[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Polyalkylbenzenes. XXVIII.[1] Physical Properties of the Tetraethylbenzenes

BY LEE IRVIN SMITH AND CYRUS O. GUSS[2]

The three tetraethylbenzenes, prepared as described in the previous and following papers,[1,3] by hydrolysis of their purified sulfonic acids, were further purified by two fractional distillations through a packed column, rejecting the first and last 25% each time. Densities were determined by the pycnometer method, the pycnometer having a volume of 10 cc. Refractive indices were determined by means of an Abbe refractometer over a range of 28°. *sym-* and *unsym*-tetraethylbenzenes gave practically identical refractive indices throughout the range studied; mixtures of these two hydrocarbons could not be analyzed by making use of this property.

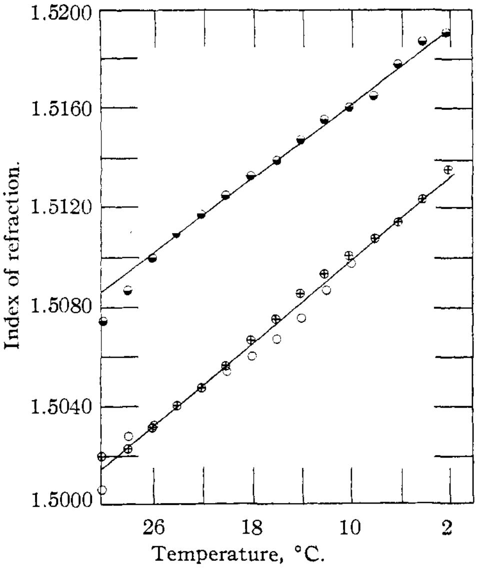

Fig. 1.—Refractive indices of the tetraethylbenzenes with temperature: ⊕, *unsym;* ○, *sym;* ◒, *vicinal.*

Freezing points of 1,2,3,5- and 1,2,4,5-tetraethylbenzenes, as well as the freezing point diagram of mixtures of the two hydrocarbons, were determined in an apparatus essentially like that used by Smith and MacDougall.[4] For the symmetrical hydrocarbon, an ice-bath was used; the thermometer was carefully checked against a thermometer calibrated by the Bureau of Standards. For 1,2,3,5-tetraethylbenzene, a bath of acetone and dry-ice was used. Because this hydrocarbon supercooled excessively, it was difficult to determine the freezing point. The thermometer had a range of +50° to −50° and, while not calibrated, it was believed to be an accurate one. The thermometer could not be held in the supercooled hydrocarbon, because the thermometric substance also froze. But by quickly introducing the bulb of the thermometer into the liquid at the instant it was crystallizing, it was possible to record part of the plateau and the second slope of the usual cooling curve. A melting point curve was also obtained by allowing the seeded liquid to crystallize partially and then melt. The mixtures of hydrocarbons did not supercool greatly and the individual points on the freezing point diagram were obtained in the usual way without undue difficulty. The eutectic mixture, containing about 25% of *sym*-tetraethylbenzene, froze at −28°.

Vapor pressures of the pure hydrocarbons were determined by taking the boiling points under different pressures in an apparatus like that used by MacDougall and Smith.[5] The modified distilling flask was immersed in a bath of Wood's metal, and a fine stream of air was passed through the liquid to avoid superheating. The pressure was regulated by a capillary tube in the vacuum line, and was read on a closed tube manometer having a range of one atmosphere which could be read with an accuracy of 0.5–1.0 mm. The thermometer, calibrated by the Bureau of Standards, was marked in 1° intervals and was wholly immersed in the vapors.

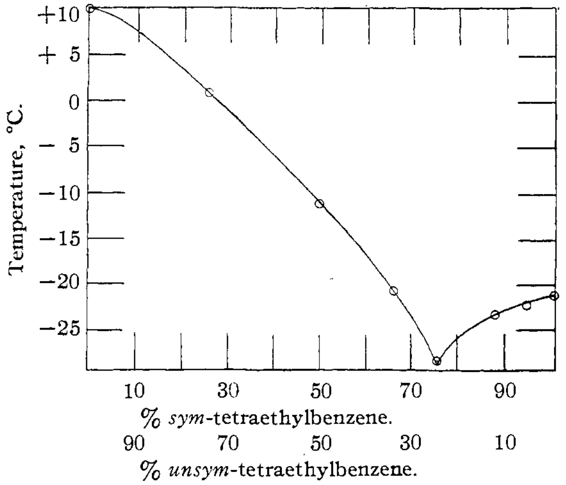

Fig. 2.—Freezing point diagram of mixtures of *sym-* and *unsym*-tetraethylbenzenes.

Only one curve could be drawn from the data for *sym-* and *unsym*-tetraethylbenzenes. Empirical equations derived from the data and relating the vapor pressure to the absolute temperature are as follows:

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(1) XXVII, THIS JOURNAL, **62**, 2625 (1940).

(2) Abstracted from a thesis by Cyrus O. Guss, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, January, 1940.

(3) Ref. 1, p. 2625; XXIX, p. 2631.

(4) THIS JOURNAL, **51**, 3001 (1929).

(5) THIS JOURNAL, **52**, 1998 (1930).

For 1,2,4,5-tetraethylbenzene:

$$\log p = 54.6612 - 5905.5/T - 14.8886 \log T$$

For 1,2,3,5-tetraethylbenzene:

$$\log p = 18.1202 - 3756/T - 2.9332 \log T$$

For 1,2,3,4-tetraethylbenzene:

$$\log p = 17.4635 - 3637/T - 2.8165 \log T$$

These equations, however, are only approximate, the average deviations of the first being ±2 mm., of the second, omitting the two largest values which were much too large, ±2.5 mm. and of the third ±6 mm.

TABLE I

PHYSICAL PROPERTIES OF THE TETRAETHYLBENZENES

	Symmetrical	Unsymmetrical	Vicinal
B. p., °C.	246.8 (734 mm.)[a] 250[c] 248 (755 mm.)[b]	247.4 (734 mm.)[a]	251.1 (734 mm.)[a] 254[c]
F. p., °C.	+10[a] +13[c]	−21[a]	Does not freeze[a] at −50
$n^{20}D$	1.5054[a] 1.5041 (16°)[b]	1.5056[a]	1.5125[a] 1.50845[d]
d^{20}	0.8788[a] .8884 (16°)[b]	0.8799[a]	0.8875[a] .88664 (19.6°)[d]

[a] New results reported in the present study. [b] Klages and Keil, *Ber.*, **36**, 1632 (1903). [c] Jacobsen, *ibid.*, 21, 2814, 2819 (1888). [d] Perkin, *J. Chem. Soc.*, **77**, 280 (1900).

TABLE II

VAPOR PRESSURES OF THE TETRAETHYLBENZENES

Symmetrical		Unsymmetrical		Vicinal	
Press., mm.	B. p., °C.	Press., mm.	B. p., °C.	Press., mm.	B. p., °C.
3	97.6	3	96.6	2	95.2
4	102.6	4	104.0	4	107.0
10.5	128.4	15	134.4	10	129.4
22.5	141.4	32.5	148.5	11.5	132.4
57	159.2	58	160.3	30.5	151.0
123	180.6	129.5	182.6	51	164.1
240	202.6	246	204.1	124	185.2
546	233.8	530	232.8	224.5	204.1
734	246.8	734	247.4	578.5	241.8
				734	251.1

Summary

1. The following physical properties of highly purified tetraethylbenzenes have been determined: refractive indices, densities, freezing points, vapor pressures.

2. The freezing point diagram of mixtures of 1,2,4,5- and 1,2,3,5-tetraethylbenzenes has been constructed.

3. *sym*- and *unsym*-tetraethylbenzenes have practically identical refractive indices and vapor pressures throughout the entire range studied.

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The Jacobsen Reaction. VII.[1] Polyethylbenzenes

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In the previous paper[1b] the results of a study of the Jacobsen rearrangements of some ethyltrimethylbenzenes, namely, 5-ethylpseudocumene, 3-ethylpseudocumene and ethylmesitylene, were reported. The second of these hydrocarbons did not undergo any rearrangement in contact with sulfuric acid, but the other two were rearranged into 3-ethylpseudocumene (25–35%), prehnitene (10%), an ethyl-*m*-xylene (12%) and a trimethylbenzene (5%). In these rearrangements, the ethyl group migrated more readily than one of the methyl groups, but the reaction was accompanied by three types of cleavage: loss of the ethyl group, loss of a methyl group, and cleavage of the ethyl group to a methyl group. Moreover, there was a great difference between ethylmesitylene and 5-ethylpseudocumene in the ease with which the rearrangement occurred; at 60–70°, the former required six hours for complete change, while one hour sufficed for the latter.

To obtain more information concerning the Jacobsen rearrangement of ethylated benzenes, six polyethylbenzenes, 1,2,4- and 1,3,5-triethylbenzenes, the three tetraethylbenzenes, and pentaethylbenzene, have been studied. Very few reports are to be found in the literature dealing with rearrangements of polyethylbenzenes. Jacobsen[3] dissolved pentaethylbenzene in fuming sulfuric acid; after the solution stood for several days, he noted the formation of hexa-ethylbenzene and found that the solution contained a sulfonic acid whose amide melted at 107°, and he identified this as derived from 1,2,3,4-tetraethylbenzene. Jacobsen also stated that when pentaethylbenzene was heated with sulfuric acid, neither hexa-

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(1) (a) Polyalkylbenzenes XXIX. Paper XXVIII, THIS JOURNAL, **62**, 2630 (1940); (b) Paper VI on the Jacobsen Reaction, THIS JOURNAL, **61**, 989 (1939).

(2) Abstracted from a thesis by Cyrus O. Guss, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, January, 1940.

(3) Jacobsen, *Ber.*, **21**, 2814, 2819 (1888).