Identification of Alkyl Cycloalkyl Sulfides in Petroleum

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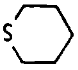
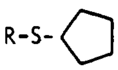
The apparent absence of alkyl cycloalkyl sulfides in petroleum has been of interest to sulfur and petroleum chemists for many years. Recently the authors have identified, in trace amounts, several alkyl cycloalkyl sulfides in Wasson, Texas, crude oil. This represents the first known identification of this class of sulfur compounds in petroleum. These identifications are described in detail and were accomplished by special techniques including the use of microdesulfurization and gas-liquid chromatography.

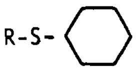
THERE IS AMPLE EVIDENCE (*3, 7, 12*) that chain sulfides of the structure R-S-R′ constitute an appreciable part of the sulfur compound content of some crude oils. It is known also (*1, 3, 11*) that cyclic sulfides in which the sulfur atoms in the ring, e.g.



are even more abundant. However, prior to this investigation, no alkyl cycloalkyl sulfide



or

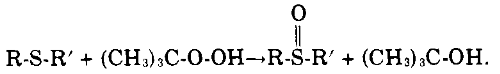


has been identified in any crude oil. This paper presents data indicating that this class of sulfur compound is present in Wasson, Texas, crude oil, although in extremely low concentration. If the amount of these compounds detected in Wasson crude oil is indicative of that present in other crude oils, it is understandable that they have not been identified previously in petroleum by other investigators. Why the quantities of chain sulfides and cyclic sulfides are so bountiful, comparatively, among the sulfur components of Wasson crude oil and of other crude oils, when quantities of the alkyl cycloalkyl sulfides are so meager, is presently unknown.

EXPERIMENTAL

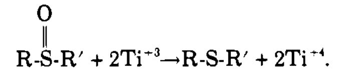
Sample Origin. The treatment used to obtain the sulfide concentrate in which the alkyl cycloalkyl sulfides were identified is shown in Figure 1. All procedural details indicated in this chart, except the final "Chemical Treatment (2)." have been described in previous reports (*6, 9, 10*). The purpose of the final procedure was to separate and recover the sulfides from the thiol-free aromatic-sulfur compound concentrate. The procedure used here, one of several methods being comparatively tested, was based on a sulfide oxidation method developed by Bateman and Hargrave (*2*), modified in the laboratories of the late S.F. Birch of the British Petroleum Co. (*4*), and varied further by the authors to suit the nature of their sample.

A 25-ml. sample of the atomatic-sulfur compound concentrate was mixed with 7-ml. of glacial acetic acid. Seven grams of *tert*-butyl hydroperoxide was then added in small increments and cooled so the temperature of reaction mixture did not exceed 40° C. The following reaction takes place,



$$\text{R-S-R}' + (\text{CH}_3)_3\text{C-O-OH} \rightarrow \text{R-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-R}' + (\text{CH}_3)_3\text{C-OH}.$$

There is no evidence that the oxidation proceeds beyond the sulfoxide stage. After standing for 24 hours, the mix was diluted with 3 volumes of pentane and washed with NaOH solution to remove the acetic acid and the excess *tert*-butyl hydroperoxide. The mixture was then washed with 10 ml. of 40% H_2SO_4, followed by four 5-ml. washes of 80% H_2SO_4. The sulfoxides formed in the oxidation reaction are soluble in the 80% H_2SO_4 and are extracted by this treatment. The acid extract was washed once with pentane and run onto ice. NaOH solution was added until the mixture was alkaline. A sulfoxide layer separated and was extracted with ether. The ether was distilled off and 200 grams of 20% $TiCl_3$ in glacial acetic acid was added. Reduction of the sulfoxides back to the original sulfides takes place according to the equation:



$$\text{R-}\overset{\text{O}}{\overset{\|}{\text{S}}}\text{-R}' + 2\text{Ti}^{+3} \rightarrow \text{R-S-R}' + 2\text{Ti}^{+4}.$$

A small amount of pentane was added (to displace air) and the mixture was heated to 80° C. under a water-cooled condenser for 1-½ hours and allowed to cool overnight. The regenerated sulfides separated as a top layer which was recovered in a separatory funnel and washed with an equal volume of water, extracted with pentane and distilled. The extract was 25%, the residue was 62%, and loss was 13%.

Analytical. Figure 2 is a chromatogram of the sulfide concentrate obtained with a ¼-inch by 25-foot stainless steel gas chromatographic column packed with 30-42 mesh

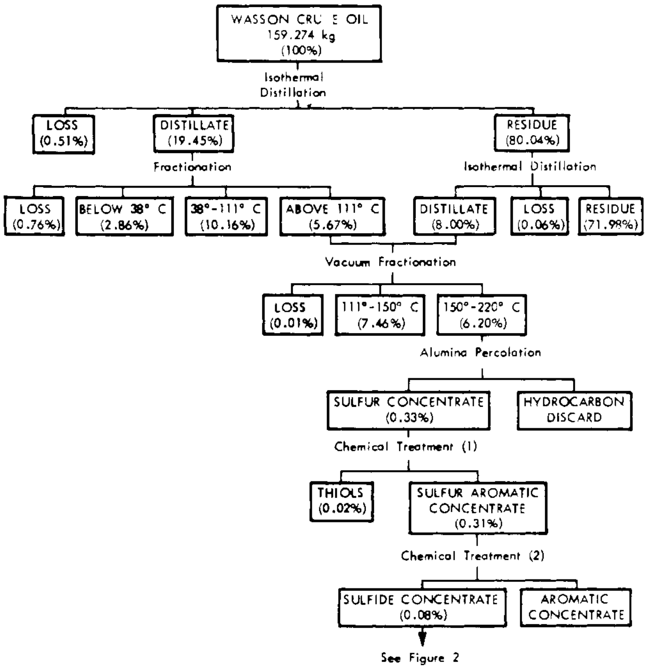


Figure 1. Treatment of Wasson crude oil to obtain 150° to 220° C. sulfide concentrate

GC Supersupport, coated with 20/100 weight ratio of Reoplex 400 and operating at 150° C. with 60 ml./min. helium flow. The chromatogram indicates clearly that the composition of the sample is quite complex. The retention time of the peak at about 22 minutes corresponds with those of several alkyl cycloalkyl sulfides and suggests their presence. To obtain some of this material for desulfurization studies, the effluent emerging between 21 and 22.5 minutes (see Figure 2) from 16 successive 25λ was collected in dry ice cooled pentane. After evaporating most of the *n*-pentane, the trapped material was rechromatographed in the same column and under the same conditions and that portion emerging between 19.2 and 24.5 minutes was collected. The significant portion of the chromatogram obtained is shown in Figure 3 in which arrows indicate the retention times of certain alkyl cycloalkyl sulfides. The concurrence of these retention times with that of the trapped material again pointed to the possible presence of these compounds in the material emerging from the column during the formation of the peak. The symmetry and simplicity of the peak are misleading, however, and the compounds sought (and eventually found) were minor constituents of the material producing it. The material emerging from the chromatograph over the time interval 19.2 to 24.5 minutes (Figure 3) was retrapped, the collected material was desulfurized by the technique of Thompson and coworkers (*13*), and the products of desulfurization were identified by gas-liquid chromatography. The hydrocarbon products were of such wide boiling range that it was necessary to use two columns, one for the detection of "light" materials (*n*-pentane and lighter) and another for "heavy" products (emerging after *n*-pentane). The light material was analyzed using a gas chromatograph equipped with a flame detector and a ⅛-inch by 20-foot stainless steel column packed with 80-100 mesh Neutraport-S, treated with 10/100 weight ratio di-*n*-butyl maleate. The "heavy" material was analyzed with another gas chromatograph equipped with a thermistor detector and a ¼-inch by 20-foot aluminum column, containing 30-42 mesh GC-22 Supersupport coated with 10/100 weight ratio of di-*n*-butyl maleate. The two chromatograms obtained are shown in Figure 4, in which the right panel is that of the low-boiling components and the left panel is that of the high-boiling components. The peaks in the chromatogram of the high-boiling components emerging at times greater than 23 minutes represent hydrocarbon fragments from sulfur compounds other than alkyl cycloalkyl sulfides, e.g., cyclic sulfides, and as such are of no immediate concern to this investigation although they probably represent a major part of the trapped material. The determined retention times of certain hydrocarbons are indicated by arrows on these charts. Because of the significance of cyclopentane in these data, the insert panel of Figure 4 (left) shows a portion of another chromatogram of a synthetic blend of cyclopentane, *n*-hexane, and methylcyclopentane, indicating that the peaks in this chromatogram of a mixture of known hydrocarbons correspond accurately with peaks in the chromatogram of the heavy products. Similarly, because of the significane of cyclohexane in the identification of certain alkyl cycloalkyl sulfides, the peak labeled "5" (which encompassed the retention times of the hydrocarbons, cyclohexane, 2,3-dimethylpentane, and 3-methylhexane) was trapped and rerun in a third GLC column capable of separating these three compounds. Figure 5 reproduces this chromatogram, indicating unmistakably that the major part of "peak 5" of Figure 4, "heavy" components, is cyclohexane and that the remainder (about 10%) is essentially all 3-methylhexane. The chromatogram of Figure 5 was produced by a gas chromatograph equipped with a ¼-inch by 40-foot

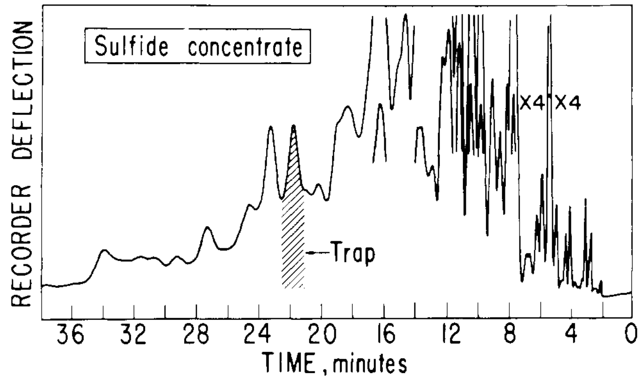


Figure 2. Chromatogram of sulfide concentrate indicating trapped area

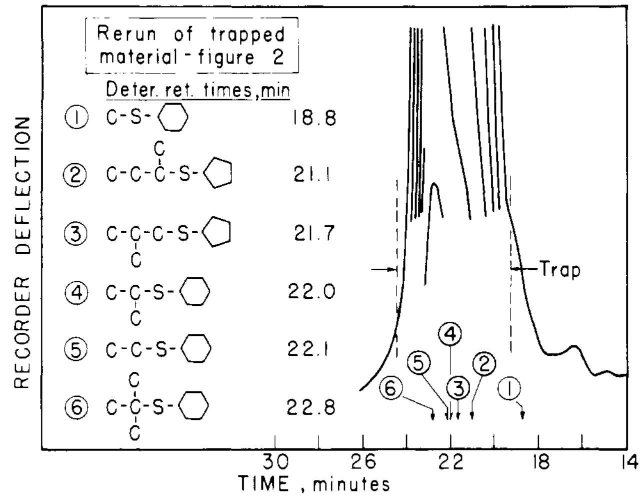


Figure 3. Chromatogram of trapped material from Figure 2

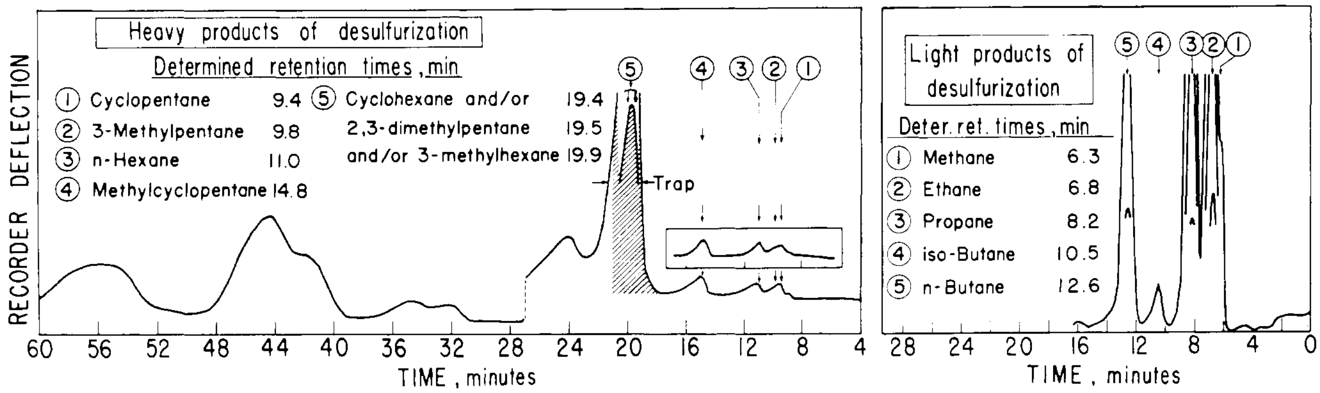


Figure 4. Chromatograms showing products of desulfurization of trapped material from Figure 3

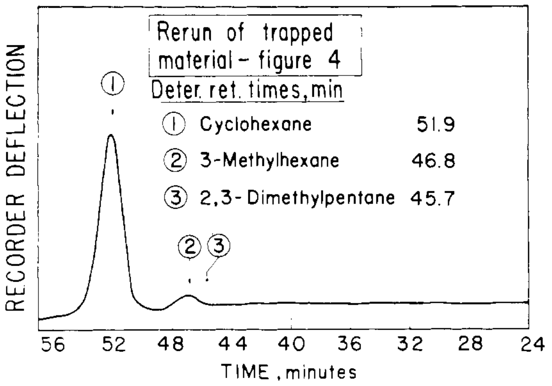


Figure 5. Chromatogram of trapped material from Figure 4

aluminum column packed with 30–42 mesh GC-22 Super-support, coated with 30/100 weight percent DC-550 silicone oil.

DISCUSSION

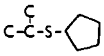
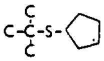
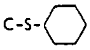
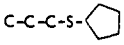
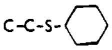
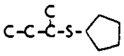
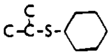
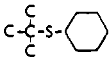
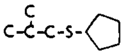
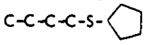
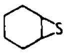
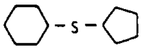
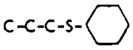
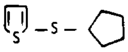
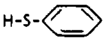
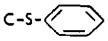
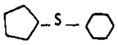
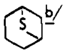
From prior sample treatment and mass spectrometer analyses the concentrate under study is known to be a thiol-free sulfide concentrate containing approximately 69% cyclic sulfides, 18% chain sulfides, small amounts of other types of sulfur compounds, and some alkylbenzenes.

The light products of desulfurization, as indicated in Figure 4, contain methane, ethane, propane, isobutane, and *n*-butane. The heavy products of desulfurization, Figures 4 and 5, contain, among other compounds, a small amount of cyclopentane and methylcyclopentane, and significant amounts of cyclohexane. With the columns employed, these identifications are exact and free from conflict with other paraffins or cycloparaffins. The number of sulfur compounds in petroleum that could produce cyclopentane or cyclohexane upon desulfurization and also have a retention time in agreement with the trapped area is very limited. Table I lists a few compounds that meet these requirements and several that will produce the required hydrocarbon but have retention times near but outside that of the trapped area. All other compounds that would produce the required hydrocarbons upon desulfurization have been eliminated by deductive reasoning based upon structural configuration and retention time data.

Individual alkyl cycloalkyl sulfides were not present in sufficient quantity for spectral study. However, from microdesulfurization and GLC data, some facts are obvious and some deductions are possible. For example, the absence of thiols, bicyclic sulfides, dicycloalkyl sulfides, and cycloalkyl thienyl sulfides in the trapped and desulfurized material is evident from determined retention times as indicated in Table I and by deductive reasoning. This leaves only alkyl cycloalkyl sulfides as possible precursors of the identified cyclopentane and cyclohexane. Having established that cyclopentane and cyclohexane were produced by desulfurization of alkyl cycloalkyl sulfides and that methane, ethane, propane, isobutane, and *n*-butane were also produced, it is now necessary to consider the retention times of possible precursors of these hydrocarbons.

In Table I only five compounds—ethylcyclohexyl sulfide, isopropylcyclohexyl sulfide, *tert*-butylcyclohexyl sulfide, isobutylcyclopentyl sulfide, and *sec*-butycyclopentyl sulfide—have retention times that include them within or near the initial trapping time interval of 21.0 to 22.5 minutes and in the rerun and retrapping at 19.2 to 24.5 minutes. From a qualitative and quantitative study of the data so far presented, the identification of ethylcyclohexyl sulfide, isopropylcyclohexyl sulfide, and *sec*-butylcyclopentyl sulfide is well established. The other two sulfides, *tert*-butylcyclohexyl sulfide and isobutyl cyclopentyl sulfide, are, up to this point, identified only on a conditional basis because the small amount of isobutane found in the light products of desulfurization could have been combined with either the cyclohexane or cyclopentane, or both, to form their respective alkyl cycloalkyl sulfides. However, in other work on the same concentrate using, consecutively, a comparatively nonpolar substrate (DC-550 silicone oil) and then a polar substrate (Reoplex 400), isobutylcyclopentyl sulfide, having a retention time of 102 min., and *tert*-butylcyclohexyl sulfide, having a retention time of 114 min., were fully separated and trapped. Upon desulfurization of the trapped materials, isobutane was identified in both instances along with other hydrocarbons, indicating the presence of both sulfides in Wasson crude oil. Therefore, these five sulfur compounds, and only these compounds, must be precursors of the identified hydrocarbons.

Table I. Possible Sulfur Compound Precursors of Cyclopentane and Cyclohexane

Cyclopentane		Cyclohexane	
Compound	Ret. time[a] in min	Compound	Ret. time[a] in min
	15.0		16.8
	16.3		18.8
	19.5		22.1
	21.1		22.0
			22.8
	21.7		
	27.8		24.2
	94		29.0
	211		32.1
			47.4
			94
		 b/	?

[a] GLC retention time data secured on same column and under same conditions as chromatograms of figures 2 and 3. [b] Compound highly reactive and not available for testing. Reported (5) to be unstable in acid and therefore if originally present would not have survived chemical treatment to which sample was subjected.

The presence of sulfides other than those just discussed is indicated by the existence of unidentified hydrocarbons in the products of desulfurization emerging beyond cyclohexane (Figure 4), but identification of these hydrocarbons or of the parent sulfides was not attempted. However, methylcyclopentane was identified, and some of the possible methylcyclopentyl alkyl sulfide precursors were synthesized and found to emerge in the previously defined area. Although no individual alkyl methylcyclopentyl sulfides were identified, the presence of this class of sulfides was tentatively established.

A sulfide concentrate prepared from another portion of the same distillate and one prepared from a slightly higher boiling distillate by sulfonium salt formation (8), a method not requiring acid treatment, also gave evidence upon desulfurization of the entire concentrate of the presence of alkyl cycloalkyl sulfides; hence it is improbable that the acid treatment (chemical treatment 2) was involved in their formation.

CONCLUSION

By a combination of microdesulfurization and gas-liquid chromatographic techniques, five alkyl cycloalkyl sulfides were identified in a 150° to 220° C. boiling range fraction from Wasson, Texas, crude oil. The individual compounds identified were ethylcyclohexyl sulfide, isopropylcyclohexyl sulfide, *tert*-butylcyclohexyl sulfide, *sec*-butylcyclopentyl sulfide, and isobutylcyclopentyl sulfide. This is the first reported identification of this type compound in any crude oil. Here, as in other ring types, the six member ring appears to predominate over the five-member ring. The concentrations, on a crude oil basis, of the five compounds identified range from 0.00000003 to 0.000009%. This represents but 0.3 to 90 parts-per-billion. These are minimum values influenced possibly by significant but not unreasonable processing losses.

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CORRECTION

In the article "Buffer Systems of Natural Fresh Waters" [J. CHEM. ENG. DATA **8**, 464 (1963)] by Walter J. Weber, Jr., and Werner Stumm, there are a number of errors. On page 466, column 1, paragraph 5, line 7, the word "production" should be "reduction." In Table I, the term "α_2" in the denominator of Equation E should be "α_1". The term "−1.15" before the large bracket in Equation G should be:

$$\frac{-2.3}{\alpha_1\left(1+\frac{2K_2}{[H^+]}\right)}$$

Under nomenclature the term "K_8" should be "K_s".

CORRECTION

In the article "Vapor Pressure of Ammonia in Aqueous Potassium Hydroxide Solutions" by T. Katan and A.B. Campa, published in the J. CHEM. ENG. DATA **8**, 574 (1963), a portion of the first sentence in the second paragraph is incomplete. The sentence should read "To extend these data regarding the vapor pressure of ammonia over aqueous KOH-NH_3 solutions to higher temperatures and concentrations, and to obtain further information of the thermodynamic properties (*7*), the solutions of ammonia at known vapor pressures is determined in 5.35*m* KOH solutions from 30° to 80° C."

CORRECTION:

In the article "Liquid Phase Enthalpy Values for the Ethane-*n*-Pentane System" by A.J. Vennix and J.H. Weber [J. CHEM. ENG. DATA **7**, 169 (1962)] there is an error in one of the figures. The ordinate values on Figure 1, "enthalpy-composition diagram for liquid phase mixtures of ethane–*n*-pentane," are 2000 B.t.u./lb. mole too high. Subtract this amount from values given on this figure to obtain correct enthalpy values.

CORRECTION:

Several corrections are to be made in the article "Activities in Alkali-Ammonia Solutions" by Philip R. Marshall [J. CHEM. ENG. DATA **7**, 399 (1962)]. Two references in Table VI are incorrect. Reference (*12*, p. 1806) should be (*3*, p. 4806) and Reference (*13*) should be (*11*). In Table IV the Na column is unlabeled and the Li column is headed Na. The molality, Li, and Na columns are reproduced below. (The K, Rb, and Cs columns are correct as they appear.)

Molality	Li	Na
0.02	5.54	. . .
0.03	5.15	. . .
0.04	4.97	8.52
0.06	4.68	6.36
0.08	4.38	5.23
0.10	4.11	4.58
0.15	3.48	3.48
0.20	3.02	2.92
0.30	2.42	2.30
0.40	1.99	1.93
0.60	1.46	1.52
0.80	1.17	1.18
1.00	1.00	1.00
1.50	0.745	0.715
2.00	0.596	0.556
3.00	0.434	0.372
4.00	0.365	0.296
6.00	0.347	0.270
8.00	0.386	0.387
10.00	0.530	0.786
10.84	. . .	1.14
12.00	0.999	. . .
14.00	3.52	. . .
15.70	9.220	. . .