[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (DIVISION OF SOCONY-VACUUM OIL CO., INC.), RESEARCH AND DEVELOPMENT DEPARTMENT]

Physical Properties of 2- and 3-Methylthiophene

BY FRANK S. FAWCETT

Thiophene is produced from *n*-butane and sulfur by a process recently developed in this Laboratory.[1] The use of pentanes results in the production of methylthiophenes.[2] The properties of thiophene from this process have been reported.[3] The two methylthiophenes have now been purified and some of their physical properties measured. A number of physical properties of the methylthiophenes have been reported in the literature.[4–9]

Purification of Methylthiophenes.—The two pilot plant products which served as the starting point for this work were examined by freezing point measurements and the preparation of chemical derivatives and each was found to contain approximately 95% of its respective isomer. Each of the two products was washed with dilute hydrochloric acid, sodium hydroxide, and distilled water and dried by distilling part of the material. Two liters of the resulting product was distilled at atmospheric pressure with a rectifying column[3] equivalent to approximately 95 theoretical plates. A reflux ratio of 50:1 was used and the distillate was collected as 100-cc. fractions (5% of charge). Central portions were selected for use on the basis of time–temperature freezing curves, since most common properties are not very sensitive to changes in the proportions of the two isomers. For each isomer approximately 300 cc. of best material was obtained by combining three fractions having the same freezing point to 0.1°; fractions before and after those combined differed in freezing point by not more than 0.1°. The selected material was then evacuated to remove gases and, under reduced pressure, a portion was distilled and rejected and other portions were distilled into ampules, which were then sealed.[10]

Determination of Properties.—The properties listed in Table I were determined using the same apparatus and procedures previously described,[3] except where otherwise noted. Time–temperature freezing curves for each isomer were determined with the 2.5-ohm platinum resistance thermometer and the Mueller bridge. From the temperature change corresponding to the freezing of a given fraction of the sample and the data of Table II, the purity of each isomer was estimated to be at least 99.8 mole%.[11]

TABLE I

OBSERVED PHYSICAL PROPERTIES OF METHYLTHIOPHENES

		2-Methylthiophene	3-Methylthiophene
B. p., °C. at	500 mm.[a]	98.5	101.3
	600 mm.	104.4	107.2
	650 mm.	107.2	109.9
	700 mm.	109.7	112.5
	760 mm.	112.5	115.4
	800 mm.	114.3	117.2
	850 mm.	116.4	119.3
	900 mm.	118.4	121.3
(d*t*/d*p*) at 760 mm., °/mm.		0.046	0.046
F. p. in air, °C.		−63.5	−68.9[b] −74.1[c]
d^t_4 at	20°	1.0194	1.0216
	25°	1.0140	1.0162
	30°	1.0086	1.0110
n^t_D at	20°	1.5203	1.5204
	25°	1.5174	1.5175
	30°	1.5144	1.5146
$10^4 (n_F - n_C)/d$ at 20°		162	159
Absolute viscosity, centipoise at	0°	0.944	0.902
	20°	.716	.687
	25°	.669	.642
	30°	.629	.607
Molecular refr. at 20°		29.29	29.23

[a] The pressures were obtained from the data of Smith[17] for benzene. [b] Higher-freezing form. [c] Lower-freezing form.

In the case of 3-methylthiophene some determinations of the freezing curve showed two distinct temperature plateaus, first the lower and then an abrupt change to the higher temperature during freezing. After from one-third to one-half of the sample had frozen, the stirrer stopped and the temperature changed to the higher value. Most determinations of the freezing point showed only the higher-freezing form, but on undercooling the stirred liquid to −78° the lower-freezing form appeared. A single form of 2-methylthiophene was obtained even when the stirred liquid was undercooled to −76°. The refrigerant used in all cases was liquid nitrogen.

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[1] Rasmussen, Hansford and Sachanen, *Ind. Eng. Chem.*, **38**, 376 (1946).

[2] Rasmussen, to be published.

[3] Fawcett and Rasmussen, THIS JOURNAL, **67**, 1705 (1945).

[4] Opolski, *Forts. von Anz. Akad. Wiss. Krakau*, 548 (1905); *Chem. Zentr.*, **76**, II, 1796 (1905).

[5] Auwers and Kohlhaas, *J. prakt. Chem.*, (2) **108**, 321 (1924).

[6] Lowry and Nasini, *Proc. Roy. Soc.* (London), **A123**, 688 (1929).

[7] Midgley, Henne and Shepard, THIS JOURNAL, **54**, 2957 (1932).

[8] Shepard, Henne and Midgley, *ibid.*, **56**, 1355 (1934).

[9] Jurjew (Yur'ev), *Ber.*, **69B**, 1002 (1936).

[10] The 3-methylthiophene sealed *in vacuo* in clear-glass vessels remained water-white after four months, while a portion similarly sealed and later opened to the atmosphere became slightly yellow on further standing for a few days. The freezing point of the colored sample had not changed by as much as 0.1°. The 2-methylthiophene remained water-white under both conditions. Thiophene behaved as 2-methylthiophene.

[11] Schwab and Wichers, in "Temperature, its Measurement and Control in Science and Industry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 256.

TABLE II

FREEZING POINT DEPRESSIONS OF METHYLTHIOPHENES WITH VARIOUS SOLUTES

Solvent	Solute		F. p., °C.
	Identity	Mole %	
2-Methylthiophene	None	..	-63.5
	3-Methylthiophene	5.1	-65.5
		9.9	-67.9
		19.6	-70.9
		27.8	-74.0
	Thiophene	5.5	-65.7
		23.1	-72.9
	Toluene	5.2	-65.7
		20.4	-72.8
3-Methylthiophene Form I[a]	None	..	-68.9
	2-Methylthiophene	3.3	-69.7
		6.7	-71.3
		12.0	-72.9
		14.9	-73.8
		18.3	-75.8
		19.7	-75.4
	Thiophene	5.4[c]	-70.7
		22.0	-77.6
	Toluene	4.3	-70.5
		20.4	-76.5
3-Methylthiophene Form II[b]	None	..	-74.1
	Thiophene	5.4[c]	-76.4

[a] Higher-freezing form. [b] Lower-freezing form. [c] The two freezing points were observed for the same solution, as was the case with 3-methylthiophene containing no solute.

The freezing point was determined for several mixtures of 2- and 3-methylthiophene in the same manner as for the pure components, using a copper-constantan thermocouple and a Rubicon Company Type B, No. 2780, potentiometer. Approximately 35-cc. samples were prepared by weighing the two components. Freezing point depressions caused by toluene and by thiophene were also measured (Table II). The thiophene used was a portion of that purified during other work.[3] J. T. Baker C.P. Analyzed toluene (n^{20}D 1.4962, d^{20}_4 0.8664) was distilled with the 95-plate column with a reflux ratio of 50:1 and one of the central portions was selected having n^{20}D 1.4967. In one instance, 5% thiophene in 3-methylthiophene, two freezing points were observed for the one solution. On undercooling the stirred solution to $-81°$ a lower freezing temperature was observed from which an abrupt, spontaneous change occurred to a higher temperature. The sample was melted and on re-freezing the higher freezing point was obtained. This behavior, here and with the 3-methylthiophene alone, is evidence for the existence of two crystalline forms of 3-methylthiophene. Cooling curves followed down to $-90°$ have not shown evidence of a solid transition. The lower-freezing form was obtained only from the undercooled liquid. The change from the higher-freezing form to the lower-freezing form was not found to occur. From the depressions of the freezing points of the two forms caused by thiophene the heats of fusion were calculated as 2500 cal./mole for the higher-freezing form and 1900 cal./mole for the lower-freezing form. Thus the vapor pressure curves for the two crystalline modifications will intersect above the melting point of either. These are the characteristics of monotropic polymorphism.[12] The phase diagram for the system 2-methylthiophene–3-methylthiophene is complicated by the occurrence of the metastable lower-freezing form, and only the data of Table II have been completed. The heat of fusion of 2-methylthiophene was calculated as 2200 cal./mole.

Viscosities and 20, 25 and 30° were determined as for thiophene.[3] Values at 0° were determined in an ice–water-bath, using the extrapolated values of the densities. The viscometer was calibrated with water and *n*-heptane at that temperature with the operating volume of charge. A measurement was made at 0° for the thiophene previously purified,[3] and the value of η_0 was 0.873 centipoise. The data for the three compounds when plotted according to a Dühring-type relationship gave nearly linear curves. Using viscosity data[13] for water, the reference liquid, the temperatures were plotted at which the compound and water have equal viscosities (fluidities). Such a plot yields an approximately linear curve for wide temperature (viscosity) ranges for a variety of materials, and is useful in extending such data. The replacement of a hydrogen by a methyl group in thiophene causes an increase in the viscosity at a given temperature, as is the case with cyclopentane.[14] Such a change with benzene,[14] cyclohexane,[14] and pyridine[15] causes a decrease in the viscosity.

For the boiling points[16] the Rubicon potentiometer was used. The copper–constantan thermocouple was calibrated against the resistance thermometer in this range. A sample of the same benzene previously prepared[3] served as reference liquid. The values in Table I were obtained from Dühring plots of the observed corresponding boiling points and published data for benzene.[17] The calculated heats of vaporization are approximately 8500 cal./mole. The ratio of the vapor pressure of 2-methylthiophene to that of 3-methylthiophene at the same temperature is 1.09 in the range 112–116°. Vapor pressure data for the 2-methyl isomer over the range 33–95° have been reported by Nasini.[18]

Derivatives of Methylthiophenes.—The tribromo derivatives were prepared from the pilot plant products by

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(12) Findlay, "The Phase Rule and its Applications," Longmans, Green and Co., New York, 1927, p. 35.

(13) Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corp., New York, N. Y., 1940, p. 184.

(14) Doss, "Physical Properties of the Principal Hydrocarbons," The Texas Co., New York, 1943.

(15) Beilstein's "Handbuch der organischen Chemie," Vol. XX, 4th ed., Julius Springer, Berlin, 1933, p. 183, 235, 239.

(16) Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945, Chap. III.

(17) Smith, *J. Research Natl. Bur. Standards*, **26**, 129 (1941).

(18) Nasini, *Proc. Roy. Soc.* (London), **A123**, 711 (1929).

the procedure of Steinkopf and Jacob.[19] The solid products crystallized from ethanol–water gave: for 2-methylthiophene m. p. 84–86° (lit. 86°), and for 3-methylthiophene m. p. 33.8–34.0° (lit. 34°). For the chloromercuri derivatives[20] the ethanol-soluble part of the solid products after crystallization from ethanol–water gave: for 2-methylthiophene m. p. 202–204° (lit. 204°) and for 3-methylthiophene m. p. 127–129° (lit. 128–129°). The literature values are quoted from McKittrick.[21]

A 30-cc. sample of each isomer was isolated from rejected distillation fractions by means of the chloromercuri derivatives.[3] The properties of the regenerated products were: 2-methylthiophene b. p. 112.6°, f. p. −63.5°, n^{20}_{D} 1.5203, d^{20}_4 1.0195, η_{20} 0.717 centipoise; 3-methylthiophene b. p. 115.5°, f. p. −69.4°, n^{20}_{D} 1.5204, d^{20}_4 1.0216, η_{20} 0.687 centipoise (*cf.* Table I). Examination of the infrared absorption spectra in the range 2 to 15 microns showed the regenerated materials to be equivalent to the corresponding samples isolated physically, with the exception that with the former there was a small amount of mutual contamination. For the regenerated materials, the 2-methylthiophene was found to contain 1 mole % of the 3-methyl isomer; the 3-methylthiophene was found to contain 2 mole % of the 2-methyl isomer. For the physically-purified samples, infrared examination indicated that the purity of each isomer was approximately 99.8 mole %.

In preparing the chloromercuri derivatives there was a noticeable difference in the rates of formation of the solid product. When a mixture of 2-methylthiophene, 3-methylthiophene and thiophene in the molar ratio 1:1:1 partially reacted with mercuric chloride under conditions similar to those described by McKittrick,[21] the portion which had reacted was found by means of infrared absorption spectra to contain the thiophenes in the molar ratio 6:4:1, respectively.

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Summary

1. The two methylthiophenes have been purified by distillation and the following properties have been determined for each: f. p., b. p. over the range 500 to 900 mm., n_{D}, d_4 and η at 20, 25 and 30°, η at 0°, specific dispersion at 20°, f. p. depressions for three solutes, and some derived constants.

2. Samples of the two isomers isolated by means of the chloromercuri derivatives showed several properties in agreement with the corresponding properties of the physically-purified specimens.

3. Two crystalline forms of 3-methylthiophene were found; the lower-freezing form has the lower heat of fusion and over the whole range of its existence is metastable with respect to the higher-freezing form.

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[19] Steinkopf and Jacob, *Ann.*, **515**, 279 (1935).

[20] Steinkopf, "Die Chemie des Thiophens," Theodor Steinkopff, Dresden, 1941, p. 109.

[21] McKittrick, *Ind. Eng. Chem.*, **21**, 585 (1929).

[CONTRIBUTION FROM THE NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

The Mechanism of Modifier Action in the GR-S Polymerization.[1] I

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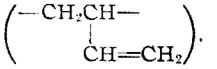
When butadiene and styrene are copolymerized in an aqueous emulsion containing only the monomers, an emulsifying agent, and a peroxidic catalyst the product obtained is an insoluble substance which is difficult to process and is of little value as a rubber. Useful copolymers are obtained by adding to the polymerization system a substance known as a "modifier." In the preparation of GR-S the modifier used is a mercaptan or a mixture of mercaptans. The copolymer produced in the presence of such a modifier is soluble in benzene, and it can be milled and processed much like natural rubber. The present work was undertaken in an effort to determine the nature of the chemical action of the modifier.

It is now generally believed that vinyl polymerizations induced by peroxidic catalysts proceed by a free radical mechanism[2,3,4] in which the essential steps are initiation, propagation, and termination. Peroxide-catalyzed polymerizations of dienes differ from those of simple vinyl monomers in that the steps of initiation and propagation may consist in either 1,4- or 1,2-addition to the diene system, or both 1,4- and 1,2-addition may occur in random fashion. Ozonization studies of polybutadiene indicate that the polymer has a structure of the third type, resulting from both 1,4- and 1,2-addition.[5,6]

At the time of the beginning of the present work two theories were under general discussion as providing possible explanations for the action of modifying agents. In one it was supposed that the modifier acted as a catalyst for 1,4- addition to the diene, or as an inhibitor for 1,2-addition, so that its use resulted in the formation of polymer of essentially linear structure. In the absence of a modifier the polymerization was supposed to yield a product in which a large proportion of the diene units were combined as vinylethylene residues



$\left(\begin{array}{l}—CH_2CH— \\ \qquad\quad | \\ \qquad\quad CH{=}CH_2\end{array}\right)$. The side-chain vinyl groups in

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] (a) Flory, THIS JOURNAL, **59**, 241 (1937); (b) Irany, *ibid.*, **62**, 2690 (1940).

[3] Price, Kell and Krebs, *ibid.*, **64**, 1103 (1942).

[4] Schulz and Husemann, *Z. physik. Chem.*, **B39**, 246 (1933).

[5] Hill, Lewis and Simonsen, *Trans. Faraday Soc.*, **35**, 1067 (1939).

[6] Alekseeva and Belitzkaya, *Rubber Chem. and Tech.*, **15**, 693 (1942).