The Preparation of Pure Stearic Acid

By J. P. Kass and L. S. Keyser

The preparation of pure stearic acid is complicated by the difficulty of removing final traces of the contaminating palmitic acid, since the separation by physical means is tedious and never unquestionably complete. In a recent study, Guy and Smith[1] considered it necessary to subject "pure" stearic acid to twenty-four recrystallizations from various solvents and to three fractional distillations to obtain a 3.8% yield of final product, m. p. 69.62°, the homogeneity of which was still not beyond question. During the course of our investigations of the chemistry of the fatty acids, we have found it convenient to prepare pure stearic acid totally free from palmitic acid by the catalytic reduction of the readily purifiable octadecenoic acids. Elaidic acid,[2] and especially the α- or β-eleostearic acids,[3] are easily available and may be brought to a high state of purity by a few recrystallizations of the free acids, while pure linoleic acid[4] of theoretical iodine value may be obtained from the crystallizable α-tetrabromostearic acid.[5] Quantitative reduction was effected by shaking the acetic acid solutions of the unsaturated acids for three hours in an atmosphere of hydrogen at room temperature and 45 lb. (3 atm.) pressure in the presence of platinum oxide catalyst. One recrystallization of the product from acetic acid or 85% alcohol yielded a stearic acid melting in a capillary tube at 69.6–70.2° (corr.) and dissolving in concentrated sulfuric acid at 70° without discoloration. A similar procedure was used by Francis, Collins and Piper[6] for the preparation of behenic acid from erucic acid.

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(1) Guy and Smith, *J. Chem. Soc.*, 616 (1939).

(2) Rankoff, *Ber.*, **64**, 619 (1931); Smith, *J. Chem. Soc.*, 976 (1939).

(3) Wan and Chen, This Journal, **61**, 2283 (1939).

(4) Rollet, *Z. physiol. Chem.*, **62**, 410 (1909).

(5) McCutcheon, *Can. J. Research*, **16**, 158 (1938).

(6) Francis, Collins and Piper, *Proc. Roy. Soc.* (London), **A158**, 707 (1937).

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The Preparation of *m*-Halogenophenols

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The author's attention has been drawn to a recent paper by S. Natelson and S. P. Gottfried[1] in which the preparation of *m*-bromophenol is described in language which implies originality, *viz.*: "Since this paper[1] was written, Smith and Haller[2] have published a method for obtaining *m*-bromophenol in good yield .... Their over-all yield is not as good as that obtained from the procedure described herein[1] nor is their procedure as simple."

It is of interest to note that from January to May of this present year (1939) the preparation of *m*-bromophenol has been described no fewer than three times,[1,2,3] and in only one of them[3] has the work of the present writer been mentioned.

The method apparently claimed as new by Natelson and Gottfried[1] was patented by the author[4] in 1923, and C. F. Koelsch[3] has stated recently that this patent of seventeen years ago is substantially true and that yields of 75–80% may be obtained thereby. Similar confirmations of the patent claim, however, have already been made to the writer by numerous chemists during the past seventeen years, who have found yields of the order of 80–90%.

Yields of over 90% of *m*-chlorophenol from *m*-chloroaniline have been obtained by the patented method[4] in large scale (kilo.) preparations. Subsequent work proved that excellent yields of *m*-fluorophenol[5] could also be obtained from *m*-fluoroaniline, while even the non-steam volatile *m*-hydroxybenzaldehyde[6] was prepared in excellent yield by the process.

The patented method[4] is substantially the same in detail as that described at length by Koelsch,[3] and is probably the best process yet devised for the preparation of steam-volatile phenols, since it is of universal application.

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(1) Natelson and Gottfried, This Journal, **61**, 1001 (1939).

(2) Smith and Haller, *ibid.*, **61**, 143 (1939).

(3) C. F. Koelsch, *ibid.*, **61**, 969 (1939).

(4) H. H. Hodgson and The British Dyestuffs Corporation, English Patent 200,714 (1923); *B. C. A.*, [i] 1005 (1923).

(5) H. H. Hodgson and J. Nixon, *J. Chem. Soc.*, 1879 (1928).

(6) H. H. Hodgson and H. G. Beard, *J. Soc. Chem. Ind.*, **45**, 91T (1926).

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The Freezing Points of Pure High Polymers

By Edwin L. Lovell and Harold Hibbert

In a recent publication[1] it was shown that the setting points of the polymer-homologous series of polyoxyethylene glycols $HO(CH_2CH_2O)_pH$ followed very exactly the *empirical* equation

$$t_s = P/(a + bP) \qquad (1)$$

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(1) Lovell and Hibbert, This Journal, **61**, 1916 (1939).

where t_s is the setting point in °C., P the number of repeating units in the chain, and a and b constants. The experimental data covered molecules with from 54 to 558 atoms in the straight chain, a much wider range than has previously been available for pure compounds. At that time it was duly noted that this homologous series did *not* follow the logarithmic freezing point equation deduced from what might be termed "kinetic" considerations by Austin[2] but the authors could offer no explanation for the form of the equation actually obtained.

Very recently, however, a publication has appeared by Huggins[3] concerning the properties of long-chain compounds; it includes the derivation on purely thermodynamic grounds of a general law relating the freezing points in a polymer-homologous series to the number of atoms in the chain. This equation is

$$T_f = (A + Bn)/(C + Dn) \qquad (2)$$

where T_f is the absolute freezing point, n the number of atoms in the straight chain and the other symbols are constants. Inspection of the empirical relationship (1), and substituting for t_s its equivalent $T_f - 273$, reveals that this equation is identical in form with that of Huggins. This provides excellent support for the latter over a very wide range of chain lengths, many times greater than is possible in the n-alkane series, agreement for which (up to C_{70}) is shown by the previous work of Garner[4] and co-workers, who also have attempted to justify their results theoretically.[5] In both series the relation fails for chains of less than 20 atoms.

The agreement thus found between Huggins' thermodynamically derived freezing point equation and the freezing point data for the higher polyoxyethylene glycols is important additional evidence for the purity (uniformity of chain length) of this series of synthetic polymers.

[2] Austin, This Journal, **52**, 1049 (1930).
[3] Huggins, *J. Phys. Chem.*, **43**, 1095 (1939).
[4] Garner, van Bibber and King, *J. Chem. Soc.*, 1533 (1931).
[5] Garner, Madden and Rushbrooke, *ibid.*, 2491 (1926).

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The Conversion of Chlorophyll to Pheophytin

By G. Mackinney and M. A. Joslyn

In a previous paper[1] we presented evidence showing the rate of conversion of chlorophyll to pheophytin in 90% acetone was of first order with respect to acid concentration (normality) and possibly of second order with respect to chlorophyll. It was necessary to consider the two chlorophylls as a single component because we did not have the individual components separated. Evidence favored the assumption that the reaction was chiefly a conversion of chlorophyll a to pheophytin a, because the reaction was rarely carried to more than 80% completion. We have now separated sufficient quantities of chlorophylls a and b[2] to repeat previous experiments. Measurements were made at 5350 Å. for chlorophyll a, at 5280 Å. for chlorophyll b, where the respective pheophytin maxima occur.

Results are condensed in Table I. The first and second order rate constants, k_1 and k_2, have been calculated, and each value represents the average of 8–13 determinations over periods of time varying from two minutes to seven hours. The temperature was 28 ± 0.5°. The column Δ indicates the mean deviation of the arithmetic mean of the individual determinations. The values of k/N, whether k_1 or k_2 is taken, clearly show the reaction is of first order with respect to acid concentration, confirming our earlier work.

Table I

Rate Constants for Chlorophyll, in 90% Acetone, with Oxalic Acid

Normality	k_1	Δ	k_2	Δ
		Chlorophyll a		
0.002	0.211	0.046	0.0069	0.0010
.004	.539	.072	.0189	.0099
.007	.907	.088	.0332	.0114
.01	1.39	.170	.0562	.0301
		Chlorophyll b		
0.01	0.148	0.021	0.0040	0.0007
.02	.328	.126	.0088	.0022
.05	.804	.180	.0271	.0049
.10	1.69	.216	.0580	.0148

We were previously at some loss to decide the order with respect to chlorophyll, because in most cases there was an apparent falling off in the calculated constants with time. The k_2 constants for oxalic acid were reasonably constant which led us to suggest a second order for chlorophyll. We knew only that pheophytin b contributed to the absorption at 5350 Å., but we could not then evaluate the extent of its absorption. Because the a and b mixture used was not highly purified, extensive recalculations are not deemed profit-

[1] Mackinney and Joslyn, This Journal, **60**, 1132 (1938).

[2] Details will be published shortly.