SCIENTIFIC SECTION

THE HEATS OF FORMATION OF THE ALCOHOLATES OF CHLORAL.

BY SAMUEL CHECHIK.*

INTRODUCTION.

As is well known, anhydrous chloral combines not only with water to form chloral hydrate, regarded structurally as trichlorethyledene glycol, but also with alcohol to form chloral alcoholate,[1] the monoethyl ether of trichlorethyledene glycol,[2] also regarded as its hemiacetal. Other alcohols are known to form similar addition products.[3] Because of the readiness with which some of these are formed, also because of the sharp or fairly sharp melting points of a few of these addition products, they have been used to identify the respective alcohols. Bromal and its addition products[4] have been used for a like purpose.

Thus far, however, the use of these two reagents appears to have depended largely upon accidental discovery.[5] No systematic study of the additive capacity of either chloral or bromal for alcohols, monatomic, diatomic,[6] triatomic,[7] etc., seems

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* Scientific Section, A. PH. A., Rapid City meeting, 1929.

[1] The discovery of chloral hydrate and of chloral alcoholate was coincident with that of chloral, first prepared by Liebig in 1832 (*Ann.*, 1, p. 182. See also "Cohen, Org. Chem.," p. 140), though he did not recongize the alcoholate as a distinct substance at that time. Personne is accredited with the observation, in 1869, that by the addition of ethyl alcohol to chloral a different substance is formed than that which results when water is added. (*Compt. rend.*, 69, p. 1363; J. (1869), p. 504.) During the same year, Roussin had found that a crystalline mass is formed when alcohol is acted upon by chlorine as in the preparation of chloral (*Compt. rend.*, 69, p. 1144; J. (1869), p. 504). This is chiefly chloral hydrate. In 1870, hence a year later, Lieben in his report "Ueber die Einwirkung von Chlor auf absoluten Alkohol" pointed out that choral alcoholate is formed as a by-product in the preparation of chloral hydrate (*Ber.*, 3, p. 907).

[2] The structure of chloral hydrate as trichlorethyledene glycol was first pronounced by Caro and Victor Meyer in 1880. (*Ber.*, 13, p. 2343; see also Meyer u. Jacobsen, I (II), p. 867.) That chloral alcoholate should be regarded as the hemiacetal or monoethyl ether of trichlorethyledene glycol followed.

[3] In his paper "Ueber die Alkoholderivate des Chlorals," Henry in 1874 discusses the addition products formed by the union of chloral, not only with water, but with the following alcohols as well, *viz.* CH_3OH, C_2H_5OH, $C_5H_{11}OH$, $C_2H_4(OH)Cl$, $C_2H_2O(OH)C_2H_5O$, $CH_2(OH)\cdot CH_2(OH)$. (*Ber.*, 7, p. 762.)

[4] The fact that bromal behaves like chloral in this respect was first recorded by Minguin in 1893 (*Compt. rend.*, 116, p. 889).

[5] 1869. Ethyl alcohol, Personne, *Compt. rend.*, 69, p. 1363.
1870. Methyl alcohol, Martius and Mendelssohn-Bartholdy, *Ber.*, 3, p. 443.
1871. Amyl alcohol, Jacobsen, *Ann.*, 157, p. 243.
1871. Cetyl alcohol, Jacobsen, *Ibid.*
1874. Allyl alcohol, Oglialoro, *Ber.*, 7, p. 1462.
1883. Thymol, Mazzara, *Gaz.*, 13, p. 272.
1891. Borneol, Heller, *Compt. rend.*, 112, p. 144.
1901. Propyl alcohol, Gabutti, *Gaz.*, 31, I, p. 86.
1901. Isopropyl alcohol, Gabutti, *Ibid.*

[6] Glycol, Henry, *Ber.*, 7 (1874), 762. Resorcinol, H. Causse, *Bull. Soc. Chim.* (3rd ser.), 3 (1890), p. 861.

[7] Glycerol.

to have been recorded.[1] A mere beginning has now been made by studying the heats of formation of the hemiacetals resulting by bringing together molecular amounts of anhydrous chloral and the alcohols of the methanol series, from the point of homology as well as that of isomerism.

For this purpose 3.2 cc. of anhydrous chloral (= 5 Gm.) freshly prepared and kept in a well-stoppered bottle, were mixed with equimolecular amounts of the respective alcohols in a double tube stoppered with a thermometer and the rise in temperature observed, also the time required to reach the maximum temperature. In addition the time required for the cooled reaction product to crystallize was recorded, also the melting point of the crystallized mass.

Methyl Alcohol.—The monomethyl ether of trichlorethyledene glycol was first prepared by Martius and Mendelssohn-Bartholdy in 1870.[2] In the next year it was prepared by Jacobsen.[3] He records its m. p. at 50° and its b. p. at 106°. In 1874 Henry[4] again reports having prepared this compound but he also reports no melting point.

To 3.2 cc. of chloral 1.4 cc. (= 1.14 Gm.) of methanol ("Absolute," E. & A.) were added. The temperature rose 56.9° (56.7°, 56.9° and 57.2°) in 6 seconds. (The three readings were 7, 6 and 6 seconds, respectively.) The reaction mixture crystallized on cooling. The product melted at 51.5°. It remained crystalline after seven months. After that time it was found to be insoluble in cold heptane, but soluble in hot heptane. From the hot solution it crystallized upon cooling. The recrystallized product melted at 46°. Recrystallized a second time from hot heptane, its melting point remained the same. The m. p. of chloral hydrate is reported as 57°. The m. p. of about 51° as reported above, may have been due to traces of chloral hydrate since the "absolute" methyl alcohol used, no doubt, contained traces of water.

Ethyl Alcohol.—The preparation of chloral alcoholate by Liebig[5] (1832), Personne[6] (1869), Roussin[7] (1869) and Lieben[8] (1870) has already been referred to.[9] Jacobsen[10] (1871) states that it melts at 56–57° and boils at 115–117°. ("Richter, Org. Chem.," 1st edition, p. 196) states that it melts at 56° and boils at 114–115°.

To 3.2 cc. of chloral 1.94 cc. (= 1.57 Gm.) of absolute ethyl alcohol (manufactured in the laboratory; d = 0.816) were added. The temperature of the reaction mixture rose 61.2° (61.0°, 61.2° and 61.4°) in 11 seconds. (The three readings were 12, 10 and 10 seconds, respectively.) Crystallization set in upon cooling. The product melted at 55° to 58°. After having stood for half a year, it was found to be insoluble in cold, but soluble in hot heptane. From the hot solution it did not crystallize immediately upon cooling, but only after long exposure to cold. The recrystallized material melted at 61°. A second recrystallization from heptane caused a lowering of the melting point to 57°. These fluctuations are not readily explained.

Propyl Alcohols.—The addition products of neither the primary nor the secondary propyl alcohols appear to have been prepared.

Primary Propyl Alcohol.—To 3.2 cc. of chloral, 2.54 cc. (= 2.05 Gm.) of a commercial article (E. & A.) obtained from stockroom were added. The rise in temperature amounted to 62.9° (63.3°, 62.9° and 62.6°) in 7 seconds (6, 7 and 6 seconds, respectively.) The product remained liquid after six months' standing.

Secondary Propyl Alcohol.—The alcohol used was that of the stockroom (E. & A.). The rise in temperature amounted to 53.7° (54.0°, 53.7° and 53.5°) in 11 seconds (10, 12 and 11 seconds,

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[1] An attempt in this direction is recorded as an undergraduate thesis by Lloyd T. Plank, "The Addition of Alcohols to Chloral," U. W., 1927, unpublished results.

[2] *Ber.*, 3, p. 443. [3] *Ann.*, 157, p. 243.

[4] *Ber.*, 7, p. 762.

[5] *Ann.*, 1, p. 182.

[6] *Compt. rend.*, 69, p. 1363; *J.* (1869), p. 504.

[7] *Compt. rend.*, 69, p. 1144; *J.* (1869), p. 504.

[8] *Ber.*, 3, p. 907. [9] See Introduction, footnote 1.

[10] *Ann.*, 157, p. 243.

respectively, in the three experiments). The product crystallized upon cooling. The crystals melted at 47°. They were soluble in heptane at room temperature from which solvent they were obtained after prolonged standing in the cold as fine needles melting at 49°. A second recrystallization from heptane gave a product with the same melting point.

Butyl Alcohols.—Not one of the addition products of the four isomeric alcohols appears to have been prepared.

Primary Normal Butyl Alcohol.—To 3.2 cc. of chloral, 3.1 cc. (= 2.74 Gm.) of a *n*-butyl alcohol from the stockroom (Industrial Chem. Co., Balto.) were added. The rise in temperature was 58.1° (57.6°, 58.8° and 58.0°) in 10 seconds (9, 10 and 10 seconds, respectively, in the three experiments). The reaction product solidified in 15 minutes. It melted at 58.5°. It was found to be soluble in cold heptane. The m. p. of the recovered crystals was 56.5°. A second recrystallization from the same solvent yielded a product with the same m. p.

Primary Iso Butyl Alcohol.—To 3.2 cc. of chloral, 3.1 cc. (= 2.50 Gm.) of *p*-isobutyl alcohol from the stockroom (Merck & Co.) were added. The temperature rose 57.2° (56.7°, 58.0° and 57.0°) in 10 seconds (11, 10 and 10 seconds, respectively). After standing for four months the reaction product was still liquid. It was soluble in heptane, from which solvent no crystals have been obtained after three weeks. The solution had a yellowish color.

Secondary Butyl Alcohol.—To 3.2 cc. of chloral, 3.05 (= 3.03 Gm.) of *s*-butyl alcohol from the stockroom (manufacturer unknown) were added. The temperature of the reaction mixture rose 52° (51.6°, 52.0° and 52.4°) in 7.5 seconds (8, 7 and 8 seconds, respectively). After standing for four months it was still liquid.

Tertiary Butyl Alcohol.—To 3.2 cc. of chloral, 3.2 cc. (= 2.5 Gm.) of *t*-butyl alcohol from the stockroom were added. The rise in temperature was 14.75° (13.5°, 15.0° and 15.2°) in six minutes ($4^{1}/_{2}$, 6 and $7^{1}/_{2}$ minutes, respectively). The reaction mixture solidified over night. It melted at 58°. It was insoluble in cold heptane but soluble in the hot solvent. After prolonged standing crystals were obtained that melted at 52°.

Amyl Alcohols.—Of the eight isomeric alcohols (isomers of position, exclusive of optical isomers) only one appears to have been used in the preparation of an addition product. No doubt, the commercial amyl alcohol was used. It was first reported by Martius and Mendelssohn-Bartholdy[1] in 1870. In the next year Jacobsen[2] reports a m. p. of 56° and a b. p. of 145–147°. Henry,[3] in 1874, also prepared it.

The alcohols used in the experiments here recorded were obtained from Eastman.

Primary Normal Amyl Alcohol.—To 3.2 cc. of chloral, 3.7 cc. (= 3.02 Gm.) of the alcohol were added. The temperature of the reaction mixture rose 50.6° (50.0°, 49.7° and 52.2°) in seven seconds (7, 7 and 7 seconds, respectively). It was still liquid after having stood four months. The reaction product was of a dark brown color.

Primary Iso Amyl Alcohol.—To 3.2 cc. of chloral, 3.7 cc. (= 3.03 Gm.) of the alcohol obobtained were added. The temperature of the reaction mixture rose 56.5° (55.5°, 56.5° and 57.7°) in seven seconds (8, 7 and 8 seconds, respectively). It solidified after standing two days. It melted at 55°. It was insoluble in cold heptane, but soluble in hot heptane. After prolonged standing crystals were obtained that melted at 55°. The recrystallized product had the same m. p.

Secondary Normal Amyl Alcohol (Methyl n-Propyl Carbinol).—To 3.2 cc. of chloral 3.7 cc. (= 3.05 Gm.) of the alcohol were added. The temperature of the reaction mixture rose 53.4° (52.7°, 53° and 53.7°) in seven seconds (7, 9 and 7 seconds, respectively). After standing four months it was still liquid.

Secondary Normal Amyl Alcohol (Diethyl Carbinol).—To 3.2 cc. of chloral, 3.7 cc. (= 3.05 Gm.) of the alcohol were added. The temperature of the reaction mixture rose 42.9° (43.0°, 42.2° and 43.5°) in eleven seconds (11, 12 and 11 seconds, respectively). After four months it was still liquid.

Tertiary Amyl Alcohol.—To 3.2 cc. of chloral, 3.7 cc. (= 3.0 Gm.) of the alcohol were added. The temperature of the reaction mixture rose 27.1° (27.2°, 27.2° and 26.9°) in twenty-five seconds (25, 27 and 24 seconds, respectively). After four months it was still liquid. It was soluble in heptane from which solvent crystals were obtained after three weeks that melted at 68°.

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[1] *Ber.*, 3, p. 443. [2] *Ann.*, 157, p. 243. [3] *Ber.*, 7, p. 762.

Hexyl Alcohols.—None of the addition products of this group of isomeric alcohols appears to have been prepared. The alcohols used in the experiments here recorded were obtained from Eastman.

Primary Normal Hexyl Alcohol.—To 3.2 cc. of chloral, 4.2 cc. (= 3.45 Gm.) of the alcohol were added. The temperature of the reaction mixture rose 48.8° (48.0°, 49.2° and 49.4°) in ten seconds (10, 10 and 9 seconds, respectively). After standing three weeks it was still liquid with a dark brown color. It was soluble in heptane but did not crystallize from this solvent after standing for three weeks. From the combined three reaction mixtures, most of the hexyl alcohol was recovered by steam distillation. From the aqueous residue the chloral was recovered as chloral hydrate by means of ether. In the distillation flask there remained an appreciable dark, sticky residue. It is this impurity of the hexyl alcohol which, no doubt, accounts for the failure of the addition product of the alcohol in question with the chloral to crystallize.

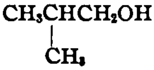
Primary Alcohols.

1. HCH_2OH
56.9°

2. CH_3CH_2OH
61.2°

3. $CH_3CH_2CH_2OH$
62.9°

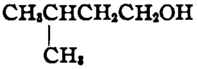
4. $CH_3[CH_2]_2CH_2OH$
58.1°



$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2OH$

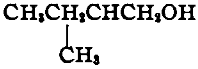
57.2°

5. $CH_3[CH_2]_3CH_2OH$
50.6°



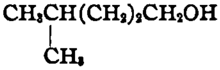
$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2OH$

57°



$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2OH$

6. $CH_3[CH_2]_4CH_2OH$
48.8°

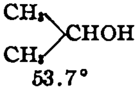


$CH_3\underset{\underset{CH_3}{|}}{C}H(CH_2)_2CH_2OH$

$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2OH$

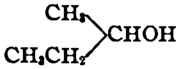
Secondary Alcohols.

3.



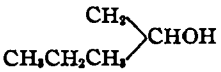
53.7°

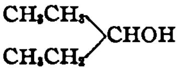
4.

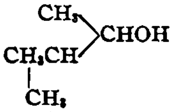


52°

5.

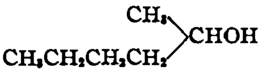






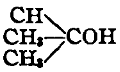
53.4°

6.



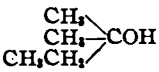
Tertiary Alcohols.

4.



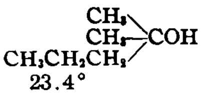
14.7°

5.



26.9°

6.



23.4°

Secondary Iso Hexyl Alcohol (Methyl n-Butyl Carbinol).—To 3.2 cc. of chloral, 4.2 cc. (= 3.5 Gm.) of the alcohol were added. The temperature of the reaction mixture rose 45.6° (46.0°, 45.6° and 45.2°) in ten seconds (10, 10 and 10 seconds, respectively). After three weeks it had not solidified.

Tertiary Iso Hexyl Alcohol (Dimethyl Normal Propyl Carbinol).—To 3.2 cc. of chloral, 4.2 cc. of the alcohol were added. The temperature of the reaction mixture rose 23.4° (23.9°, 23.7° and 22.9°) in four minutes (4, $4^1/_2$ and $4^1/_3$ minutes, respectively). No crystallization had set in after three weeks' standing, however it had assumed a dark brown coloration. It was soluble in heptane. After standing three weeks in the cold crystals were obtained that melted at 47.°

In judging these preliminary results several allowances will have to be made.

1. Although three determinations were made in each case and the average of the three recorded in the following table, greater accuracy will, no doubt, become attainable with further experience.

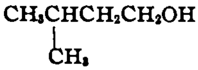
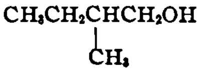
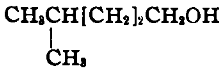
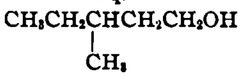
2. In the case of the isomeric alcohols, the same volume was used although the slight differences in the density called for a corresponding change in volume to yield exact molecular equivalents. However, the inaccuracies in measuring such small volumes in the ordinary way may be assumed to be even greater than the differences caused by the failure to compute each volume separately.

3. While the purest materials attainable were used, absolute purity is out of the question. This is particularly true, *e. g.*, of ethyl alcohol which always contains traces of water which influences the reaction accordingly.

4. The difference in the length of time, from five seconds to as many minutes, required to reach the maximum temperature of reaction would seem to indicate either that greater accuracy should be attainable in this measurement, or that an impurity in the alcohol may be responsible.

In studying the results obtained, each property had better be considered separately. The heats of formation are naturally of prime interest. These have been recorded with the structural formulas arranged for each series of true homology for each subtype of alcohol.

Primary Alcohols.

	Methyl		
1.	HCH_2OH 51.5°		
2.	CH_3CH_2OH 55–58°		
3.	$CH_3CH_2CH_2OH$ liq.		
4.	$CH_3[CH_2]_2CH_2OH$ 58.5°	 $CH_3\underset{CH_3}{CH}CH_2OH$ liq.	
5.	$CH_3[CH_2]_3CH_2OH$ liq.	 $CH_3\underset{CH_3}{CH}CH_2CH_2OH$ 55°	 $CH_3CH_2\underset{CH_3}{CH}CH_2OH$ liq.
6.	$CH_3[CH_2]_4CH_2OH$ liq.	 $CH_3\underset{CH_3}{CH}[CH_2]_2CH_2OH$ liq.	 $CH_3CH_2\underset{CH_3}{CH}CH_2CH_2OH$ liq.

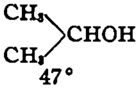
For the normal series of primary alcohols we have as many as six constants for comparison. However, any regularity that might be adduced from this series will not hold for the two series of iso primary alcohols. Moreover, the drop from 58.1° to 50.6° from butanol to pentanol seems too great. The determination of the heat of formation of higher homologues may establish the incorrectness of this constant found. Again the drop from 57.2° to 57° for the two homologous iso alcohols seems too small. Hence, in all probability the two constants for both primary pentyl alcohols require correction. It is one of the great advantages of studying these constants in the light of structure that such incongruities are brought out and may be corrected by experiments made more carefully and with the purest materials attainable.

If the results drawn from the study of the influence of homology are still unsatisfactory, partly because the series do not as yet include a sufficient number of members, those that may be drawn from the study of comparable isomeric alcohols are even more so; again, in larger part, because the desired isomers were not available.

The work, however, offers sufficient encouragement to warrant its continuation. The melting points of the addition products are tabulated in the tables.

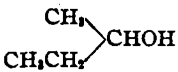
Secondary Alcohols.

3.



47°

4.



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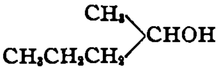
5.



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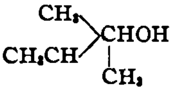

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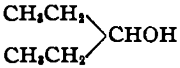
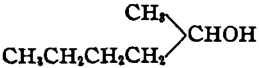


liq.

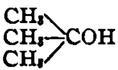
6.



liq.

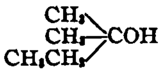
Tertiary Alcohols.

4.



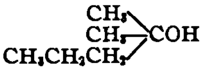
68°

5.

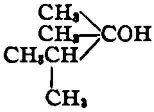


liq.

6.



liq.



Inasmuch as ten out of the sixteen compounds prepared had not solidified after seven months, generalizations with regard to this constant are even less satisfactory if not impossible, either as to the effect of homology or of isomerism.

In conclusion, it may be desirable to emphasize once more the importance or, more truly, the absolute necessity of determining physical constants not as of individual compounds but as of members of series of true homology. The resolution of one of the compounds in the group of hexyl alcohol addition products into its components reveals how unreliable even the purest reagents attainable may be. To take the individual result in such a case and to record the constants obtained, results in the lumbering up of the literature. Of this we have had altogether too much.