[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY]

The Relation of the Melting Point to the Number of Carbon Atoms in a Series of Normal Mercaptans[1]

BY DONALD EDWARD TEETS

E. E. Reid and L. M. Ellis of this Laboratory have prepared a series of mercaptans and have kindly loaned them to the author for the melting point determinations given below.

Austin[2] gave a method for selecting the values of melting points. He pointed out that when the logarithm of the molecular weight was plotted against the absolute temperature of melting, a straight line was obtained. The series of normal mercaptans affords an accurate means of checking this relation because they are pure compounds and give well-defined cooling curves.

Apparatus.—The apparatus used in determining the melting points was, with a few exceptions, as described by Andrews, Kohman and Johnson.[3] A description is shown in Fig. 1. A is a copper–constantan thermocouple (no. 36 copper wire and no. 30 constantan wire both double silk insulated), passing through a small glass tube, with the naked couple directly immersed in the melt. B is a similar thermocouple attached to the side of the shield D by means of a small rubber band. The difference of the two couple readings gives the temperature head. C is a sample tube which is attached to a longer tube by a piece of rubber tubing. E is a cylindrical copper shield wound with approximately 100 ohms of constantan resistance wire. F is an evacuated shield partly filled with activated charcoal. K is a liquid air bath, and G is another evacuated silvered Dewar bulb. The shield D above is allowed to drop in temperature in the usual manner.

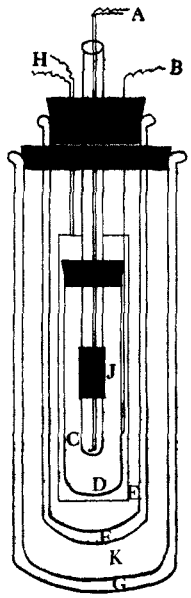

Fig. 1.—Melting point apparatus.

The thermocouples were calibrated against a platinum resistance thermometer furnished by Southard and Andrews,[4] and against pure samples of toluene and benzene.

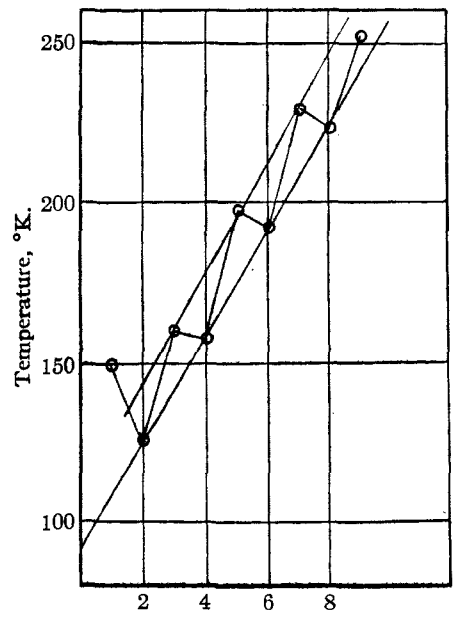

Fig. 2.—Melting points.

Experimental Procedure.—The sample under consideration (approx. 0.75 cc.) was placed in C (Fig. 1) and surrounded by a liquid air bath as shown. As the temperature dropped the e. m. f. of the melt couple and shield couple was read one a minute for each couple.

Experimental Results and Discussion.—The series of mercaptans were subjected to the above procedure and Table I gives a summary of the results. The compounds show exceptional purity as a whole.

If we plot the melting temperatures against the number of carbon atoms in the chain a zigzag curve is obtained as given in Fig. 2. If the curve is examined more closely we see that the odd numbered members, with the exceptions of methyl and nonyl mercaptans, lie on a straight line. The even numbered members give another straight line. We see that the melting point is a two-fold function of the number of carbon atoms in the chain when the number is small. When the

(1) This article is a part of a paper entitled "The Relation of the Melting Point to Molecular Symmetry in some Series of Related Organic Compounds" and was presented by Dr. D. H. Andrews for the author at the Atlanta meeting of the American Chemical Society.

(2) J. B. Austin, THIS JOURNAL, **53**, 1049 (1930).

(3) Andrews, Kohman and Johnson, *J. Phys. Chem.*, **29**, 914 (1925).

(4) Southard and Andrews, *J. Franklin Inst.*, **207**, 323 (1929).

molecular weight becomes high the addition of another carbon atom does not produce such marked changes in the melting point.

TABLE I

Compound, mercaptan	M. p., °C.		Half time drop of curve, °C.
Nonyl	− 20.1		0.0
Octyl	− 49.2		.0
Heptyl	− 43.4		.0
Hexyl	− 81.03		.0
Amyl	− 75.7		.0
Butyl	−115.9		.03
Propyl	−113.3	−115.5[a]	.19
Ethyl	−147.3		1.04
Methyl	−123.1	−121.0[a]	0.19

[a] Values from literature "I. C. T."

Since we know accurately the melting points of the normal mercaptans we have a method to test

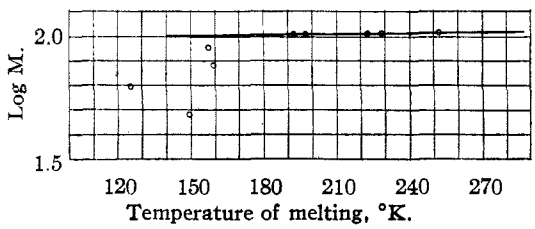

Fig. 3.—Normal mercaptans, Austin method.

the accuracy of the Austin method.[2] A plot of log M against the temperature of melting is given in Fig. 3, where we see that when the logarithm of the molecular weight is two or more the points do lie on a straight line. In Fig. 2 we notice that nonyl mercaptan deviates from the simple linear function, indicating that if we were to plot more members the simple addition rule would break down. Figure 3 shows that Austin's method breaks down completely for the lower members of the series. This indicates that the method applies when the molecular weight is above 100 and that the lower members of the chain series obey the linear addition method.

In Fig. 2 the even membered line has been extended to obtain a value for the melting temperature of methane, which is equivalent to removing two carbon atoms or one sulfur atom. The value obtained is 91°K. while the value given in the literature ("I. C. T") is 89°K.

The author wishes to express his appreciation to Dr. D. H. Andrews, who has given valuable advice in this investigation. Thanks are also due Drs. Reid and Ellis for supplying the compounds.

Summary

1. A modification of the melting point apparatus of Andrews and co-workers is given.

2. The melting temperatures of a series of normal mercaptans are reported.

3. The relation of the melting temperature to the number of carbon atoms in the chain is discussed.

BALTIMORE, MARYLAND RECEIVED JANUARY 15, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Synthesis of Alpha-Nicotine and Alpha-Nornicotine

BY LYMAN C. CRAIG[1]

The results of a previous paper indicate[2] that toxicity in the alpha substituted N-methylpyrrolidine series increases as the negativity of the alpha substituting radical increases. Nicotine may be considered a member of the series and is more toxic than the synthetic preparations. However, the beta pyridyl radical is far more negative than the other alpha substituting radicals in the series. The alpha pyridyl radical has been shown to be of a like order of negativity as the beta[3] and the alpha pyrrole radical somewhat less negative but yet more negative than any of the radicals in the series prepared above. In view of this it seemed interesting to prepare and study the physiological properties of α-(α-pyridyl)-N-methylpyrrolidine (α-nicotine) and α-(α-pyrrole)-N-methylpyrrolidine. This paper reports the synthesis of the former compound and some intermediates in the synthesis of the latter. The literature contains two accounts[4] in which a proposed synthesis of α-nicotine was partially completed.[5]

For the preparation of these compounds the

(1) National Research Fellow.

(2) Craig, THIS JOURNAL, **55**, 2543 (1933).

(3) Craig and Hixon, *ibid.*, **53**, 4367 (1931).

(4) Wibaut and Dingemanse, *Rec. Trav. Chim.*, **42**, 1033 (1923); Tschitschibabin and Bylinkin, *Ber.*, **56**, 1745 (1923).

(5) Shortly after the completion of the experimental work reported in this paper Wibaut and Oosterhuis, *Rec. Trav. Chim.*, **52**, 941 (1933), reported the synthesis of α-nicotine although according to their analytical data a final pure product was not isolated. Their method of synthesis is entirely different from the one reported here.