gram, but is cut off at the limit of 70% for each salt.

A different view of the tetrahedron, bringing out something of the water content of the saturated solution, is shown in Fig. 6, which is a Schreinemakers projection,[18] obtained by superimposing the H_2O and $(NH_4)_2SiF_6$ corners of the tetrahedron and projecting parallel to the edge H_2O–$(NH_4)_2SiF_6$. Finally, the salt proportions (water neglected) of the saturated solutions are projected, radially from the H_2O corner upon the salt base, in the Jänecke diagram of Fig. 7. This represents the relative weight percentage of each salt in the total salt content.

Of the two 3-solid invariant points, point *2*, lying, as seen in Fig. 7, in the triangle of its three solids, A, B, D, is congruently saturated with them and is the congruent drying-up point, at equilibrium, for all solutions with salt proportions in the triangle ABD, with the phase reaction Liquid → A + B + D + $H_2O\uparrow$ in isothermal evaporation. Point *1*, lying outside the triangle of its solids, B, C, D, is incongruently saturated. Its phase reaction is of the transition type, Liquid + C → B + D + $H_2O\uparrow$. It is, therefore, the incongruent drying-up point, at equilibrium, for isothermal evaporation of solutions with salt proportions in triangle BCD. Solutions reaching point *1* from the region D*1*B would lose solid C in the invariant reaction (for complete equilibrium) and then travel on curve *1* → *2* to point *2*, to dry up to A + B + D. With a rate too high for complete equilibrium, solid C will not be consumed at point *1*, and all liquids reaching point *1* proceed to point *2*, which is therefore the practical drying-up point for the whole system. Point *2* is therefore the only minimum of vapor pressure of the isothermal solubility surfaces and curves, and the arrows on the curves indicate the direction followed during isothermal evaporation of the solutions saturated with two solids. The phase reaction on curve *c* → *1* is the same as that at the ternary point *c* itself, Liquid + C → D + $H_2O\uparrow$, except that the liquid now contains NH_4Cl in addition. This transition curve is therefore crossed, in isothermal evaporation with complete equilibrium, only by solutions with original salt proportions in the region *c1*D, when, with the liquid traveling on the curve, C comes to be completely consumed. For practical conditions, however, it is crossed by any solution reaching it, or from the region *c1*C, and the unchanged C takes hardly any part in the ensuing phase reactions.

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[18] F. A. H. Schreinemakers, *Z. physik. Chem.*, **59**, 642 (1907).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, ANGLO-IRANIAN OIL CO., LTD.]

The Preparation and Properties of Sulfur Compounds Related to Petroleum. I. The Dialkyl Sulfides and Disulfides[1]

BY D. T. MCALLAN, T. V. CULLUM, R. A. DEAN AND F. A. FIDLER

The preparation of fourteen dialkyl sulfides and eleven dialkyl disulfides is given, together with some of their physical properties. For purposes of characterization, mercuric chloride derivatives and sulfones have been prepared from the sulfides. It has been shown that under certain conditions, a mixture of two symmetrical disulfides will disproportionate to give an equilibrium mixture containing the unsymmetrical compound. This reaction is extremely useful for the preparation of certain unsymmetrical disulfides.

Introduction

The growing interest which the petroleum industry is taking in the gradually increasing production of high sulfur crude oils has been pointed out recently in numerous articles in the scientific press. An examination of the tables of physical properties of sulfur compounds recently compiled by the Bureau of Mines,[2] shows that the data for even the simplest members are far from complete and of questionable accuracy. Although the deleterious effects of some of the sulfur compounds in petroleum products are well known and many refinery processes have been developed for their removal, yet the fundamental knowledge of their chemical properties is extremely limited. A program designed to assist in filling this gap was therefore begun in these laboratories. The present program has been confined to the synthesis of those sulfur compounds which have been identified in straight run distillates, which means that thiophenes and unsaturated sulfur compounds have not been included. A quantity of 500 g. of the pure compound in each case was aimed at, of which 200 g. was allocated as a standard sample.

Discussion

Dialkyl Sulfides.—Fourteen dialkyl sulfides have been prepared and their physical properties determined. These include all the possible members, both symmetrical and unsymmetrical, having methyl, ethyl, *n*-propyl and isopropyl radicals attached to the sulfur atom. In addition, all the four possible ethyl butyl sulfides were synthesized.[3] Of these four isomers, ethyl *s*-butyl sulfide is a new compound and has not been described previously.

In order to avoid the possibility of the final sulfides being seriously contaminated with impurities which might prove difficult to remove, care was taken to ensure that the starting materials were of an extremely high degree of purity. Even so, it was found that some purification, before final fractionation through 100-plate columns, was beneficial in giving compounds whose purity could be guaranteed.

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[1] Presented before the Petroleum Division of the American Chemical Society at the 117th National Meeting, Houston, Texas (March, 1950).

[2] W. E. Haines, W. J. Wenger, R. V. Helm and J. S. Ball, U. S. Bureau of Mines, Report of Investigation 4060.

[3] The ethyl rather than the methyl radical was chosen for this series since the necessary starting materials were more readily available.

For characterization purposes, two derivatives of each sulfide have been prepared, these being the sulfone and the mercuric chloride complex. In preparing the latter, it was found advisable to use always a considerable excess of mercuric chloride over that theoretically required to give a 1:1 molar complex. This was necessary because in some cases the stable complex had a smaller proportion of sulfide than would be given by a 1:1 ratio and on recrystallization to constant melting point, the composition of the complex would change and sulfide would be lost. However, it was found that whatever proportions of mercuric chloride to sulfide were used for the preparation of the derivative, crystallization to constant melting would always result in one and the same stable complex from each sulfide provided that the same solvent was always employed. This is important, since it has been shown that changing the solvent has in certain cases brought about a change in the composition of the complex. All the mercuric chloride derivatives, the properties of which are quoted in this paper, have been prepared in and crystallized from ethanol.

Dialkyl Disulfides.—The general method employed in the present work for the synthesis of dialkyl disulfides was the oxidation of an individual mercaptan or a mixture of two mercaptans. When an individual mercaptan was employed the product contained only one disulfide which was a symmetrical one, but if a mixture of two different mercaptans was oxidized, the product then consisted of two symmetrical disulfides and an unsymmetrical one. In all, eleven disulfides have been synthesized and their physical properties determined, four being symmetrical and seven unsymmetrical. Only one of the latter has been induced to crystallize and consequently freezing points and estimated purities can only be given for the former and this single unsymmetrical compound.

In general, the products from the oxidation of a mixture of two mercaptans contained the three possible disulfides in the molar ratio 1:2:1, the unsymmetrical one predominating. When one of the mercaptans used was *s*-butyl or *t*-butyl mercaptan, however, the molar ratios of the disulfides in the products varied widely from this value and the divergence seemed at first sight to be anomalous. The most reasonable explanation was that one of the mercaptans was reacting with one of the symmetrical disulfides to produce an unsymmetrical compound.[4] In order to check this hypothesis, experiments were carried out with a symmetrical disulfide and a mercaptan in the presence of alkali. It was found that by refluxing this latter mixture in alcoholic solution, an exchange between the two molecules readily occurred to form the unsymmetrical compound and the mercaptan from the original disulfide. A disproportionation reaction had therefore taken place which can be represented by the equation

$$\mathrm{RSSR} + \mathrm{R'SH} \rightleftharpoons \mathrm{RSSR'} + \mathrm{RSH}$$

Following on this, it was also shown that two symmetrical disulfides will disproportionate amongst themselves under certain conditions to give the unsymmetrical disulfide, *e.g.*

$$\mathrm{RSSR} + \mathrm{R'SSR'} \rightleftharpoons 2\mathrm{RSSR'}$$

The molar ratios of the two symmetrical compounds and the unsymmetrical disulfide at equilibrium are approximately those which are obtained by oxidizing a mixture of the corresponding mercaptans. It was found that for this reversible action to take place the presence of a small amount of mercaptan was essential.

Purity Estimation.—The determination of the purities of sulfur compounds has proved much more difficult than was previously experienced with hydrocarbons. It is believed that in the majority of cases this is not because the compounds contain relatively large percentages of impurities but is due to the lack of establishment of equilibrium between the solid and liquid phases during the freezing point determination. In a number of cases it has been quite impossible to obtain any figure whatever for their freezing points since, on cooling, the compounds either set to glasses or became so viscous as to render stirring impossible. Even where satisfactory values could be obtained, these had in every case to be estimated from the melting curves and not from the freezing curves. Of the unsymmetrical disulfides, only one could be induced to crystallize and give a reasonably good melting curve.

In order to obtain concordant values for the melting point for zero impurity, the determinations had to be repeated many times for each compound and even then two of the dialkyl sulfides gave melting curves of such a slope that although the actual melting point of the sample could be estimated, the corresponding value for zero impurity could not be given. It was found that considerable improvement in the ease of establishment of equilibrium between the solid and liquid phases was achieved if a rotary rather than a reciprocating stirrer was employed in the determination. Also, it was found necessary to maintain very slow rates of heat transfer to the melting or freezing compound which resulted in melting times in some cases of three hours or more.

In the case of three of the compounds, direct comparison can be made between the freezing points obtained in this work and values quoted by the workers on the A.P.I. Research Project 48.[5] For methyl ethyl sulfide both groups of workers obtained exactly the same value for the freezing (or melting) point for zero impurity, namely, −105.91°. For diethyl sulfide and diethyl disulfide the corresponding figures are −103.90°, −103.94°, −101.46° and −101.55°, respectively, the A.P.I. values being the second figure in each case.

The cryoscopic constants employed in this work for the calculation of the purities were determined by one of two methods. The first method is one which is commonly employed for these estimations and depends on the determination of the lowering of the freezing point which occurs on the addition of a known amount of impurity to the pure sample. The

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(4) H. Lecher, *Ber.*, **53B**, 591 (1920).

(5) W. E. Haines, R. V. Helm, W. J. Wenger and J. S. Ball, paper presented before the Petroleum Division of the A. C. S., San Francisco Meeting (April, 1949).

second method has only recently been adopted in these laboratories and depends on the direct measurement of the latent heat of fusion of the specimen. Not only is this second method regarded as being more accurate than the former, but in addition it avoids contamination of the sample.

During the course of this work on the synthesis of sulfur compounds, one or two examples have emerged which have tended to show the weakness of the bond formed between a tertiary carbon atom and a sulfur atom. For instance, it was observed that the mercuric chloride derivative formed from ethyl *t*-butyl sulfide was extremely unstable and on crystallization from ethanol it decomposed to a considerable extent to form *t*-butyl chloride and the stable complex of ethyl mercaptan and mercuric chloride

$$t\text{-}C_4H_9SC_2H_5\cdot HgCl_2 \rightleftarrows t\text{-}C_4H_9Cl + C_2H_5SHgCl$$

The rupture of this carbon–sulfur bond is also effected to a certain extent by reduction with zinc and acetic acid. A sample of ethyl *t*-butyl sulfide after refluxing for 3 hours with powdered zinc and glacial acetic acid gave, on steam distillation, a product containing mercaptan. This is of considerable interest since it introduces a possible error in the method of estimating disulfides by the reduction method,[6] if any sulfides containing tertiary carbon–sulfur linkages are present in the sample being analyzed.

Experimental[7]

Dialkyl Sulfides.

General Methods of Preparation.—Two main routes were employed for the synthesis of the fourteen dialkyl sulfides, details of which are presented below.

Method I. The Reaction of an Alkyl Halide with Aqueous Sodium Sulfide Solution.—A 50% theoretical excess of sodium sulfide nonahydrate (1.5 moles) was dissolved in water (250 g.) in a three-necked flask fitted with a condenser, an efficient water-sealed stirrer and a dropping funnel. The alkyl halide or equimolar mixture of alkyl halides (2 moles) was slowly added to the vigorously stirred solution when a strongly exothermic reaction ensued. The addition was regulated to maintain a reasonable reflux and when complete the stirred reaction mixture was refluxed for a further three hours by the application of external heat. The product was then steam distilled and the crude material so obtained was successively washed with water and 10% sodium hydroxide solution and was then given a final water wash before being dried with calcium chloride.

Method II. The Reaction of an Alkyl Halide with an Aqueous Alkaline Solution of a Mercaptan.—A slight excess over the theoretical amount of sodium hydroxide (1.025 moles) was dissolved in water (250 g.) in the same type of apparatus as described for Method I and the mercaptan (1 mole) was slowly added to this vigorously stirred solution. When this reaction was complete, the alkyl halide (1 mole) was added as fast as the resultant exothermic reaction would permit. On completion of the addition, the stirred mixture was refluxed for three hours with external heating and then the product was steam distilled and treated in the manner described previously.

Purification of the Sulfides.—In addition to fractionation in 100-plate metal-packed columns, the dialkyl sulfides were purified through their mercuric chloride complexes. Mercuric chloride (1 mole) was dissolved in alcohol (1250 ml.) and the sulfide was slowly added to the boiling alcoholic solution. A solid complex was formed which was then recrystallized to constant melting point. The ratio of mercuric chloride to sulfide was adjusted in each case to that required for the stable complex (Table II).

The sulfide was regenerated by heating the complex (500 g.) with dilute hydrochloric acid (250 ml. of concentrated

TABLE I: PHYSICAL CONSTANTS AND PURITIES OF THE DIALKYL SULFIDES

Sulfide	Dimethyl	Methyl ethyl	Methyl isopropyl	Diethyl	Methyl *n*-propyl	Ethyl isopropyl	Ethyl *n*-propyl	Diiso-propyl	Ethyl *t*-butyl	Propyl isopropyl	Ethyl *s*-butyl	Ethyl isobutyl	Di-*n*-propyl[a]	Ethyl *n*-butyl
B.p., °C.	37.3	66.6	84.8	92.0	95.6	107.3	118.5	119.8	120.4	132.1	133.6	134.2	142.8	144.2
M.p., °C.	−98.25	−105.91	−101.48	−103.91	−112.98	−122.19	−117.04	−78.08	−88.95	......	......	......	......	−95.13
Estimated for zero impurity *Cryos. const. deg.*$^{-1}$	*0.027*	*0.040*	*0.043*	*0.056*	*0.040*	*0.046*	*0.052*	*0.034*	0.025	......	......	......	......	0.047
d^{20}, g./ml.	0.8483	0.8422	0.8291	0.8363	0.8424	0.8246	0.8370	0.8146	0.8206	0.8269	0.8353	0.8306	0.8377	0.8376
d^{25}, g./ml.	0.8424	0.8369	0.8251	0.8313	0.8375	0.8199	0.8324	0.8104	0.8161	0.8225	0.8307	0.8261	0.8332	0.8332
$n^{20}\text{D}$	1.4353	1.4403	1.4392	1.4427	1.4442	1.4407	1.4461	1.4388	1.4417	1.4440	1.4477	1.4450	1.4487	1.4491
$n^{25}\text{D}$	1.4319	1.4372	1.4362	1.4400	1.4415	1.4382	1.4434	1.4362	1.4390	1.4414	1.4451	1.4424	1.4461	1.4463
$n^{20}\text{c}^{b}$	1.4322	1.4374	1.4363	1.4398	1.4413	1.4376	1.4432	1.4360	1.4390	1.4412	1.4450	1.4424	1.4458	1.4463
$n^{25}\text{c}^{b}$	1.4289	1.4343	1.4335	1.4371	1.4387	1.4353	1.4407	1.4335	1.4362	1.4387	1.4426	1.4397	1.4434	1.4436
$n^{20}\text{F}^{b}$	1.4427	1.4475	1.4461	1.4497	1.4512	1.4473	1.4529	1.4455	1.4485	1.4507	1.4545	1.4518	1.4552	1.4557
$n^{25}\text{F}^{b}$	1.4393	1.4444	1.4431	1.4470	1.4485	1.4450	1.4503	1.4429	1.4457	1.4481	1.4518	1.4492	1.4529	1.4530
$n^{20}\text{e}^{b}$	1.4378	1.4428	1.4416	1.4452	1.4466	1.4430	1.4484	1.4411	1.4440	1.4463	1.4500	1.4474	1.4509	1.4514
$n^{25}\text{e}^{b}$	1.4345	1.4397	1.4386	1.4424	1.4440	1.4406	1.4459	1.4385	1.4413	1.4438	1.4475	1.4448	1.4484	1.4486
$n^{20}\text{g}^{b}$	1.4485	1.4532	1.4516	1.4553	1.4566	1.4530	1.4583	1.4509	1.4538	1.4562	1.4598	1.4569	1.4606	1.4612
$n^{25}\text{g}^{b}$	1.4452	1.4500	1.4486	1.4525	1.4540	1.4504	1.4558	1.4482	1.4510	1.4535	1.4571	1.4544	1.4585	1.4583
Estimated purity, mole %	99.95	99.90	99.8	99.8	99.96	99.85	99.8	99.93	99.97	......	......	......	......	99.8

[a] Approx. m.p. for di-*n*-propyl sulfide, −102.6°. [b] The wave lengths (Å.) of these lines were: c 6562 (hydrogen), F 4861 (hydrogen), e 5460 (mercury), g 4358 (mercury).

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[6] J. S. Ball, U. S. Bureau of Mines, Report of Investigation 3591.

[7] Microanalyses by Weiler and Strauss, Oxford.

TABLE II

PROPERTIES OF THE SULFONES AND MERCURIC CHLORIDE DERIVATIVES OF THE DIALKYL SULFIDES

		Mercuric chloride derivatives									
				Analyses, %							
				Calculated				Found			
Sulfide	Sulfone m.p., °C. (cor.)	M.p., °C. (cor.)	Formula	C	H	S	Cl	C	H	S	Cl
Dimethyl	106.5	158	$2C_2H_6S{\cdot}3HgCl_2$[a]	5.11	1.28	6.82	22.62	5.8	1.4	6.7	21.2
Methyl ethyl	32.5	104	$C_3H_8S{\cdot}HgCl_2$	10.35	2.26	9.21	20.37	11.0	2.2	8.6	19.4
Methyl isopropyl	*ca.* 16 (n^{20}D 1.4525)	144.5	$C_4H_{10}S{\cdot}HgCl_2$	13.28	2.78	8.86	19.62	12.7	2.6	6.5	19.1
Diethyl	69.0	119.5	$C_4H_{10}S{\cdot}2HgCl_2$	7.57	1.60	5.05	22.36	8.0	1.6	4.6	21.7
Methyl *n*-propyl	28.0	165	$C_4H_{10}S{\cdot}2HgCl_2$	7.57	1.60	5.05	22.36	7.2	1.6	3.2	22.2
Ethyl isopropyl	*ca.* −5 (n^{20}D 1.4532)	82.5	$C_5H_{12}S{\cdot}HgCl_2$	15.97	3.23	8.53	18.88	16.7	3.3	8.5	19.4
Ethyl *n*-propyl	23.0	106	$C_5H_{12}S{\cdot}2HgCl_2$	9.26	1.86	4.95	21.92	9.3	1.3	5.0	22.7
Diisopropyl	35.0	148.5	$C_6H_{14}S{\cdot}HgCl_2$	18.48	3.62	8.22	18.21	19.2	3.8	8.1	18.6
Ethyl *t*-butyl	33.0	83	$C_6H_{14}S{\cdot}HgCl_2$	18.48	3.62	8.22	18.21	17.1	3.8	8.8	19.6
Propyl isopropyl	*ca.* −8 (n^{20}D 1.4539)	75.5	$C_6H_{14}S{\cdot}HgCl_2$	18.48	3.62	8.22	18.21	18.6	3.6	7.6	17.3
Ethyl *s*-butyl	Below −60 (n^{20}D 1.4565)	50	$C_6H_{14}S{\cdot}HgCl_2$	18.48	3.62	8.22	18.21	17.6	3.7	8.4	19.0
Ethyl isobutyl	*ca.* −15 (n^{20}D 1.4495)	79	$C_6H_{14}S{\cdot}HgCl_2$	18.48	3.62	8.22	18.21	19.0	3.9	8.5	18.5
Di-*n*-propyl	28.0	88	$C_6H_{14}S{\cdot}HgCl_2$	18.48	3.62	8.22	18.21	18.8	3.6	8.2	19.3
Ethyl *n*-butyl	49.0	47.5	$C_6H_{14}S{\cdot}HgCl_2$	18.48	3.62	8.22	18.21	19.0	3.6	8.1	19.1

[a] The ratio of sulfide to mercuric chloride determined for this complex is in agreement with that found by Faragher, Morrell and Comay, THIS JOURNAL, 51, 2774 (1929).

acid in 750 ml. of water) and after washing with water and 10% sodium hydroxide solution, it was dried with calcium chloride.

Preparation of the Ten Sulfides Containing Methyl, Ethyl and Propyl Groups. Dimethyl Sulfide, Diethyl Sulfide, Di-*n*-Propyl Sulfide and Diisopropyl Sulfide.—These sulfides were prepared by treating methyl iodide, ethyl bromide, *n*-propyl bromide and isopropyl bromide, respectively, with an aqueous solution of sodium sulfide. In the case of the first three compounds, the yields of sulfides before purification were between 95 and 98%. The rate of reaction with isopropyl bromide was found to be much slower than with the other halides and it was found necessary, after the normal procedure had been followed, to treat the product with a further fresh batch of sodium sulfide solution for another four hours. In this case the yield of diisopropyl sulfide was 87%.

Methyl *n*-Propyl Sulfide, Methyl Isopropyl Sulfide, Ethyl *n*-Propyl Sulfide, Ethyl Isopropyl Sulfide and *n*-Propyl Isopropyl Sulfide.—Satisfactory preparations of these sulfides were made by treating methyl iodide, ethyl bromide or isopropyl bromide with an aqueous alkaline solution of ethyl mercaptan *n*-propyl mercaptan or isopropyl mercaptan. The yields of crude sulfides after steam distillation from the reaction mixtures and washing with caustic soda were, in each case, greater than 90%.

Methyl Ethyl Sulfide.—This sulfide was prepared by both routes, the sample from methyl iodide and an alkaline solution of ethyl mercaptan having a final purity of 99.90 mole per cent.

Preparation of the Four Ethyl Butyl Sulfides.—All four sulfides containing an ethyl and one of the isomeric butyl radicals were prepared according to Method II. The yields of crude sulfides before purification varied between 95 and 99%. Purification of each material was effected through the mercuric chloride derivative which was perfectly satisfactory for all cases except for the ethyl *t*-butyl sulfide.

A quantity of this latter compound was also prepared using the method of Fehnel and Carmack.[8] The procedure adopted varied from that given by these workers in that ethyl mercaptan was substituted for *t*-butyl mercaptan. The unsymmetrical sulfide was obtained from this reaction in excellent yield.

Fractionation of these four sulfides in metal-packed 100-plate columns gave products which, although having constant refractive indices and boiling points, contained traces of mercaptans. The fractionated products were therefore washed with 30% aqueous potassium hydroxide solution until free from mercaptan, repurified through their mercuric chloride derivatives (ethyl *t*-butyl sulfide excepted) and refractionated under reduced pressure in a 20-plate glass-packed column. From this final distillation, the usual standard samples were taken.

Physical Properties of the Dialkyl Sulfides.—The physical constants which have been determined on the 14 synthetic dialkyl sulfides are given in Table I. As previously mentioned, the few gaps in the freezing points and purities are due to the fact that in these cases the compounds set to glasses on cooling instead of crystallizing in a normal manner.

Determination of the Latent Heats of Fusion.—The apparatus used for the measurement of the latent heat of fusion is the same as that used for the determination of the freezing point except that the stirrer is replaced by an electrically heated element. The sample is completely frozen, allowed to melt and the total time of melting accurately measured. The melting curve is followed for a short time and the electrical heater is then switched on. From the change in the slope of the curve it is possible to calculate the specific heat of the liquid and from the previous part of the curve, the heat input from the surroundings of the system can be calculated. From the heat input and the total time of melting, it is possible to calculate the latent heat of fusion of the specimen and hence the cryoscopic constant.

Preparation of Derivatives. (a) Mercuric Chloride Complex.—The melting points, molar compositions and analyses of the various mercuric chloride derivatives which were prepared as described previously, are given in Table II. Some of the determined microanalyses are not as close to the calculated values as desired, but the molecular formulas shown in the table give the closest agreement between the calculated and the observed results.

(b) **Sulfones.**—The sulfones were prepared by oxidizing the dialkyl sulfides with an excess of hydrogen peroxide in acetic acid solution. The sulfide (0.1 mole) was dissolved in glacial acetic acid (200 ml.) and 30% hydrogen peroxide solution (100 ml.) was slowly added to the cooled solution, which was allowed to stand at room temperature for 48 hours. After refluxing for 4 hours, the acetic acid was removed by heating the solution on a water-bath under reduced pressure and the residual sulfone was crystallized to constant melting point. The solvents used for crystallization were a mixture of benzene and petroleum ether, or diethyl ether.

Many of the sulfones were liquids or low melting solids, the melting points being given in Table II.

Dialkyl Disulfides

Preparation by Oxidation of Mercaptans.—The general method used for the disulfides was the oxidation of an individual mercaptan or a mixture of mercaptans with iodine or hydrogen peroxide.

Method I. Oxidation with Iodine.—Caustic soda (320 g., 8 moles) and potassium iodide (20 g.) were dissolved in distilled water (2000 ml.) and the solution cooled in a bath of iced water. A mixture of 4 moles of each of the two mercaptans or 8 moles of a single mercaptan was added with stirring. This mixture of the sodium salts of the mercaptans was cooled and stirred for a further 30 minutes when iodine (1016 g., 4 moles) was added in small portions until a permanent red color persisted. This color was removed

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[8] E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 84 (1949).

TABLE III

PHYSICAL CONSTANTS AND PURITIES OF THE DIALKYL DISULFIDES

Disulfide	Dimethyl	Diethyl	Ethyl isopropyl	Ethyl *n*-propyl	Diisopropyl	Ethyl *t*-butyl	Ethyl *s*-butyl	Ethyl isobutyl	Propyl isopropyl	Di-*n*-propyl	Ethyl *n*-butyl
B.p., °C.[a]	110	154	165	173	174	175	181	184	184	195	193
M.p., °C.	−84.69	−101.46	Glass	Glass	−69.08	−66.71	Glass	Glass	Glass	−85.59	Glass
Estimated for zero impurity											
Cryoscopic const. deg.$^{-1}$	0.026	0.024	......	......	0.034	0.028	......	......	......	0.019	.....
d^{20}, g./ml.	1.0623	0.9933	0.9661	0.9746	0.9427	0.9471	0.9603	0.9543	0.9506	0.9596	0.9594
d^{25}, g./ml.	1.0570	0.9882	0.9613	0.9700	0.9381	0.9425	0.9556	0.9497	0.9462	0.9549	0.9548
n^{20}_D	1.5259	1.5072	1.4988	1.5019	1.4917	1.4942	1.4986	1.4951	1.4943	1.4980	1.4984
n^{25}_D	1.5227	1.5046	1.4963	1.4995	1.4891	1.4916	1.4964	1.4926	1.4920	1.4954	1.4961
n^{20}_C	1.5215	1.5034	1.4952	1.4983	1.4882	1.4907	1.4952	1.4916	1.4908	1.4945	1.4948
n^{25}_C	1.5183	1.5009	1.4927	1.4959	1.4857	1.4880	1.4929	1.4889	1.4886	1.4920	1.4924
n^{20}_F	1.5367	1.5167	1.5079	1.5109	1.5002	1.5030	1.5074	1.5037	1.5029	1.5066	1.5068
n^{25}_F	1.5334	1.5140	1.5053	1.5085	1.4977	1.5004	1.5052	1.5012	1.5007	1.5040	1.5045
n^{20}_e	1.5295	1.5105	1.5020	1.5051	1.4947	1.4972	1.5017	1.4982	1.4973	1.5010	1.5014
n^{25}_e	1.5263	1.5080	1.4995	1.5026	1.4922	1.4947	1.4995	1.4956	1.4950	1.4984	1.4990
n^{20}_g	1.5457	1.5244	1.5150	1.5180	1.5074	1.5099	1.5145	1.5105	1.5098	1.5135	1.5141
n^{25}_g	1.5423	1.5217	1.5126	1.5156	1.5046	1.5074	1.5120	1.5081	1.5075	1.5103	1.5117
Est. purity, mole %	99.96	99.8	......	......	98.9	99.1	......	......	......	99.94	......

[a] The boiling points are extrapolated values to 760 mm.

by adding a trace of one of the mercaptans used in the reaction. The crude mixture of disulfides was recovered from the product by ether extraction and then distilled in a 20-plate glass-packed column under reduced pressure. The individual compounds were then refractionated in a glass-packed 40-plate column, again under reduced pressure.

Method II. Oxidation with Hydrogen Peroxide.—A mixture of 3 moles of each of the two mercaptans was slowly added to a cooled solution of caustic soda (1150 g. of NaOH in 5600 ml. of water) contained in a 10-liter three-necked flask fitted with a condenser, stirrer and dropping funnel. During the addition the temperature of the solution was maintained between 10 and 14°. When solution of the mercaptans in the alkali had been completed, hydrogen peroxide (34% weight/volume) was run in at such a rate that the temperature of the solution did not rise above 30°. In order to obtain a permanent slight peroxide content in the mixture, it was found necessary to add about 10% excess of hydrogen peroxide over that theoretically required. After addition was complete, the reaction mixture was stirred for a further 30 minutes, the disulfide being removed by steam distillation.

Diethyl Disulfide, Ethyl *n*-Propyl Disulfide, Di-*n*-Propyl Disulfide, Ethyl Isopropyl Disulfide, Diisopropyl Disulfide and *n*-Propyl Isopropyl Disulfide.—These disulfides were prepared by the oxidation of mixtures of ethyl and *n*-propyl mercaptans, ethyl and isopropyl mercaptans and *n*-propyl and isopropyl mercaptans according to Method I. The separate portions of the various symmetrical compounds from the several preparations were bulked before final fractionation. The yields of the crude mixtures of disulfides from each reaction were of the order of 90% and the molecular ratio of unsymmetrical disulfide to either of the symmetrical ones was approximately 2:1.

Dimethyl Disulfide, Methyl Ethyl Disulfide and Ethyl *s*-Butyl Disulfide.—These three disulfides were prepared according to Method II. A mixture of methyl mercaptan and ethyl mercaptan gave the former disulfides and diethyl disulfide in the normal molecular ratio of 1:2:1. Ethyl mercaptan and *s*-butyl mercaptan gave, however, diethyl disulfide, ethyl *s*-butyl disulfide and di-*s*-butyl disulfide in the molecular ratio of 1:4.5:1. Neither the dimethyl disulfide nor the methyl ethyl disulfide were pure and a further sample of the former was prepared using the Bunte salt.

Methyl iodide (380 g., 2.68 moles) was slowly added to a solution of sodium thiosulfate (720 g., 2.90 moles) in aqueous ethanol (3000 ml. of a 1:1 mixture) with vigorous stirring. The solution was stirred under reflux for one hour, and alcohol (1500 ml.) then distilled off. The solution was cooled to about 40° and solid iodine (325 g., 2.56 moles) slowly added with vigorous stirring.

The product was steam distilled and the product separated, washed with thiosulfate solution, water and dried with calcium chloride. By this method, a total of 747 g. of crude product was obtained, which corresponded to a 100% yield as disulfide. However, fractionation of this product in a glass-packed column under reduced pressure gave in addition to pure dimethyl disulfide (460 g., 61% yield based upon the methyl iodide), a quantity (210 g.) of dimethyl trisulfide b.p. 41° at 4 mm.; n^{20}_D 1.601.

Ethyl *t*-Butyl Disulfide.—A mixture of ethyl mercaptan (1 mole) and *t*-butyl mercaptan (1 mole) was dissolved in a solution of caustic soda (320 g. of NaOH in 1700 ml. of water) and the mixture oxidized by the addition of potassium ferricyanide solution (670 g. of $K_3Fe(CN)_6$ in 20% aqueous solution). The solution was stirred while the addition was proceeding and the temperature maintained at 20°. The ferricyanide represented a slight excess over the theoretical.

Distillation of the crude product, which was obtained in 93% yield, gave the following ratio of disulfides: diethyl disulfide: ethyl *t*-butyl disulfide: di-*t*-butyl disulfide 1:6:1.

Preparations by the Disproportionation Reaction

Ethyl *t*-Butyl Disulfide.—A solution containing diethyl disulfide (325 g., 2.7 mole), *t*-butyl mercaptan (240 g., 2.7 moles), ethanol (600 ml.), water (10 ml.) and potassium hydroxide (10 g., 0.18 mole) was refluxed in a flask fitted with a short glass-packed column and vapor off-take. The column-head temperature fell to 32.5° and distillate was then taken off at such a rate that the overhead temperature did not exceed 35°, the boiling point of ethyl mercaptan. When, after 4 hours refluxing, the temperature began to rise, 155 g. (2.5 moles) of ethyl mercaptan had distilled over which indicated that the reaction

$$t\text{-}C_4H_9SH + C_2H_5{\cdot}S{\cdot}S{\cdot}C_2H_5 \rightleftharpoons C_2H_5{\cdot}S{\cdot}S{\cdot}t\text{-}C_4H_9 + C_2H_5SH$$

had virtually gone to completion. The solution was diluted with water and the disulfide extracted with pentane and recovered in the usual manner. The product, which was obtained in 95% yield, consisted almost entirely of the unsymmetrical disulfide.

Ethyl Isobutyl Disulfide and Ethyl *n*-Butyl Disulfide.—A solution containing the appropriate symmetrical dibutyl disulfide[9] (595 g., 3.3 moles), diethyl disulfide (408 g., 3.3 moles), ethanol (2600 ml.) ethyl mercaptan (20 g., 0.32 mole), water (18 ml.) and potassium hydroxide (18 g., 0.32 mole), was refluxed for a period of 10.5 hours. The disulfide products which were obtained in 96% yield, were recovered as described previously and fractionated under reduced pressure. Fractions of constant boiling point and refractive index were bulked together, the molar ratio of the three disulfides in the product, in each case being approximately 1:2:1, the unsymmetrical ones predominating as usual.

Physical Properties of the Dialkyl Disulfides.—The physical properties of the dialkyl disulfides are given in Table III. No values are given for the physical constants of methyl ethyl disulfide since no specimen was obtained of sufficient purity for the figures to be reliable.

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[9] The diisobutyl disulfide and di-*n*-butyl disulfide were prepared by oxidizing the appropriate mercaptans according to Method II.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, ANGLO-IRANIAN OIL CO. LTD.]

The Preparation and Physical Properties of Sulfur Compounds Related to Petroleum. II. Cyclic Sulfides[1]

BY E. V. WHITEHEAD, R. A. DEAN AND F. A. FIDLER

The preparation and physical properties of thiacyclopentane, 2- and 3-methylthiacyclopentanes, *cis*- and *trans*-2,5-dimethylthiacyclopentanes, thiacyclohexane and the 2-, 3-, and 4-methylthiacyclohexanes are given. The two forms of the 2,5-dimethylthiacyclopentane have been prepared pure for the first time. Considerable care was taken to purify the starting materials and the intermediates and in all cases the final sulfides were purified through their solid mercuric chloride derivatives before fractionation.

Introduction

The first paper of this series dealt with the syntheses and physical properties of alkane sulfides and alkane disulfides, both of which have been isolated from straight run petroleum distillates. The present paper deals with still another class of organic sulfur compounds found in these products, namely, the saturated cyclic sulfides.

The presence of this type of compound in Iranian distillates has been known for some considerable time[2] and further evidence of their presence has recently been obtained by the isolation of relatively pure specimens of thiacyclopentane, 2- and 3-methylthiacyclopentanes and thiacyclohexane from a tar oil obtained from the sulfuric acid treatment of an aromatic concentrate. It is interesting to note that the only cyclic sulfides which have been identified in or isolated from petroleum distillates have contained either 5- or 6-membered rings as is the case with the naphthene hydrocarbons.

The most interesting sulfide prepared in the present work was 2,5-dimethylthiacyclopentane. This compound can exist in *cis* and *trans* modifications and both these forms have been synthesized in a reasonably high and known degree of purity for the first time.

As in the case of the alkane sulfides, derivatives have been prepared to assist in the characterization of the compounds. The three derivatives used were the methiodides, the sulfones and the stable mercuric chloride complexes. The methiodides, as a rule, volatilize without melting and their temperatures of volatilization are given. Future work may find more satisfactory derivatives for the characterization of these compounds.

Experimental[3]

General Methods of Preparation

Preparation of Dibromides.—For the majority of the syntheses, the required dibromides have been prepared by hydrobromination of a cyclic oxide or a glycol.

Anhydrous hydrogen bromide was passed into the appropriate oxide or glycol at 100–120° until absorption was complete and the crude dibromide was purified by washing a pentane solution of it with concentrated sulfuric acid followed by fractionation under reduced pressure.

Preparation of the Sulfides

Method 1. Cyclization Using Aqueous Alcoholic Solution.—An aqueous alcoholic solution of sodium sulfide was prepared by dissolving 1203 g. (5.0 moles) of sodium sulfide nonahydrate in 1100 ml. of water and 1370 ml. of ethanol. A portion (1100 ml.) of this solution was refluxed in a five-liter three-necked flask fitted with a reflux condenser and two dropping funnels. The remainder of the sodium sulfide solution was placed in one of the funnels and the dihalide (3.35 moles) in the other. The liquids in the funnels were then run into the refluxing sulfide solution at such a rate that the addition of both was completed at the same time, which was approximately 30 minutes.

Method II. Cyclization Using Aqueous Solution.—The solution of sodium sulfide nonahydrate (1410 g., 5.88 moles) in water (2820 ml.) was prepared and reacted with dihalide (3.38 moles) in a similar manner to the above, with the exception that vigorous stirring was maintained throughout the reaction.

In each of the above methods, after the addition was completed, the mixture was refluxed for a further period, the length of time depending on the compound being prepared. The desired cyclic sulfide was steam distilled[4] from the reaction product and the steam distillate was added to a boiling solution of mercuric chloride in ethanol with vigorous stirring. The mercuric chloride derivative was crystallized to constant melting point from ethanol and the cyclic sulfide regenerated from this compound by steam distillation from 15% hydrochloric acid.

Purification of the Cyclic Sulfides.—The crude cyclic sulfides were purified by crystallization of their mercuric chloride derivatives to constant melting point. Initially, the sulfides, after regeneration from the complexes, were fractionated at atmospheric pressure in 100-plate metal-packed columns but it was found that a certain amount of decomposition occurred which reduced the purities of the final products. As a result, the fractions from the distillations were repurified through their mercuric chloride complexes and were given final distillations through 20-plate glass-packed columns under reduced pressure. With the later preparations, the 100-plate column distillation was omitted.

Thiacyclopentane

Tetrahydrofuran.—Commercial tetrahydrofuran was fractionated in a 50-plate glass helix packed column. Fractions boiling 65.9–66.2° with refractive index $n^{20}\text{D}$ 1.4077 and density d^{20} 0.8890 were bulked.

1,4-Dibromobutane.—From tetrahydrofuran in 71% theoretical yield; b.p. 88.0–89.0° (20 mm.); f.p. −16.53°; $n^{20}\text{D}$ 1.5190; d^{20} 1.8269; estimated purity 99.85 mole per cent. Thiacyclopentane was prepared from this dibromide by Method I in 91% yield.

2-Methylthiacyclopentane

2-Methyltetrahydrofuran.—Commercial 2-methylfuran was hydrogenated at 175–185° using a Raney nickel cata-

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[1] Presented before the Petroleum Division of the American Chemical Society at the 117th National Meeting, Houston, Texas, March, 1950.

[2] E. H. Thierry, *J. Chem. Soc.*, **127**, 2756 (1925).

[3] Microanalyses by Weiler and Strauss, Oxford.

[4] After complete removal of the cyclic sulfide, a thick oil remained in the flask. This material would not crystallize nor would it distil under a pressure of 1 mm. but began to decompose at around 250°. It is probably a linear polymer due to intermolecular condensation.