

GAS-CHROMATOGRAPHIC STUDY OF THE DECOMPOSITION OF THIO-CARBAMIC COMPOUNDS AS A FUNCTION OF TEMPERATURE

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INTRODUCTION

It is well known that the decomposition of thio-carbamic compounds in the cold and in acidic media can yield various sulphur compounds. In the specific case of ethylene bis-dithiocarbamates, the products may include hydrogen sulphide besides carbon disulphide and ethylenediamine sulphate, particularly if the decomposition is carried out below 100°.

The gas-chromatographic determination of carbon disulphide was studied in earlier investigations, which have already been reported by one of the present authors^{1,2}. It was also desired to determine hydrogen sulphide and, possibly, to investigate other sulphur compounds which, according to the literature, might be formed in the decomposition of the thio-organic compounds in question. A method was therefore developed for the determination of hydrogen sulphide which would eliminate any interference by sulphur compounds other than hydrogen sulphide.

Many analytical methods have been described for the determination of hydrogen sulphide, carbon disulphide, mercaptans, alkyl sulphides, etc., in mixtures. Such methods are, however, rather difficult to carry out, and are not always completely reproducible.

Gas-chromatographic methods, which are based on physical rather than chemical characteristics, are particularly suitable, owing to their high sensitivity and to their selectivity, which permits the elimination of interference frequently encountered in other methods.

Excellent results were obtained using gas-chromatographic methods, by COOPE AND BRYCE³ in their study of the pyrolysis of dimethyl disulphide, and by RYCE AND BRYCE⁴ and EDWARDS *et al.*⁵ in petrochemical analysis. The work on petrochemical analysis⁴ was carried out with a view to obtaining a gas-chromatographic adsorption system specific for sulphur-bearing compounds. Of the various adsorbents tested, RYCE AND BRYCE⁴ found that tricresyl phosphate on Celite, in the proportions recommended by JAMES AND MARTIN⁶, was suitable for the fractionation of acidic sulphur compounds.

In the above-mentioned gas-chromatographic investigation on carbon disulphide^{1,2}, it was observed that, below the temperature recommended by CLARKE⁷ (100°), the yield of carbon disulphide varied according to the temperature at which the dithiocarbamates were distilled.

There is no general agreement regarding the products which may be formed during the decomposition of these compounds.

In the present work it was intended to examine, by a gas-chromatographic method, such decomposition as a function of temperature. For such an investigation a reliable method was necessary and if possible simultaneous determination of hydrogen sulphide and carbon disulphide would be advantageous.

DETERMINATION OF HYDROGEN SULPHIDE AND CARBON DISULPHIDE

Preliminary experiments showed that tricresyl phosphate perfectly fulfilled the requirements for the case in question as the stationary phase, and was also found to be suitable not only for hydrogen sulphide, as shown by RYCE AND BRYCE⁴, but also for carbon disulphide.

In contrast to most literature reports concerned with the investigation of gaseous mixtures, the object of the present work was the gas-chromatographic analysis of substances displaced as gases from solids or solutions by chemical reactions. Such gases should be condensed at low temperatures, to allow their rapid introduction *in toto* into the adsorption equipment for the quantitative determination.

TABLE I

EXPERIMENTAL CONDITIONS FOR THE DETERMINATION OF HYDROGEN SULPHIDE BY GAS CHROMATOGRAPHY

Apparatus	Fractovap model B (C. ERBA-Milan)
Support	Celite C22, 30-60 mesh
Column	Length 4 m; I.D. 0.6 cm
Stationary phase	Tricresyl phosphate (25 %)
Carrier gas	Helium
Current	5.3 l/h
Temperature of thermostat chamber	20° ± 0.2°
Bridge current	8 mA
Speed of recording chart	1.25 cm/min
Retention time of hydrogen sulphide	5 min 12 sec

The optimum retention time, which has permitted the complete isolation of hydrogen sulphide, and hence its reliable detection, as well as the measurement of the corresponding peak without the need for extrapolation, can be obtained by working at 20° under a helium current of 5.3 l/h. Table I shows the experimental conditions used, and an example of the hydrogen sulphide peaks obtained is reproduced in Fig. 1.

Hydrogen sulphide used for the calibration was produced from alkaline solutions (5 % sodium hydroxide) containing known concentrations of sodium sulphide, from which samples were removed with a microsyringe to introduce the desired quantity of the material into the distillation apparatus.

The hydrogen sulphide was evolved by means of sulphuric acid, and was condensed from a current of helium carrier gas, in a liquid air trap, where it solidified together with other products which possibly included small quantities of water vapour. The trap was then connected to the gas chromatography equipment (ERBA Fractovap model B), and the contents were vaporised and transferred to the adsorption column by entrainment in a current of helium.

To meet the requirements of this work the design of the trap must be such that it is sufficiently accurate in operation to permit the determination of hydrogen sulphide in the concentration range of 10^{-7} to 10^{-4} moles per litre.

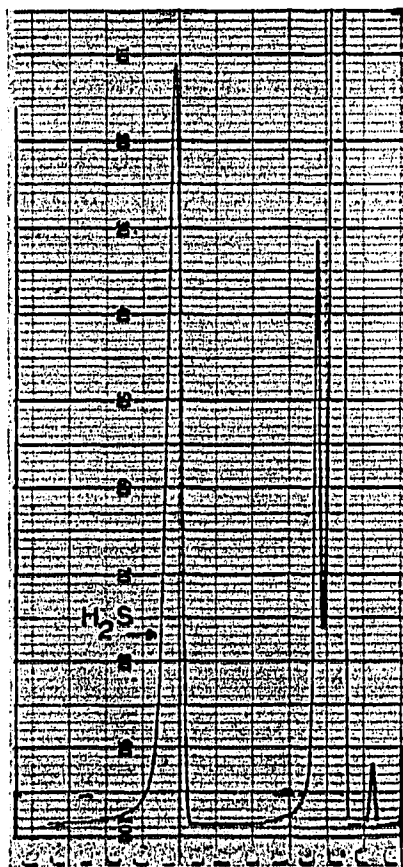


Fig. 1. Hydrogen sulphide peak.

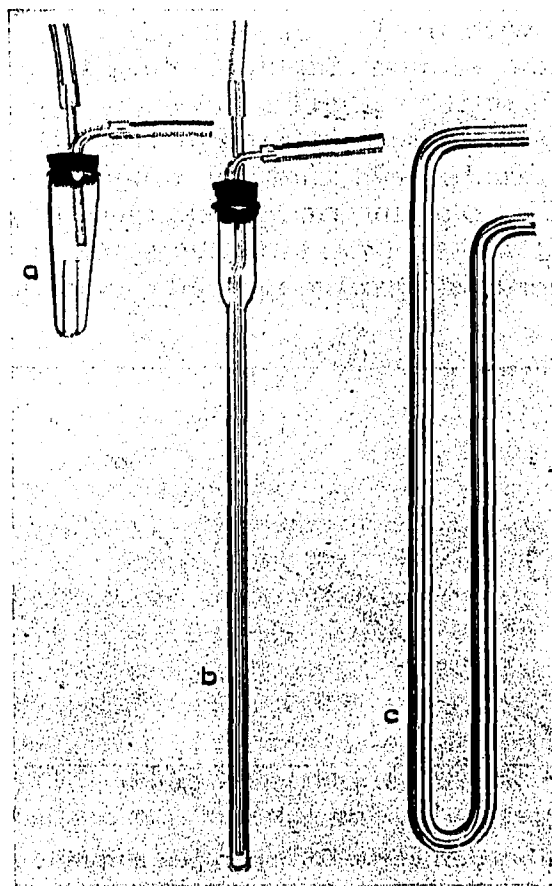


Fig. 2. Types of trap used.

Investigation of types of trap

Fig. 2 shows three types of traps studied for suitability in the present work. Type (a) was inserted directly into the chromatographic apparatus in an attempt to simplify the displacement of the hydrogen sulphide, by avoiding the need for distillation and trapping in liquid air, which takes about an hour. This trap is so designed that direct contact between the reagents is achieved at the desired moment. However, owing to the excessive quantity of water vapour displaced during the reaction and the slowness of the latter, the use of this trap is not recommended, particularly in the case of quantitative work.

Trap (c), which has a capillary section and has been described in an earlier note⁸, was also found to be unsuitable for this work; when it was inserted directly into the end of the distillation apparatus, as illustrated earlier⁸, or totally immersed in liquid air or nitrogen in a Dewar flask, it allowed appreciable quantities of the gas being examined to escape before it had completely solidified. It should be remembered that the distillation was carried out with gentle suction in a current of helium.

The peculiar structure of trap (b) permitted a gradual cooling of the hydrogen sulphide, and solidification along the internal capillary tube coaxial with the outer envelope. A cadmium acetate detector, buffered to pH 6 and inserted immediately after the trap, gave no indication of any escape of gas, in contrast to the behaviour observed with the U-shaped trap (c).

Using sodium sulphide solutions, made alkaline as described above to avoid hydrolysis of the sulphide, it was possible to construct a calibration curve, shown in Fig. 3, from the results listed in Table II.

It can be seen that the range of concentration which can be quantitatively analysed by planimetric measurement of areas under the peaks lies between 10 and 1000 γ . It was considered unnecessary to extend the curve to higher concentrations, since other less sensitive methods could be used in such cases.

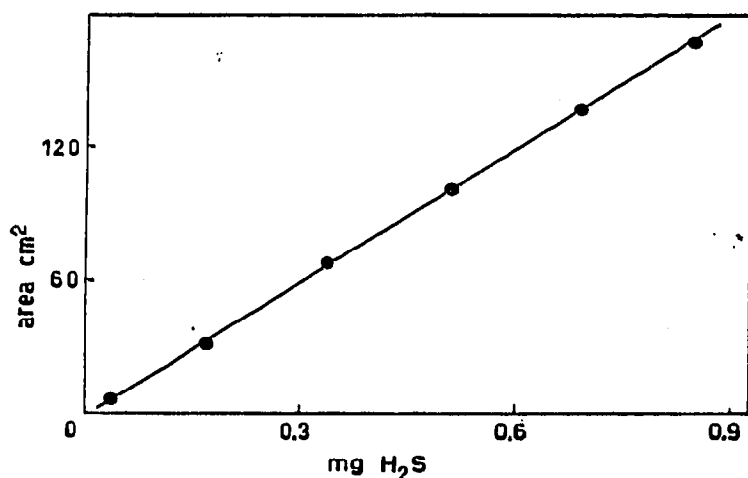


Fig. 3. Calibration curve for hydrogen sulphide.

Although the gas-chromatographic technique adopted in the present work reduced the limits of detection for hydrogen sulphide to about 3-4 γ , such results are, however, of only qualitative value, since appreciable errors are introduced in the determination of the areas under the peaks at these concentration levels.

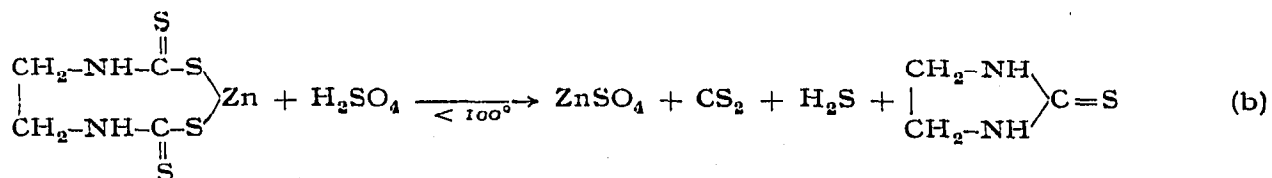
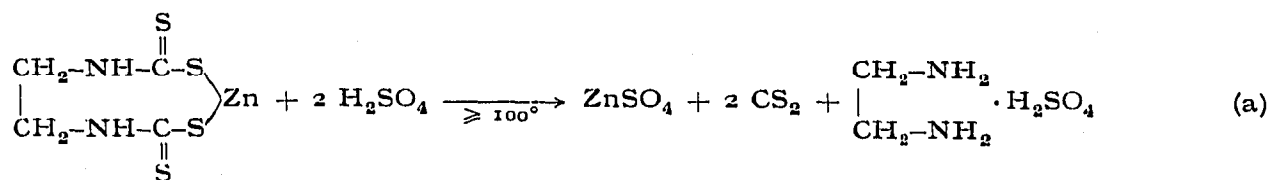
TABLE II

DATA RELATING HYDROGEN SULPHIDE CONCENTRATION WITH PEAK AREA

<i>mg of hydrogen sulphide</i>	<i>Area under the peak in cm²</i>
0.034	6.8
0.170	33.2
0.340	68.0
0.510	102.0
0.680	136.4
0.850	168.5

INVESTIGATION OF DECOMPOSITION REACTION

As is known from the literature⁷, the decomposition of ethylene bis-dithiocarbamates can proceed by two different paths, according to the temperature:



Earlier work carried out by one of the present authors^{1,2,8} was concerned with the development of a gas-chromatographic method, based on reaction mechanism (a), for the determination of CS_2 in such a way as to eliminate any source of error resulting from the possible presence in the system of other interfering sulphur compounds. Mechanism (b) was considered in the present work, the aim being to determine, under otherwise identical conditions, the temperature at which reaction (b) leading to the formation of hydrogen sulphide could be detected to the greatest extent.

The first step was naturally to prepare zinc ethylene bis-dithiocarbamate in the purest possible state, particularly as regards sulphur to ensure that the hydrogen sulphide evolved during the acid decomposition was not even partly derived from sulphur present in any form as an impurity in the finished product.

The method used in the preparation of the compounds in question has been reported in an earlier paper⁹ relating to investigations carried out by one of the authors on the amino-base constituents of dithiocarbamic acid derivatives.

With regard to the ethylene thiourea reported among the decomposition products of reaction (b) above, it was shown chromatographically that this compound could not be found in the residue from the distillation of acidic solutions of the ethylene bis-dithiocarbamates under an atmosphere of helium.

When pure ethylene thiourea is subjected to the same treatment with thiourea at the same temperature as that at which the various distillation residues are obtained, it gives an R_F value, on chromatographic examination, exactly the same as that obtained by chromatography of pure ethylene thiourea.

Ethylene thiourea can also be detected when pure ethylene bis-dithiocarbamates, not subjected to any previous treatment, are chromatographed under the conditions reported below (see Table III). It thus appears that the ethylene thiourea is already present in the ethylene bis-dithiocarbamates, and is not formed during the thermal decomposition of the dithio compound with sulphuric acid, so that this decomposition must give rise to sulphur compounds of another type. The experimental conditions shown in Table III were derived, with some modifications, from those described for an earlier investigation carried out at this Institute¹⁰.

TABLE III

EXPERIMENTAL CONDITIONS AND R_F VALUES FOR CHROMATOGRAPHY OF ETHYLENE THIOUREA AND THIOUREA

Method	Descending, on paper
Paper	Whatman 3 MM
Developer	Isobutyl alcohol-isopropyl alcohol-formic acid-water (40:30:10:20)
Temperature	22°
Time	12 h
Detector	Ammoniacal solution of silver nitrate
R_F for ethylene thiourea	0.72
R_F for thiourea	0.55

In order to avoid even slight losses in the determination of the hydrogen sulphide, we thought of substituting the switching apparatus supplied for the chromatographic apparatus for the introduction of the gaseous products with another device to eliminate the disadvantage of inevitable dead spaces. The preferred method was to insert the condensation cell in the sockets of the apparatus by a fairly simple device consisting of two suitably clamped glass Y-pieces fitted with polythene connections (Fig. 4).

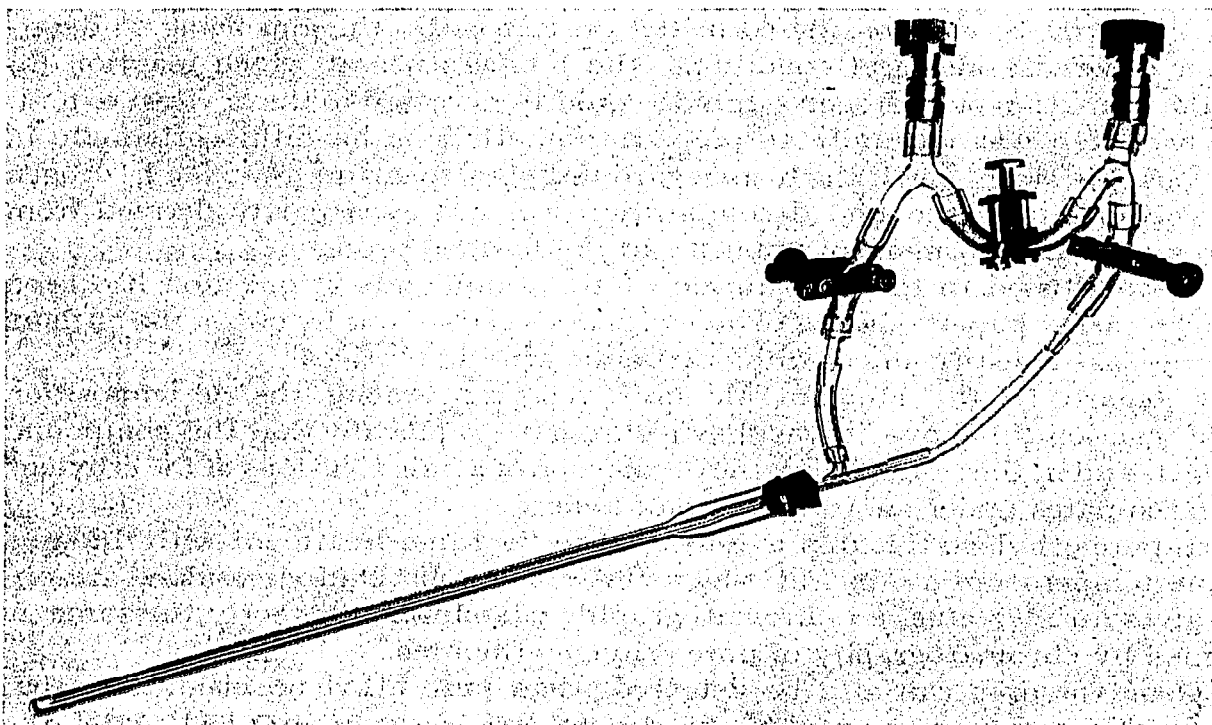


Fig. 4. Trap with connection to chromatographic apparatus.

Effect of temperature

The products of acidic decomposition of the ethylene bis-dithiocarbamates were distilled for about 1 h in a current of pure nitrogen to avoid any possible oxidation, at 50°, 60°, 70°, 80° and 90°. The sulphuric acid used in all tests was 1.1 N, *i.e.* at

the concentration recommended for CLARKE's method⁷ for the determination of dithiocarbamic acid derivatives.

To facilitate following the course of the decomposition of the thio-organic compounds in question, the hydrogen sulphide and carbon disulphide were detected simultaneously by gas chromatography, under the conditions described earlier for hydrogen sulphide. For this purpose, it was sufficient to construct a calibration curve for carbon disulphide at 20°, which is shown in Fig. 5 and which was derived

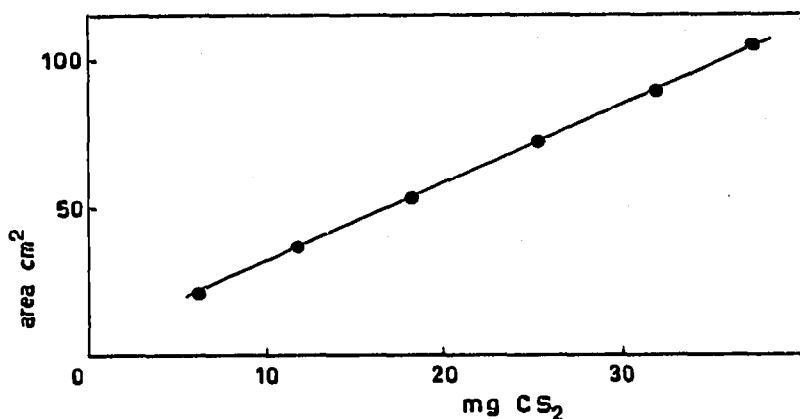


Fig. 5. Calibration curve for carbon disulphide.

from the data given in Table IV. The concentrations of carbon disulphide, which had solidified from time to time together with the hydrogen sulphide in the trap immersed in liquid air during distillation, were obtained from this curve. The retention time of the carbon disulphide increased under the conditions described to 45 min, as compared with 9 min 45 sec at 80° in the investigation mentioned earlier¹.

TABLE IV

DATA FOR CONSTRUCTION OF CALIBRATION CURVE FOR CARBON DISULPHIDE

mg of carbon disulphide	Area under peak in cm ²
6.0	11.0
12.7	36.2
19.1	53.4
25.5	72.5
31.8	89.0
37.2	105.3

Simultaneous detection of the two sulphur compounds speeded the determination of their respective concentrations and of their ratio. It was then possible to verify whether, and under what conditions, the molar ratio between hydrogen sulphide, carbon disulphide, and ethylene thiourea was effectively 1:1:1, as reported in the literature, *i.e.* according to reaction (b) above.

Reaction products and their molar ratios

Table V shows the percentages of the various sulphur compounds, deduced

TABLE V

PERCENTAGE OF CS₂, H₂S AND OTHER MONOSULPHUR COMPOUNDS AS A RESULT OF DECOMPOSITION OF ETHYLENE BIS-DITHIOCARBAMATES AT VARIOUS TEMPERATURES

<i>Decomposition temperature</i>	<i>Per 25.694 mg of sulphur</i>	<i>%</i>
50°	17.519 mg as carbon disulphide	68.18
	0.020 mg as hydrogen sulphide	0.08
	8.155 mg as other monosulphur compounds	31.74
60°	20.214 mg as carbon disulphide	78.67
	0.016 mg as hydrogen sulphide	0.08
	5.464 mg as other monosulphur compounds	21.26
70°	20.908 mg as carbon disulphide	81.37
	0.021 mg as hydrogen sulphide	0.08
	4.765 mg as other monosulphur compounds	18.55
80°	21.477 mg as carbon disulphide	83.59
	0.038 mg as hydrogen sulphide	0.15
	4.179 mg as other monosulphur compounds	16.26
90°	24.509 mg as carbon disulphide	95.39
	0.038 mg as hydrogen sulphide	0.15
	1.147 mg as other monosulphur compounds	4.46

TABLE VI

VARIATION OF MOLAR RATIOS OF REACTION PRODUCTS WITH TEMPERATURE

<i>Decomposition temperature</i>	<i>Moles</i>	<i>Molar ratio</i>
50°		
Ethylene thiourea	0.255	1
Carbon disulphide	0.274	1.07
Hydrogen sulphide	0.0005	0.002
60°		
Ethylene thiourea	0.171	1
Carbon disulphide	0.316	1.85
Hydrogen sulphide	0.0005	0.003
70°		
Ethylene thiourea	0.149	1
Carbon disulphide	0.327	2.19
Hydrogen sulphide	0.0005	0.003
80°		
Ethylene thiourea	0.131	1
Carbon disulphide	0.336	2.56
Hydrogen sulphide	0.001	0.008
90°		
Ethylene thiourea	0.036	1
Carbon disulphide	0.386	10.64
Hydrogen sulphide	0.001	0.028

from the sulphur concentrations due to each of the compounds determined by gas chromatography, and related to the total sulphur content of the dithiocarbamate analysed from time to time.

From the results, it was possible to deduce that at 50° the molar ratio of reaction (b) approached the value of 1:1 for the carbon disulphide and ethylene thiourea (or a compound containing one atom of sulphur) whilst the molar ratio of hydrogen sulphide with respect to the other two compounds was found to be 0.002. At 80° the molar ratios between ethylene thiourea, carbon disulphide, and hydrogen sulphide become 1:2.5:0.007, changing at 90° to 1:10.6:0.03. The molar ratios at the various temperatures are shown in Table VI.

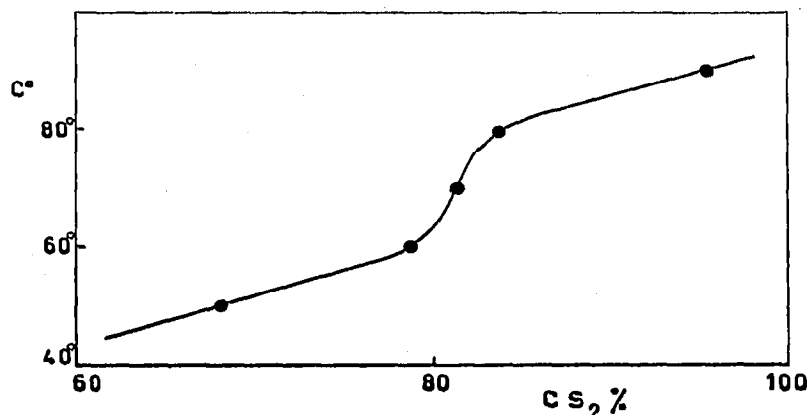


Fig. 6. Percentages of carbon disulphide at various temperatures.

Even assuming that the fraction of sulphur other than that due to carbon disulphide and hydrogen sulphide is a constituent of the ethylene thiourea, or at least of some compound containing one atom of sulphur (mercaptan or isothiocyanate), the reaction in question only gives a ratio of 1:1 around 50°, and then only for carbon disulphide and the monosulphur compound, whatever the latter may be. The molar ratio of hydrogen sulphide corresponding to reaction (b) was never observed at temperatures between 50° and 90°.

Fig. 6 shows a graph of the percentages of carbon disulphide found by analysis, as a function of the decomposition temperature of the dithiocarbamate. It can be seen that the variation follows the same course below 60 and above 80°, being rather less pronounced between these temperatures.

SUMMARY

A description is given of the experimental procedure developed for the simultaneous determination of hydrogen sulphide and carbon disulphide, evolved during the decomposition of metal ethylene bis-dithiocarbamates in acid media, at temperatures between 50° and 100°. The limits of sensitivity obtained with the apparatus used for the quantitative determination of these gaseous products are described.

The various reaction mechanisms proposed for the decomposition of the ethylene bis-dithiocarbamates are considered, and the molar ratios of the experimentally obtained sulphur compounds in relation to the total sulphur content of the original thio-organic compound are discussed.

REFERENCES

- 1 C. BIGHI, *Atti Accad. Sci. Ferrara*, 38 (1961) 1.
- 2 C. BIGHI, *Ann. Chim. (Rome)*, 53 (1963) 1061.
- 3 J. A. R. COOPE AND W. A. BRYCE, *Can. J. Chem.*, 32 (1954) 768.
- 4 S. A. RYCE AND W. A. BRYCE, *Anal. Chem.*, 29 (1957) 925.
- 5 W. R. EDWARDS, D. E. NICHOLSON AND G. A. REIDLAND, *Gas-Chromatog. Abstr.*, 44 (1959) 271.
- 6 A. T. JAMES AND A. J. P. MARTIN, *Biochem. J.*, 50 (1952) 979.
- 7 D. G. CLARKE, H. BAUM, E. L. STANLEY AND V. F. HESTER, *Anal. Chem.*, 23 (1951) 1842.
- 8 C. BIGHI, *J. Chromatog.*, 14 (1964) 348.
- 9 C. BIGHI AND L. PENZO, *Ann. Chim. (Rome)*, 53 (1963) 1068.
- 10 G. TRABANELLI, *Atti Accad. Sci. Ferrara*, 35 (1958) 157.

J. Chromatog., 17 (1965) 13-22