[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE UNION OIL COMPANY OF CALIFORNIA]

Identification of Alkylthio Groups by Infrared Spectroscopy

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Characteristic absorption bands have been found for CH_3S-, C_2H_5S-, n-C_3H_7S-, i-C_3H_7S-, and n-C_4H_9S- groups in a study of the infrared spectra of mercaptans, sulfides, disulfides, and alkyl phosphorothioate compounds. Spectra of several phosphorothioate compounds are shown.

Infrared spectra of a number of compounds containing sulfur were examined recently in an attempt to interpret the spectra of several phosphorothioate compounds. During this study it was found that individual alkylthio groups have specific identifying absorption bands. Although related spectral studies[1-8] have been made on many sulfur compounds, spectra-structure correlations for alkylthio groups have not been published.

The spectra of four mercaptans, twenty-nine sulfides, fourteen disulfides, eight trialkyl phosphorotetrathioates, four dialkyl hydrogen phosphorotetrathioates, and one trialkyl phosphorotrithioite show that corresponding members of each series have absorption bands in the same spectral regions. This is true for symmetrical as well as unsymmetrical compounds. For example, the spectra of diethyl sulfide, diethyl disulfide, and triethyl phosphorotetrathioate are all quite similar. Likewise the spectra of ethyl *i*-propyl sulfide, ethyl *i*-propyl disulfide, and methyl ethyl *i*-propyl phosphorotetrathioate have a strong resemblance.

On the basis of these data we have assigned a number of identifying absorption bands to the following groups: methylthio, ethylthio, *n*-propylthio, *i*-propylthio, and *n*-butylthio. These correlations are listed in Figure 1, which shows the spectral range within which each characteristic absorption band occurs. This chart has proved very helpful as an aid in assigning structural formulas for trialkyl phosphorotetrathioates. The characteristic bands were used not only to identify specific alkylthio groups present, but also to distinguish between compounds of the type $(RS)(R'S)_2PS$ and $(RS)_2(R'S)PS$. This was done by comparing the intensities of bands related to one group with the intensities of bands related to the other group. Further study might yield average absorbance indices for different alkylthio groups, thereby making it possible to estimate the amount of these groups present in high molecular weight compounds or mixtures. Similar methods have been developed for alkyl groups not bonded to sulfur.[9,10] Work is being continued to evaluate these possibilities more completely.

The complexity of the molecules studied makes

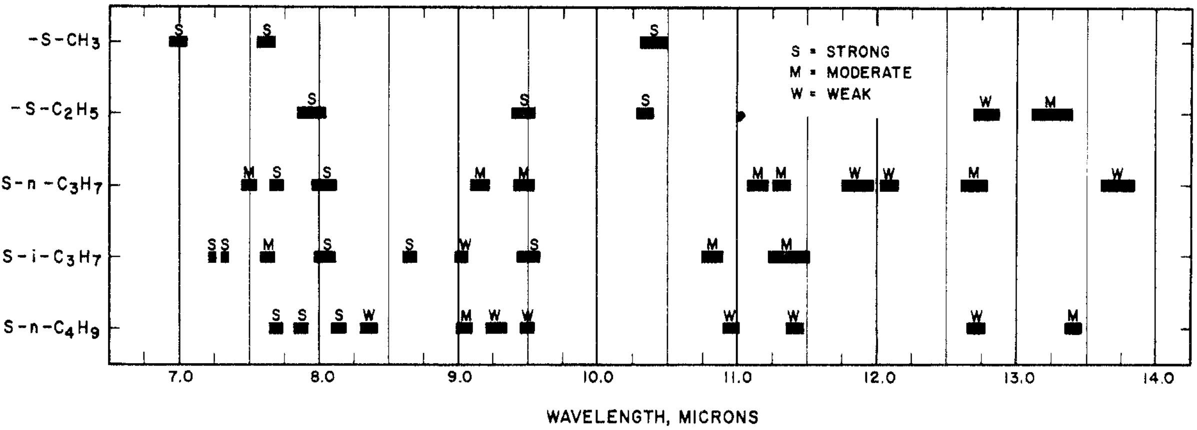

FIG. 1. SPECTRA-STRUCTURE CORRELATION CHART FOR ALKYLTHIO GROUPS

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(1) I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, p. 481 (1946).

(2) S. Venkateswaran, *Indian J. Physiol.*, **5**, 219 (1930).

(3) F. Köppl and K. W. F. Kohlrausch, *Wien. Ber.*, **142**, 11b, 477 (1933).

(4) N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950).

(5) J. H. Hibben, *The Raman Effect and its Chemical Applications*, Reinhold Publishing Corp., New York, N. Y., 256 (1939).

(6) J. Cymerman and J. B. Willis, *J. Chem. Soc.*, p. 1332 (1951).

(7) N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).

(8) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 288, (1954).

(9) S. A. Francis, *J. Chem. Phys.*, **18**, 862 (1950).

(10) S. H. Hastings, A. T. Watson, R. B. Williams, and J. A. Anderson, *Anal. Chem.*, **24**, 611 (1952).

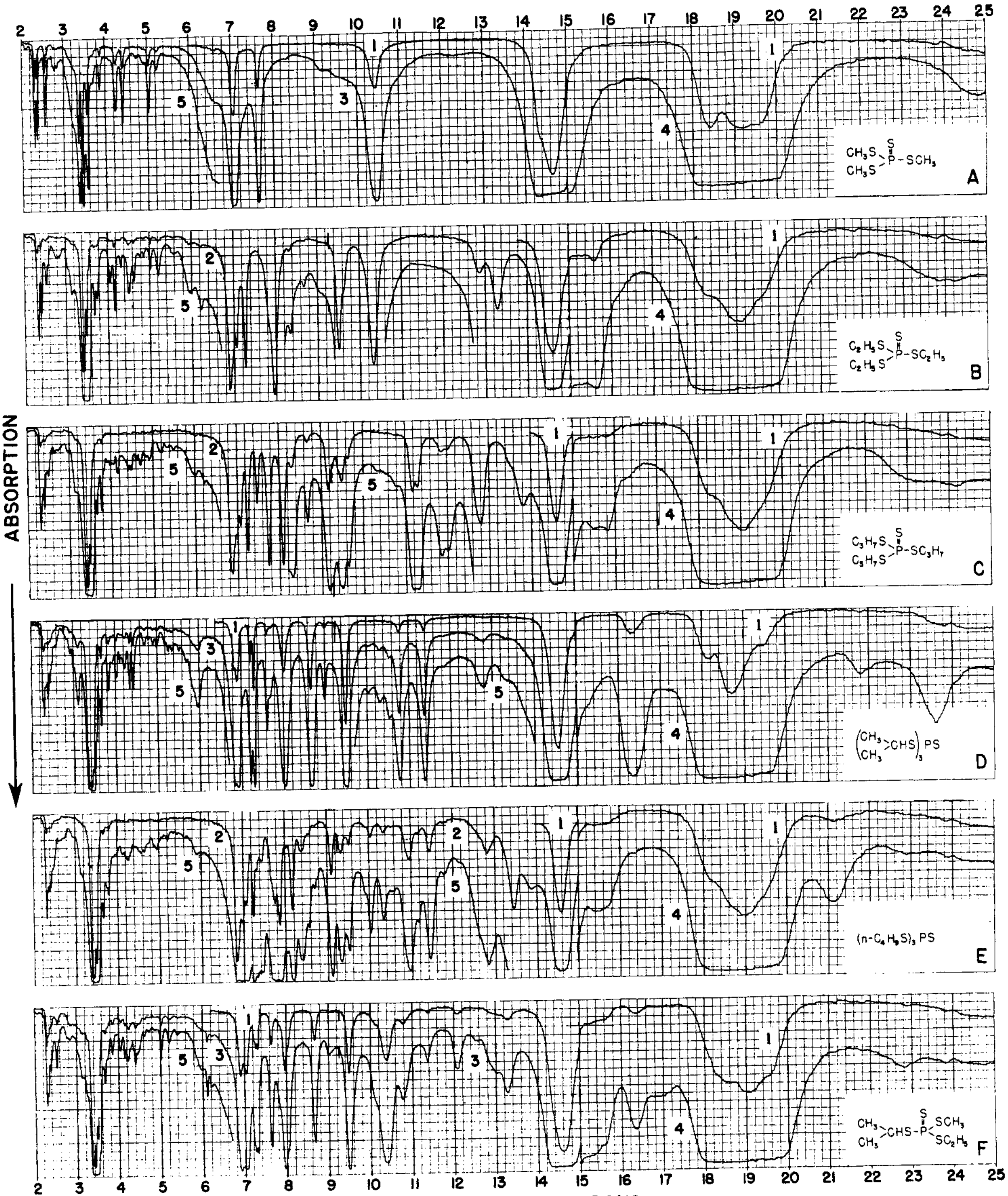

FIG. 2. INFRARED SPECTRA OF (a) trimethyl phosphorotetrathioate, (b) triethyl phosphorotetrathioate, (c) tri-*n*-propyl phosphorotetrathioate, (d) tri-*i*-propyl phosphorotetrathioate, (e) tri-*n*-butyl phosphorotetrathioate, and (f) methyl ethyl *i*-propyl phosphorotetrathioate. Cell lengths: (1) capillary, (2) 0.025 mm. (3) 0.054 mm. (4) 0.078 mm. and (5) 0.210 mm.

a unique assignment of the observed absorption bands to particular molecular vibrations extremely difficult. For this reason, we have not attempted to make definite frequency assignments to any specfic vibrations. We believe, however, that most of the characteristic bands listed in Figure 1 originate from C–H vibrations.[11,12,13] For example, the absorption band near 8 microns which is characteristic of ethylthio groups might be due to methylene wagging or twisting vibrations.[14] We have attributed absorption near 7.65 microns in the spectra of

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[11] (11) H. W. Thompson and P. Torkington, *Proc. Roy. Soc.* (*London*), A184, 3, (1945).

[12] (12) B. L. Crawford, W. H. Avery, and J. W. Linnett, *J. Chem. Phys.*, **6**, 682 (1938).

[13] (13) H. L. McMurray and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

[14] (14) N. Sheppard and D. M. Simpson, *Quart. Revs.*, **7**, 19 (1953).

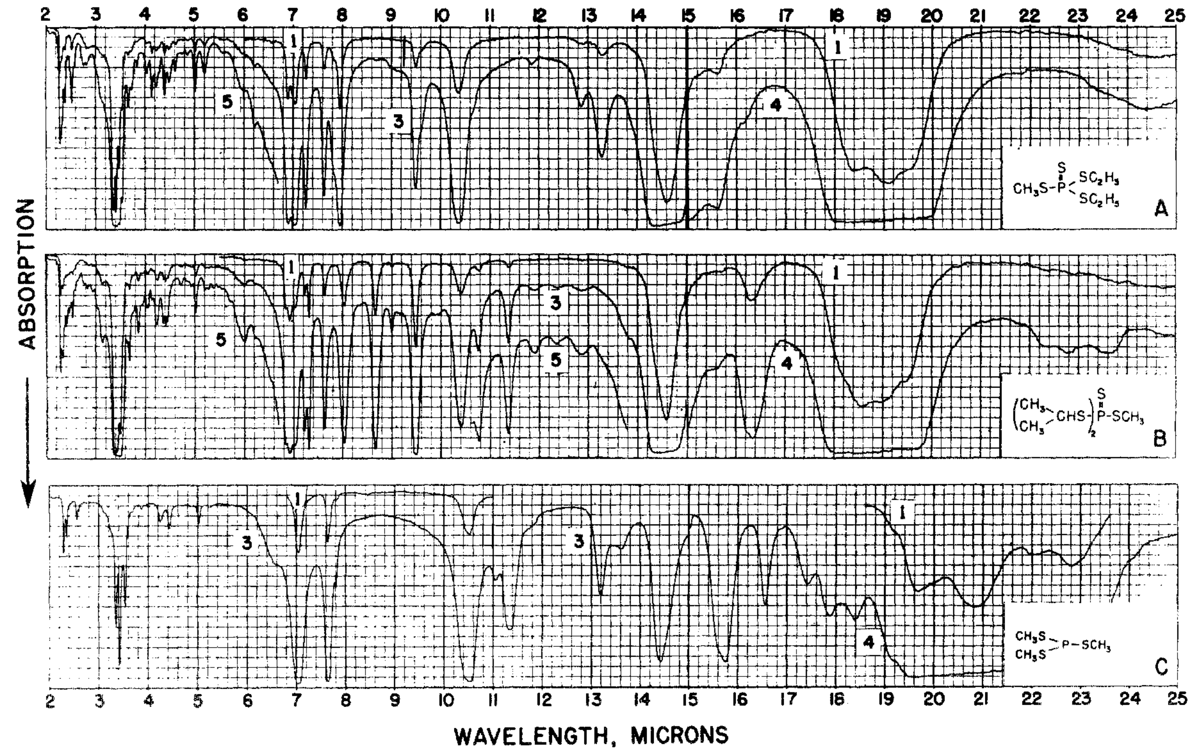

FIG. 3. INFRARED SPECTRA OF (a) methyl diethyl phosphorotetrathioate, (b) methyl di-*i*-propyl phosphorotetrathioate, and (c) trimethyl phosphorotetrathioate. Cell lengths: (1) capillary, (3) 0.054 mm, (4) 0.078 mm, and (5) 0.210 mm.

methylthio compounds to the symmetric methyl deformation vibration for reasons outlined in Sheppard's article on methyl group frequencies.[15] Absorption near 7.05 microns is attributed to the asymmetric deformation vibration of methyl groups attached to sulfur.

As an aid in interpreting spectra of the phosphorus compounds, approximation rules were used to estimate the spectral region in which certain absorption bands should occur. For example, Gordy's Rule,[16]

$$k = 1.67\,N\left[\frac{Xa\,Xb}{d^2}\right]^{3/4} + 0.30$$

where:

k = force constant × 10^{-5} dynes/cm.
N = bond order
Xa and Xb = electronegativities of atoms A and B
d = internuclear distances in Angstroms, Å

was used to estimate the wave length of the C—S stretching vibration in the methylthio group. Using a mass of 15 for the methyl group, a bond order of 1, a bond distance of 1.82 Å, electronegativity values of 2.55 for both carbon and sulfur and assuming simple harmonic oscillation, a wave length of 14.2 microns can be calculated for this vibration. Similarly, a wave length of 14.9 microns can be calculated for the P=S stretching vibration. Absorption bands are found near these wave lengths in the spectrum of trimethyl phosphorotetrathioate (Figure 2). We have attributed the intense band at about 14.6 microns to the P=S stretching vibration,[17] while the shoulder at about 14.4 microns on the side of this intense band is attributed to C—S stretching in the methylthio group. The 14.6-micron band associated with the P=S stretching vibration is present in the spectra of all phosphorotetrathioate compounds (see Figures 2 and 3). The spectrum of trimethyl phosphorotrithioite, which has no P=S group, shows absorption near 14.4 microns, but does not show the intense band near 14.6 microns.

Broad absorption bands near 19 microns in the spectra of phosphorotetrathioates are attributed to P—S— stretching vibrations. The spectrum of trimethyl phosphorortrithioite shows a similar broad band near 21 microns.

Other absorption bands near 15.6 microns and 16.4 microns are attributed to C—S stretching vibrations in ethylthio and *i*-propylthio groups, respectively.[4]

EXPERIMENTAL

Infrared spectra of mercaptans, sulfides, and disulfides published by American Petroleum Institute Research Projects 44 and 48 provided most of the data for this work. All

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(15) N. Sheppard, *Trans. Faraday Soc.*, **51**, 1465 (1955).

(16) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

(17) A paper by R. A. McIvor, G. A. Grant, and C. E. Hubley (*Can. J. Chem.*, **34**, 1611, November 1956), which appeared after this manuscript was completed, discusses this band but makes no assignment.

(18) C. B. Scott, A. B. Menefee, and D. O. Alford, *J. Org. Chem.*, **22**, 789 (1957).

organophosphorus compounds were synthesized in our laboratories.[18] Because of the possible toxic nature of the phosphorus compounds, they were handled with rubber gloves in a fume hood. Also, a small Plexiglas fume hood was placed over the sample space of the spectrophotometer to remove the strong odor characteristic of many of the samples. The spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer equipped with interchangeable sodium chloride and potassium bromide optics.

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Porphyrins in Gilsonite

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A crystalline porphyrin, isolated from gilsonite, was identified to be deoxophyllerythroetioporphyrin or an isomer. The isolation creates the inference that it is the porphyrin originally present. It occurs in the form of the Ni(II) complex.

A knowledge of types of porphyrins in asphaltic materials can provide useful information in interpreting their origin and mode of formation. The presence of pyrroles[1] in the products of pyrolysis of gilsonite and the occurrence of nickel[2] in fractions of gilsonite soluble in organic solvents suggested the presence of porphyrin-nickel complexes in this asphaltite. Accordingly, a study was initiated to clarify this possibility.

A preliminary concentration procedure was found to be desirable to decrease the requirements for hydrogen bromide in acetic acid. An exhaustive extraction of gilsonite with ethyl acetate removed porphyrins into the soluble fraction, which constituted about one fourth of the total. A colorimetric method was used to follow the efficiency of the extraction procedure. A series of six extractions at room temperature removed the major portion of the desired compounds. The colorimetric analysis indicated the porphyrin content in gilsonite to be 0.03%.

The reaction of the porphyrin-metal complex in the concentrate with hydrogen bromide in acetic acid released the free porphyrins. The treatment with hydrogen bromide in acetic acid was assumed to have no effect on the porphyrin moiety of the metal complex. Using a sealed tube for this reaction, as described by Treibs,[3] was found to be unnecessary, when the reaction was repeated once. The modified approach permitted processing larger batches than would otherwise be possible. Basic porphyrin molecules were carried into the aqueous acid phase by this procedure. Accompanying neutral compounds were extracted partially with benzene. The porphyrin fraction was then placed in ether, and basic compounds removed by aqueous hydrochloric acid, leaving behind a further amount of contaminants.

Basic compounds, aside from porphyrins, in gilsonite[4] were contained in the main, in the crude fraction at this point. A procedure was devised to extract these compounds from the desired porphyrins by forming the porphyrin-nickel complex. The latter is not basic and is stable to mineral acids in general but cleaved by concentrated sulfuric acid.[5] Accordingly, the crude extract was treated with Ni(II) ion, and the resulting Ni(II) porphyrins in an ether solution were extracted with hydrochloric acid. The complex was cleaved with concentrated sulfuric acid, and the cycle was repeated to remove essentially all of the nonporphyrin bases.

Additional purification and separation of types of porphyrins were effected by applying a hydrochloric acid fractionation[6] and by chromatography. Using 2.5, 4, and 7% aqueous acid solutions, the porphyrins were separated into fractions, amounting approximately to 80%, 10%, and 10%, respectively. Final purification and separation were achieved by chromatography on calcium carbonate. Each of the fractions gave chromatograms with two red colored zones, moving away from small amounts of dark material adsorbed more tightly on the column. The major component from the 2.5% hydrochloric acid fraction amounted to about 73% of the total porphyrins.

Visible spectra were determined for the major and minor components in the 2.5% acid fraction

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(1) J. M. Sugihara and D. P. Sorenson, *J. Am. Chem. Soc.*, **77**, 963 (1955).

(2) P. L. Morse, American Gilsonite Co., private communication.

(3) A. Treibs, *Ann.*, **509**, 103 (1934); **510**, 42 (1934); **517** 172 (1935).

(4) D. P. Sorensen, Ph.D. dissertation, University of Utah, 1955.

(5) W. S. Caughey and A. H. Corwin, *J. Am. Chem. Soc.*, **77**, 1509 (1955).

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