

elsewhere.² Hg 4358 Å. was used for excitation, and the slit width of the spectrograph was 0.08 mm.

In order to determine whether mixing had altered disproportionately the intensity of the S-H line, the strength of the 2570 line was compared with that of the 700 cm.⁻¹ line of thiophenol on the same spectrogram. This latter line was chosen as a comparison line because it is neither too weak nor too strong for accurate intensity measurement, because it does not coincide with any lines of the various solvents employed, and because comparison of the intensity ratio of this line to lines other than 2570 cm.⁻¹ indicated no noticeable effect due to association. Semi-quantitative comparison was attained by use of a set of standard lines of regularly varied intensity.³

The results are listed in Table I. The number in parentheses following the Raman frequency represents intensity. The 700 cm.⁻¹ line which was used as a standard is arbitrarily given the value of 4 on each spectrogram. No attempt was made to compare the different spectrograms with each other. In general, the solutions employed were more dilute than those used by Gordy and Stanford. This was for the purpose of giving the mercaptan molecules as much chance to form hydrogen bonds as was experimentally feasible, since preliminary experiments indicated that the 50% by volume solutions did not show so large an effect as had been anticipated from the infrared data.

TABLE I
THE EFFECT OF DONOR SOLVENTS UPON THE S-H FREQUENCY OF THIOPHENOL

Solvent	Hours of exposure	Volume, % of thiophenol	S-H frequency Raman cm. ⁻¹ I	Infrared cm. ⁻¹
Thiophenol (pure)	1	100	2569(7)	2577
Benzene	4	25	2571(7)	2577 ^a
Diisobutyl ketone	4 and 11	25	2570(6)	..
Diisopropyl ether	4	25	2570(5)	2557 ^b
Pyridine	4	50	2569(6)	2463 ^b
Pyridine	4 and 9	25	2571(3)	2463 ^b
Dioxane	4 and 8	25	2569(3)	..
			2536(2)	
Dibenzylamine	1	25	2571(6) ^c	2475 ^b

^a Dilute solution. ^b Fifty % by volume solution. ^c Solid separated from this solution at the end of one hour. Intensity reading somewhat in doubt.

As in the infrared work of Gordy and Stan-

(2) Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, **8**, 153 (1940); Cleveland, Murray, Coley and Komarewsky, *ibid.*, **10**, 18 (1942).

(3) Cleveland and Murray, *ibid.*, **7**, 396 (1939).

ford,¹ benzene was found to have negligible effect on the S-H frequency in the thiophenol-benzene solution. For mixtures of the mercaptan in diisobutyl ketone and diisopropyl ether the Raman line for the S-H stretching vibration is unchanged in frequency, somewhat broadened and only slightly decreased in intensity. For thiophenol-pyridine solutions the results are at complete variance with the infrared findings. In neither the 50% nor the 25% solutions is there Raman spectra evidence for an altered frequency. Furthermore, although in the 25% solution there is considerable decrease in the strength of the S-H line, it is evident that even in this more dilute solution the S-H groups of a sizable proportion of the thiophenol molecules are little affected by the presence of pyridine. The infrared results showed not only a shift of 114 cm.⁻¹ but also a large increase in absorptive power as compared to the pure mercaptan. The infrared showed no evidence for a band due to the unmodified S-H frequency in pyridine solution, but this may in part be caused by lack of resolution.

The Raman spectra results for the solution of thiophenol in dioxane are most striking. In this case the S-H frequency appears as a doublet composed of the original, unshifted, slightly broadened line and a new line (not observed in the spectra of either of the pure compounds) at 2536 cm.⁻¹ which is somewhat weaker and broad but clearly resolved from the 2569 cm.⁻¹ line. This is the only one of the compounds studied for which there is Raman spectra evidence of a modified frequency. In all the other cases tested in this investigation, if modified frequencies result they must be very weak or so broad and diffuse that they failed to register on the photographic emulsion in the time allotted.

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Boiling Point-Composition Data of the Methyl Alcohol-Dioxane System

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In order to further extend the data of the methyl alcohol-dioxane system given by Amis,

(1) Now employed by Ethyl Gasoline Corporation, Baton Rouge, La.

(2) Now employed by Tennessee Coal, Iron and Railway Company, Birmingham, Alabama.

Choppin and Padgitt³ the boiling point-composition curve has been determined.

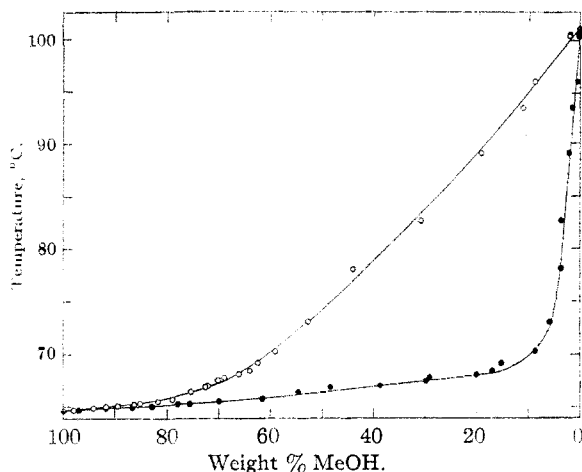


Fig. 1.—Vapor phase, O; liquid phase, ●.

The methyl alcohol and dioxane were purified as previously described³; the apparatus used was that of Othmer.⁴ Equilibrium between the vapor and liquid phases was established after

TABLE I
BOILING POINT-COMPOSITION DATA FOR THE METHYL ALCOHOL-DIOXANE SYSTEM AT ONE ATMOSPHERE

B. p., °C.	Wt., % liquid	MeOH vapor
64.60	100	100
64.72	96.5	98.1
64.90	91.9	94.2
64.96	86.7	91.9
65.10	82.9	89.4
65.27	78.0	86.3
65.34	75.7	85.2
65.55	69.7	81.7
65.78	61.7	77.9
66.50	54.6	75.7
66.94	48.4	72.6
67.10	38.8	72.2
67.60	29.8	70.2
67.89	29.0	67.9
68.20	20.0	66.1
68.50	17.0	63.9
69.30	15.4	62.5
70.40	9.7	59.0
73.20	6.0	52.7
78.20	3.9	44.1
82.80	3.7	30.8
89.20	2.4	19.1
93.50	1.6	11.1
96.04	0.7	8.7
100.38	.3	1.9
100.54	.3	1.8
101.05	.0	0.0

(3) Amis, Choppin and Padgitt, *THIS JOURNAL*, **64**, 1207 (1942).

(4) Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928).

about three hours for each determination. Temperatures were measured with calibrated thermometers graduated in 0.05° with a precision of $\pm 0.05^\circ$. The liquid and vapor phases were analyzed by means of refractive index using the values reported by Amis, Choppin and Padgitt.³ The results are tabulated in the table and represented graphically in the figure.

CONTRIBUTION FROM THE
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Addition Compounds of Tetrahydrothiopyran

BY HARRY J. WORTH AND HELMUT M. HAENDLER

Two addition compounds of tetrahydrothiopyran (pentamethylene sulfide) and inorganic metal salts have been reported: $\text{HgCl}_2 \cdot (\text{CH}_2)_5\text{S}$ by Grischkewitsch-Trochimowski¹ and $x\text{HgI}_2 \cdot (\text{CH}_2)_5\text{S}$ by Bost and Conn.² This sulfide forms addition compounds with other metal halides, offering comparison with dithiane,³ dioxane,⁴ and morpholine.⁵ Tetrahydrothiopyran exhibited less tendency to form addition compounds than did dithiane or dioxane, but greater tendency than morpholine.

The compounds are crystalline, somewhat sensitive to water, and are white, except for the yellow gold(III) chloride, tin(IV) bromide, and platinum(II) iodide, the red-brown gold(III) bromide, and the orange-red palladium(II) chloride compounds. There was some indication of reaction with silver iodide, silver bromide, and tin(IV) iodide, but no compounds could be isolated. The following compounds gave no results: copper(II) fluoride, cadmium halides, zinc chloride, iron(III) chloride, arsenic(III) iodide, antimony(III) iodide and chloride, germanium(IV) chloride, and silicon(IV) chloride.

The thiopyran was prepared by a modification of the methods of von Braun⁶ and Clarke,⁷ using 100 g. of benzoylpiperidine and 110 g. of phosphorus pentachloride. The benzonitrile was hydrolyzed by warming under reflux, the dichloropentane steam distilled, and converted to tetra-

(1) Grischkewitsch-Trochimowski, *Chem. Zentr.*, **37**, I, 1503 (1923).

(2) Bost and Conn, *Ind. Eng. Chem.*, **23**, 93 (1931).

(3) Bouknight and Smith, *THIS JOURNAL*, **61**, 28 (1939).

(4) Rheinboldt, Luyken and Schmittmann, *J. prakt. Chem.*, **149**, 30 (1937).

(5) Haendler and Smith, *THIS JOURNAL*, **63**, 1164 (1941).

(6) von Braun, *Ber.*, **37**, 2915 (1904).

(7) Clarke, *J. Chem. Soc.*, **101**, 1785 (1912).