated is 200°.

GC is used to follow the formation of carbon dioxide, sulphur dioxide, carbonyl sulphide, hydrogen sulphide and carbon disulphide; however, the presence of sulphur dioxide is of the greatest importance.

Conditions of the GC are the same as in previous cases except that silica gel has to be more often activated.

From chromatograms obtained in the course of identifying the decomposition products of compounds with different types of sulphur bonds, it can be seen that sulphur dioxide is the major product of the reaction with boron trifluoride. This is rather surprising as usually a relatively high temperature and an oxygen atmosphere are required to convert a sulphur-containing organic compound to sulphur dioxide. Although only a limited variety of compounds was examined, it seems that carbonyl sulphide is formed in addition to sulphur dioxide when the sulphur is bound in the form of $=C=S$.

Sulpho-, sulphony- and sulphamido groups yield essentially no decomposition product that contains sulphur. Also, sulphur bound to the organic residue as well as elementary sulphur can yield no decomposition product. This difference can help to decide in certain cases, whether the sulphur is bound in an organic or an inorganic compound.

DETECTION METHODS

Another way of distinguishing sulphur bonds in molecules, and possibly of revealing their presence, involves detection methods in which chromatographic paper is used.

Detection with fuming nitric acid can be considered first. This method was found by the authors in studies on the detection of organosilicon compounds having a phenyl group. In the course of the detection with the fuming nitric acid, elementary carbon is produced (as a black spot on the chromatogram) only by decomposition of the phenyl group and only small amounts of nitro compounds can be observed. The authors attempted to use this procedure for compounds containing sulphur and the results revealed that with most of these compounds elementary sulphur is formed, giving a yellow spot on the chromatographic paper. The sensitivity of this detection method is as high as 2–4 μg of sulphur. This limit may be lowered further when the paper is immersed into 10% sodium hydroxide solution immediately after dipping it in the fuming nitric acid. A faint, violet spot is formed in this case.

Another method involves spraying the chromatogram with Pinacryptol yellow. It can be seen from Table I that sulphur-containing compounds commonly give a yellow or orange to brown coloration.

Another, more selective, spraying may be performed with a copper(I) chloride which reacts with certain sulphur-containing compounds, forming brown to black spots.

In the case of the detection with fuming nitric acid, the sulphur-containing compound is applied to the chromatographic paper in an amount corresponding to

TABLE II

REACTIONS OF SULPHUR-CONTAINING COMPOUNDS WITH FUMING NITRIC ACID

Sample	Type of bond	Sample dissolved in	Reaction
4,4'-Diamino-3,3'-disulphodiphenyl	-SO ₃ H	Pyridine + ether	—
3-Diphenylsulphonic acid	-SO ₃ H	Pyridine + ether	—
Thiosalicylic acid	-SH	Ether + benzene	++
Triethoxymercaptosilane	-SH	Ether + pyridine	+++
<i>n</i> -Propylbenzyl sulphone	=SO ₂	Pyridine + ether	++
Dibenzyl sulphone	=SO ₂	Ether	++
<i>n</i> -Butylbenzyl sulphone	=SO ₂	Ether	+++
Isopropylbenzyl sulphone	=SO ₂	Ether	+++
Dimethyl sulphone	=SO ₂	Ether + pyridine	+++
Dibenzyl disulphone	-SO ₂ -SO ₂ -	Ether	+++
Dibenzyl sulphoxide	=SO	Ethanol	—
Thioacetamide	=C=S	Ether	++
Ethyl ethylxanthoacetate	-C=S	Ether + pyridine	+
Sodium thiocarbonate	$\begin{array}{c} \\ \text{S}- \\ -\text{CS}_3^{2-} \end{array}$	Benzene	+
Saccharin	C-SO ₂ -NH	Ether	++
<i>p</i> -Toluenesulphonic acid			
<i>N</i> -benzylamide	-SO ₂ NH-	Pyridine	++
<i>p</i> -Aminobenzenesulphamidothiazole	-SO ₂ NH-	Ethanol + ether	++
3-Methoxy-6-sulphanilamidopyridazine	-SO ₂ NH-	Ether	+
Sulphanilacetamide	-SO ₂ NH-	Pyridine	—
<i>o</i> -Toluenesulphamide	-SO ₂ NH ₂	Ether	+
<i>p</i> -Acetaminobenzenesulphamide	-SO ₂ NH ₂	Benzene + pyridine	+
Thianthrene	S	Ethanol	—
Potassium sulphocyanide	-SCN	Ethanol + water	—
<i>p</i> -Methylbenzene sulphochloride	-SO ₂ Cl	Benzene	+
Bis(<i>p</i> -nitrophenyl)sulphide	-S-	Pyridine + ether	++

10 µg of sulphur. The paper is then dipped into the fuming nitric acid (sp.gr. = 1.50) and then, immediately into distilled water. Naturally, the same detection can be performed with a chromatogram. The spots are yellow; for reactions of individual compounds, see Table II.

The detection with Pinacryptol yellow is carried out by spraying the paper with a 0.05% solution of this reagent. The spots are observed under UV light.

In the third method, a saturated solution of copper(I) chloride is used for spraying the chromatographic paper with the compounds of interest.

All the above detection methods offer a further differentiation with respect to the types of sulphur bonds (Table III). Whereas essentially all compounds containing sulphur react with Pinacryptol yellow, the detection methods with fuming nitric acid or copper(I) chloride are not always positive.

CONCLUSIONS

The above methods, whose final results are summarized in Table III, represent good, but not yet perfected possibilities of identifying the type of sulphur bond in an organic compound. A disadvantage is that the variety of available standard compounds is limited, as certain deviations can occur from the behaviour described in Table III.

TABLE III

REVIEW OF SULPHUR BONDS FROM THE STANDPOINT OF THE SYSTEMATIC ANALYSIS OF SULPHUR-CONTAINING COMPOUNDS

Checked only with compounds which were used in the systematic analysis. + = positive reaction; - = negative reaction; blank = not tested; * = the tested standards were volatile; () = sometimes positive and sometimes negative.

Bond	Combustion		Catalytic hydrogenation	Decomposition on Raney nickel	Fusion with NaOH	Decomposition with BF_3	Detection		
	Oxygen	Air					Fuming HNO_3	Pinacryptol yellow	Copper(I) chloride
$=\text{SO}_2$	+	+	-	-	-	+	+	+	-
$=\text{SO}$	+	+	+	-	-	-	-	+	-
$=\text{C}=\text{S}$	+	+	+	+	+	+	+	+	+
Heterocyclic									
C-S-C	+	+	-	+	-	+	-	+	-
$-\text{SO}_2\text{NH}-$	+	-	-	-	-	+	+	+	-
$-\text{SO}_2\text{NH}_2$	+	-	-	-	-	-	+	+	-
$-\text{SO}_3$	+	-	-	-	-	-	-	+	-
$-\text{SCN}$	+	-	+	(\pm)	+	-	-	+	+
$-\text{SH}$	+	-	+	(\pm)	+	(+)	+	+	-
$-\text{S}-$	+	-	+	+	+	+	+	+	*

During these investigations, it must be remembered that a negative reaction can result from the high volatility of the sample, from its inadequate solubility in the solvent chosen, etc.

Nevertheless, the authors consider the procedure to be as useful as other methods based on the reaction GC principle, in spite of certain drawbacks and the incomplete character of the data obtained.

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