From 20 g. of hydroquinone and also of *p*-phenylenediamine 13 to 14 g. of pure chloranil could be obtained; from 20 g. trichlorophenol, a yield of 10 g. could be realized and from 20 g. of sulfanilic acid, a yield of 6–7 g. could be secured.

CALCUTTA, INDIA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRYN MAWR COLLEGE.]

THE REVERSIBLE REPLACEMENT OE ALCOHOLS IN ALDEHYDEALCOHOLATES.[1]

BY MARGUERITE WILLCOX AND ROGER F. BRUNEL.

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I. Introduction.

Few systematic attempts have as yet been made to study the variation of the equilibrium in reactions of organic compounds with alteration of the constitution of one of the reacting substances. Such an investigation has been undertaken here with the hope of gaining a more definite knowledge of the relation existing between the structure of aliphatic compounds and their chemical affinity, and of determining what factors play an important part in governing this relationship.

Ostwald[2] believed that the dissociation constants of acids, bases, and salts were determined by the constitution and composition of the substance, and could be considered as a measure of chemical affinity. He investigated the dissociation constants of organic acids at some length; but the relation between the affinity of organic acids, as expressed by their dissociation constants in solution, and their affinity, as exhibited in organic reactions, is by no means clear. In particular such attempts as that of Derick[3] to explain the reactions of all sorts of organic compounds by a consideration of ionization constants cannot be regarded as convincing.

Davis[4] has recently investigated the effect of constitution on chemical affinity by studying the equilibria reached in the hydrolysis of various substituted formanilides into amines and formic acid. Since, however, his paper deals primarily with substitution in the benzene ring, the results obtained are not directly comparable with those given in this paper.

The influence which constitution exerts upon the velocity and limit of esterification of several classes of compounds, including saturated and

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[1] Dissertation presented by Marguerite Willcox to the Faculty of Bryn Mawr College in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] "Outlines of General Chemistry," p. 373 (1890). This subject has been extensively discussed in the chemical literature. Michael, *J. prakt. Chem.*, N. S., 60, 333, made such data the original basis of his scale of combined influence. Among others who have discussed this subject Wegscheider is particularly to be mentioned *Mon.*, **23**, 287; **26**, 1265; *Z. Elektrochem.*, **18**, 277, and in THIS JOURNAL, Derick, **32**, 1333 (1910).

[3] THIS JOURNAL, **32**, 1333 (1910).

[4] *Z. physik. Chem.*, 78, 353, 369 (1911).

unsaturated, aliphatic and aromatic alcohols and acids, was studied by Menschutkin.[1] Table I gives the limit of esterification reached when a limited number of primary and secondary alcohols were esterified with acetic acid and a number of acids with isobutyl alcohol.

TABLE I.

Alcohols with acetic acid.

Name.	Pct. ester.
Primary.	
Methyl alcohol	69.59
Ethyl alcohol	66.57
Propyl alcohol	66.85
n-Butyl alcohol	67.30
Isobutyl alcohol	67.38
Octyl alcohol	72.34
Cetyl alcohol	80.39
Secondary.	
Dimethylcarbinol	60.52
Methylisopropylcarbinol	59.31
Ethylmethylcarbinol	59.28
Diethylcarbinol	58.66
Hexylmethylcarbinol	62.03

Acids with isobutyl alcohol.

Name.	Pct. ester.
Primary.	
Formic acid	64.32
Acetic acid	67.38
Propionic acid	68.70
n-Butyric acid	69.52
Capronic acid	69.81
Caprylic acid	70.87
Secondary.	
Isobutyric acid	69.51
Methylethylacetic acid	73.73
Tertiary.	
Trimethylacetic acid	72.60
Dimethylethylacetic acid	74.15

When the tertiary alcohols were esterified with acetic acid, decomposition took place and unsaturated hydrocarbons were formed; consequently the percentage of ester produced was much too low. Only two general conclusions were drawn: first, that the primary, secondary, and tertiary alcohols and acids fell in three separate groups; and second, that an increase in the molecular weight in a homologous series of primary alcohols or acids was accompanied by an increase in the amount esterified. No particular explanation was given for these facts, or for the differences in the amounts of ester formed with isomeric alcohols and acids in the same group. Unfortunately, the differences between the end points reached must, in a number of cases, be less than the experimental error; therefore, there is little opportunity to draw any conclusions regarding the influence of constitution and composition upon the amount of ester formed.

It would appear that any exact knowledge of the relation between chemical affinity, on the one hand, and constitution and composition, on the other, must be based on the investigation of reversible reactions between comparatively simple compounds in which the constitution of but one of the substances is allowed to alter. In this way the effect of changes in constitution on the equilibrium point of the reaction can be clearly traced. With this end in view, the further investigation of a reaction studied by Gadamer[2] and Kuntze,[3] the course of which can be followed

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[1] *Ann. chim. phys.*, [5] **20**, 289; **23**, 14; **30**, 81 (1889).

[2] *Arch. pharm.*, **243**, 12 (1905).

[3] *Ibid.*, **246**, 91 (1908).

polarimetrically, was undertaken. When chloral-*l*-amylalcoholate is treated with any aliphatic alcohol a reaction takes place according to the following equation:

$$CCl_3.CH(OH)O—\mathbf{C_5H_{11}} + R—OH \rightleftarrows CCl_3.CH(OH)O—R + \mathbf{C_5H_{11}}—OH$$

Kuntze carried out two series of experiments with eight inactive alcohols and reached practically the same end point from whichever side of the reaction he started, from which it is evident that a true equilibrium was attained. He measured the rotation of the pure active alcoholate and alcohol in the solvent used and assumed that a linear relation existed between all intermediate values of rotations and percentages of active constituents present. This relationship he made use of in following the velocity and in measuring the end point reached in all the reactions. Proof will be given later that this assumption of a linear relationship was not correct. Since some of his readings were taken two minutes after the constituents were mixed, it seems probable that in preparing the solutions so quickly, accuracy was in some instances sacrificed; consequently no attempt has been made in this work to measure the reaction velocity, an effort being made, rather, to determine the end point of the reaction as accurately as possible. Kuntze[1] has more recently calculated velocity constants for four of these reactions.

II. Method and Procedure.

In this investigation two series of experiments were carried out, in which chloral-*l*-amylalcoholate and butylchloral-*d*-sec.-butylalcoholate, respectively, were treated with twenty-two inactive alcohols. The reactions are as follows, the optically active radicals being indicated by heavy type:

$$CCl_3.CH(OH)O—\mathbf{C_5H_{11}} + R—OH \rightleftarrows CCl_3.CH(OH)O—R + \mathbf{C_5H_{11}}—OH,$$

and

$$CH_3.CHCl.CCl_2.CH(OH)O — \mathbf{C_4H_9} + R — OH \rightleftarrows$$
$$CH_3.CHCl.CCl_2.CH(OH)O — R + \mathbf{C_4H_7} — OH$$

The determinations were carried out in benzene solution at 25°. In every case 0.025 mol of active alcoholate and an equivalent amount of inactive alcohol were accurately weighed into a measuring flask and diluted to 20 cc. The measurements were all taken in a 2-dm. jacketed polarimeter tube, maintained at 25° by a current of water from the thermostat. The polarimeter[2] was a Landolt-Lippich instrument with a half-shade field and with direct vision spectroscope. The source of light was a lime candle heated by an oxy-illuminating gas flame, light corresponding approximately to the sodium D lines being used. The rotations of the solutions could be read to 0.005°. In the series carried out with chloral-*l*-amylalcoholate, duplicates of all but two of the determinations were

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[1] *Z. Electrochem.*, 18, 1015 (1912).

[2] No. 58 in the Schmidt and Haensch catalog.

made, which were identical in most cases and never varied by more than 0.01°. In the butylchloral-*d*-sec.butylalcoholate series duplicates of many of the determinations were made, but since the *d*-sec.butyl alcohol is difficult to obtain in large quantities, only one determination was made with part of the alcohols.

The reactions with primary and secondary alcohols were completed within thirty or forty minutes, the rotations having become constant. The tertiary alcohols, however, reacted more slowly, constant rotations not being obtained in some cases for nearly two hours. Whenever duplicates were made one of the solutions was allowed to stand several hours or even overnight, but no further change in the rotation ever occurred.

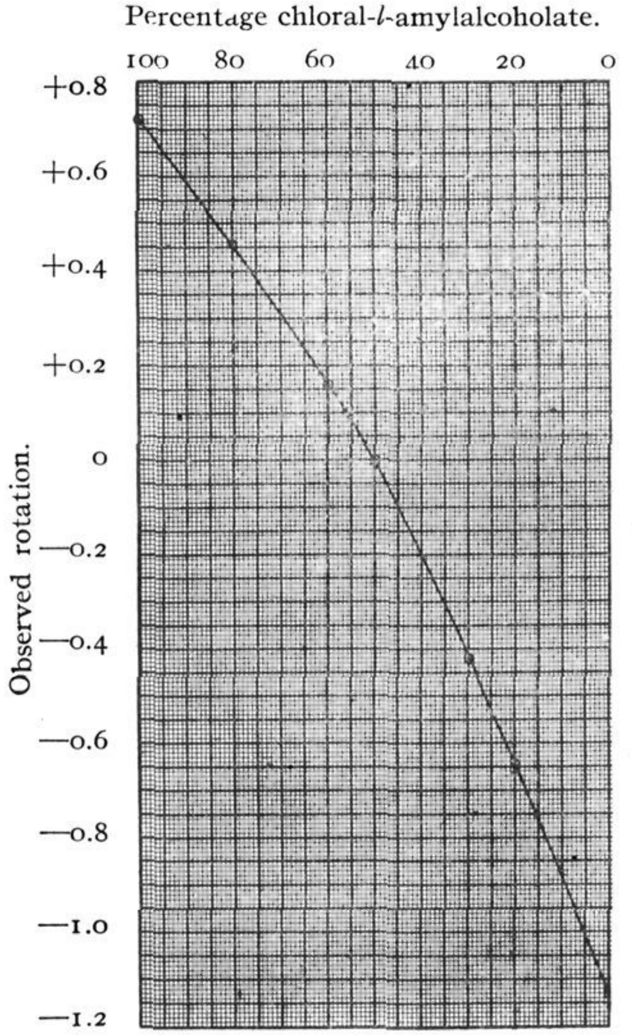

Fig. 1.

The determination of the end point in these reactions depends upon the fact that the active alcoholates do not have the same rotations as the active alcohols from which they are formed. It will be noticed that the difference between the rotations of butylchloral-*d*-sec.butylalcoholate and *d*-sec. butyl alcohol is much greater than that between the rotations of chloral-*l*-amylalcoholate and *l*-amyl alcohol; consequently a greater degree of accuracy is afforded by the former series of reactions. For 0.025 mol, 2.2028 g., *l*-amyl alcohol in 20 cc. benzene solution, $\alpha_D^{25°} = -1.13°$; for 0.025 mol, 5.8871 g., chloral-*l*-amylalcoholate in 20 cc. benzene solution, $\alpha_D^{25°} = +0.72°$, the difference being 1.85°. For 0.025 mol, 1.8520 g., *d*-sec.butyl alcohol in 20 cc. benzene solution, $\alpha_D^{25°} = +2.60°$; for 0.025 mol, 6.2375 g., butylchloral-*d*-sec.butylalcoholate in 20 cc. benzene solution, $\alpha_D^{25°} = +10.20°$, the difference being 7.60°.

As the reaction proceeds, the active alcoholate is partly converted into alcoholate of the inactive alcohol and free active alcohol, with a resulting change in the rotation. The course of the reaction can be followed by determining graphically the percentage of free active alcohol and active alcoholate. Fig. 1 gives the curve for the rotation of mixtures of *l*-amyl alcohol and chloral-*l*-amylalcoholate; Fig. 2, that for *d*-sec.butyl alcohol and butylchloral-*d*-sec.butylalcoholate. The ordinates represent the angles of rotation and the abscissae, from left to right, the percentages of active alcohol. The curves are not linear as assumed by Kuntze.

It is to be observed that these curves were determined for solutions containing only the optically active substances, whereas in the following experiments, where the curves were used for determining the end points of reactions, other (optically inactive) substances were present which might affect the rotations. It will be seen, however, that the absolute value of the equilibrium point of the reactions is not the matter of primary importance, but rather the order in which the end points with the different alcohols fall. The end point of the reaction cannot, in fact, be exactly determined by the method used since, on account of the high velocity of the interaction between the alcohols and alcoholates concerned, it is impossible to determine the correction to be applied to the observed rotation for the effect of all the substances in the solutions on the rotatory power of the optically active substances. It can be shown, however, that there is no reason to suspect any disturbance from this cause which could affect the order in which the end points with the various alcohols fall. In the case of alcohols sufficiently near together in the series, so that such slight disturbances would be of consequence, the nature and concentration of the substances present is either the same, or so nearly so, that this effect upon the rotation of the active compounds present should be the same. The following tests confirm this expectation. It will be seen that the rotatory power of *d*-sec.butyl alcohol is unaffected by the

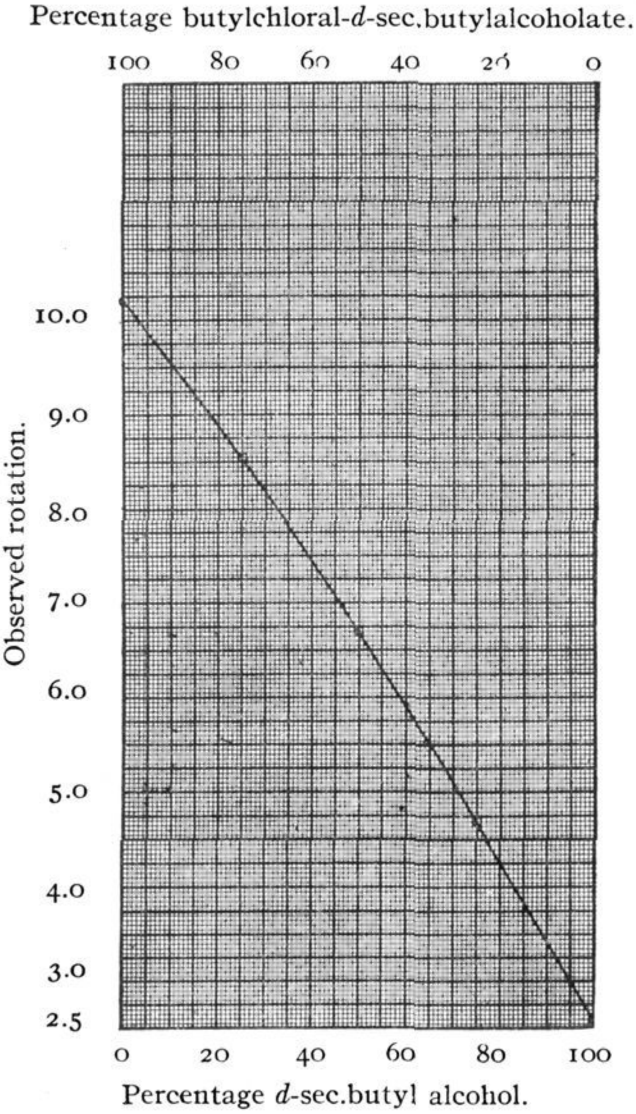

Fig. 2.

presence of other alcohols. In the case of butylchloral-*d*-sec.butylalcoholate the rotation is affected by other alcoholates, but the effect is small and is the same for the alcoholates tried.

The following experiments were carried out in 20 cc. of benzene solution at concentrations approximately the same as those occurring in the experiments below:

	$\alpha_D^{25°}$.
0.5 × 0.025 mol *d*-sec.butyl alcohol	1.28°
Upon addition of 0.5 × 0.025 mol methylisobutylcarbinol	1.28°
Upon addition of 0.5 × 0.025 mol methylisopropylcarbinol	1.28°
0.68 × 0.025 mol *d*-sec.butyl alcohol	1.77°
Upon addition of 0.32 × 0.025 mol ethyl alcohol	1.77°
Upon addition of 0.32 × 0.025 mol *n*-propyl alcohol	1.77°

The following experiments were carried out with a specimen of butylchloral-*d*-sec.butylalcoholate differing slightly in rotatory power from the purest product, but the similarity in effect in the two cases is unmistakable.

0.5 × 0.025 mol. active alcoholate	4.78°
Upon addition of 0.5 × 0.025 mol alcoholate of methylisobutylcarbinol	4.84°
Upon addition of 0.5 × 0.025 mol alcoholate of methylisopropylcarbinol	4.84°

It appears certain that, although the end point of the reaction cannot be exactly determined, the order in which the end points with the different alcohols fall must be correctly given.

Marckwald[1] probably obtained *l*-amyl alcohol pure, finding $[\alpha_D^{20°}] = -5.90°$. For the alcohol used here $[\alpha_D^{20°}] = -5.496°$ and $[\alpha_D^{25°}] = -5.428°$, in benzene solution, $[\alpha_D^{25°}] = -5.12°$. The impurity in the *l*-amyl alcohol, a fusel oil product, is not the *d*-isomer, but chiefly isoamyl alcohol, which must be present to the extent of about 6.85%. Since isoamyl alcohol is present, it must enter into all the equilibria, but the following considerations show that its presence cannot change the order of the end points reached with the various aliphatic alcohols. Letting Chl stand for $CCl_3.CH(OH)O—$, R_a for the active amyl radical, R_i for the isoamyl radical, R for any inactive radical; and indicating the equilibrium constants by K_1, K_2, and K_3, and the concentrations by expressions in brackets; for the reaction,

$$\text{Chl—R}_a + \text{R—OH} \overset{K_1}{\rightleftarrows} \text{Chl—R} + \text{R}_a\text{—OH},\ K_1 = \frac{[\text{Chl—R}][\text{R}_a\text{—OH}]}{[\text{Chl—R}_a][\text{R—OH}]};$$

for

$$\text{Chl—R}_i + \text{R—OH} \overset{K_2}{\rightleftarrows} \text{Chl—R} + \text{R}_i\text{—OH},\ K_2 = \frac{[\text{Chl—R}][\text{R}_i\text{—OH}]}{[\text{Chl—R}_i][\text{R—OH}]};$$

and for

$$\text{Chl—R}_a + \text{R}_i\text{—OH} \overset{K_3}{\rightleftarrows} \text{Chl—R}_i + \text{R}_a\text{—OH},\ K_3 = \frac{[\text{Chl—R}_i][\text{R}_a\text{—OH}]}{[\text{Chl—R}_a][\text{R}_i\text{—OH}]}.$$

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[1] *Ber.*, 34, 485 (1901).

Hence

$$\frac{K_1}{K_2} = \frac{[Chl—R_i][R_a—OH]}{[Chl—R_a][R_i—OH]} = K_3, \text{ and } \frac{[Chl—R_i]}{[Chl—R_a]} = K_3\frac{[R_i—OH]}{[R_a—OH]}.$$

The ratio of the isoamyl- and active amylalcoholates must, therefore, remain proportional to the ratio of the isoamyl and active amyl alcohols, independently of the nature of the alkyl radical R.

TABLE II.

Primary alcohols.

Butylchloral-*d*-sec.butylalcoholate.

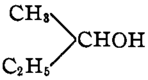
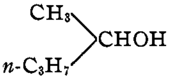
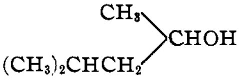
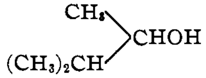
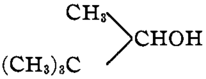
Formula.	8 H	7 H	6 H	5 H	4 H	3 H	2 H.	$\alpha_D^{25°}$.	Pct. act. alcohol.
C_2H_5OH						3	2	+5.20°	68.8%
C_4H_9OH				3	2	2	2	5.24	68.4
C_3H_7OH					3	2	2	5.28	67.8
$C_7H_{15}OH$	3	2	2	2	2	2	2	5.29	67.7
$C_6H_{13}OH$		3	2	2	2	2	2	5.30	67.6
$(CH_3)_2CHCH_2OH$					6	1	2	5.33	67.3

Chloral-*l*-amylalcoholate.

Formula.	8 H	7 H	6 H	5 H	4 H	3 H	2 H.	$\alpha_D^{25°}$.	Pct. act. alcohol.
$C_7H_{15}OH$	3	2	2	2	2	2	2	—0.025°	51.2%
$C_6H_{13}OH$		3	2	2	2	2	2	—0.020	50.9
C_2H_5OH						3	2	+0.065	45.9
C_3H_7OH					3	2	2	0.075	45.3
$(CH_3)_2CHCH_2OH$					6	1	2	0.085	44.7
C_4H_9OH				3	2	2	2	0.095	44.1
CH_3OH							3	0.120	42.6
$(CH_3)_2CHCH_2CH_2OH$				6	1	2	2	0.190	38.1

Secondary alcohols.

Butylchloral-*d*-sec.butylalcoholate.

Formula.	5 H	4 H	3 H	2 H.	$\alpha_D^{25°}$.	Pct. act. alcohol.
$(CH_3)_2CHOH$			6	1	6.23°	56.0%
 $\begin{matrix}CH_3\\C_2H_5\end{matrix}>CHOH$		3	5	1	6.42	53.6
 $\begin{matrix}CH_3\\n\text{-}C_3H_7\end{matrix}>CHOH$	3	2	5	1	6.44	53.2
 $\begin{matrix}CH_3\\(CH_3)_2CHCH_2\end{matrix}>CHOH$	6	1	5	1	6.46	52.9
 $\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}>CHOH$		6	4	1	6.50	52.4
$(C_2H_5)_2CHOH$		6	4	1	6.52	52.0
 $\begin{matrix}CH_3\\(CH_3)_3C\end{matrix}>CHOH$		9	3	1	6.74	49.6
$(C_3H_7)_2CHOH$	6	4	4	1	6.86	47.8
$[(CH_3)_2CHCH_2]_2CHOH$	12	2	4	1	7.27	42.5

Chloral-*l*-amylalcoholate.

	5 H	4 H	3 H	2 H.	$\alpha_D^{25°}$.	Pct. act. alcohol.
$(CH_3)_2CHOH$			6	1	0.290°	31.7%
$\begin{matrix}CH_3\\C_2H_5\end{matrix}\Big\rangle CHOH$		3	5	1	0.300	30.9
$(C_2H_5)_2CHOH$		6	4	1	0.365	26.5
$\begin{matrix}CH_3\\(CH_3)_2CH\end{matrix}\Big\rangle CHOH$		6	4	1	0.370	26.0
$\begin{matrix}CH_3\\(CH_3)_3C\end{matrix}\Big\rangle CHOH$		9	3	1	0.380	25.2
$\begin{matrix}CH_3\\n\text{-}C_3H_7\end{matrix}\Big\rangle CHOH$	3	2	5	1	0.400	23.9
$\begin{matrix}CH_3\\(CH_3)_2CHCH_2\end{matrix}\Big\rangle CHOH$	6	1	5	1	0.410	23.1
$(C_3H_7)_2CHOH$	6	4	4	1	0.420	22.5
$[(CH_3)_2CHCH_2]_2CHOH$	12	2	4	1	0.450	20.3

Tertiary alcohols.

Butylchloral-*d*-sec.butylalcoholate.

	5 H	4 H	3 H	2 H.		
$(CH_3)_3COH$			9	0	8.41°	26.8%
$\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}\Big\rangle COH$		3	8	0	8.53	25.2
$\begin{matrix}(CH_3)_2\\n\text{-}C_3H_7\end{matrix}\Big\rangle COH$	3	2	8	0	8.68	23.1
$\begin{matrix}(CH_3)_2\\(CH_3)_2CHCH_2\end{matrix}\Big\rangle COH$	6	1	8	0	8.75	22.0
$\begin{matrix}CH_3\\(C_2H_5)_2\end{matrix}\Big\rangle COH$		6	7	0	8.86	20.6

Chloral-*l*-amylalcoholate.

	5 H	4 H	3 H	2 H.		
$(CH_3)_3COH$			9	0	0.620°	7.7%
$\begin{matrix}(CH_3)_2\\C_2H_5\end{matrix}\Big\rangle COH$		3	8	0	0.630	6.9
$\begin{matrix}CH_3\\(C_2H_5)_2\end{matrix}\Big\rangle COH$		6	7	0	0.635	6.6
$\begin{matrix}(CH_3)_2\\n\text{-}C_3H_7\end{matrix}\Big\rangle COH$	3	2	8	0	0.640	6.0
$\begin{matrix}(CH_3)_2\\(CH_3)_2CHCH_2\end{matrix}\Big\rangle COH$	6	1	8	0	0.655	5.9

d-Sec.butyl alcohol was also probably obtained pure by Pickard and Kenyon,[1] who found that $[\alpha_D^{27°}] = +13.52°$ and $[\alpha_D^{21°}] = +13.85°$; by interpolation $[\alpha_D^{25°}] = +13.63°$. For the alcohol used here $[\alpha_D^{25°}] = +13.11°$, in benzene solution, $[\alpha_D^{25°}] = +14.04°$. The impurity in the *d*-sec.butyl alcohol is probably chiefly the *l*-isomer which cannot change the order of the end points reached with the different aliphatic alcohols. If the impurity is wholly the *l*-isomer, the *d*-sec.butyl alcohol is 98.08% pure.

Table II gives a list of the aliphatic alcohols which were allowed to react with butylchloral-*d*-sec.butylalcoholate and chloral-*l*-amylalcoholate. The alcohols are arranged in order corresponding to the percentage of active alcohol set free, which is equivalent to the percentage of alcoholate of the inactive alcohols formed. In both series the first column gives the formula of the alcohol; the second column, the number of hydrogen atoms occurring in the various positions in the molecule (explained more fully below); the third column, the average observed rotations; and the fourth column, the percentage of active alcohol set free, determined graphically from Figs. 1 and 2.

III. Discussion of Results.

It will be seen at once from the foregoing table that the three classes of alcohols fall in separate groups, as in the work of Menschutkin. Also, the change in the end point of the reaction is roughly parallel to the molecular weights of the alcohols. Since, however, there are marked exceptions to the latter statement and since isomeric compounds do not give the same values, it is necessary to look for a more exact basis for the observed relationships.

Passing down the list of alcohols in both series of experiments,

$$CCl_3.CH(OH)O—C_5H_{11} + R—OH \rightleftarrows CCl_3.CH(OH)O—R + C_5H_{11}—OH,$$

and

$$CH_3.CHCl.CCl_2.CH(OH)O—C_4H_9 + R—OH \rightleftarrows CH_3.CHCl.CCl_2.CH(OH)O—R + C_4H_9—OH$$

the equilibrium point is gradually shifted to the left. This must mean that the affinity of the alkyl radicals, R, for the hydroxyl group is increasing more than their affinity for the chloral group. The assumption that the affinity for negative groups is increasing in this direction is justified by the investigation carried out in this laboratory and elsewhere on the equilibrium, $(CH_3)_2CH.CHBr \rightleftarrows (CH_3)_3CBr$. In the gaseous condition, 18% of isobutyl bromide is in equilibrium with 82% of tertiarybutyl bromide, indicating that the radical in the latter has the greater affinity for bromine. It, therefore, appears reasonable to assume that its affinity will be correspondingly greater for any negative radical;

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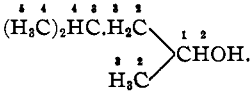
[1] *J. Chem. Soc.*, **99**, 64 (1911).

i. e., that the affinity of the radicals for negative groups increases as we pass downward in the table; the increase with respect to the hydroxyl group, however, is the greater. For the sake of brevity the radicals will be called more positive as we pass downward in the table.

Since in the reactions studied different alkyl radicals are joined to oxygen both in the alcoholates and in the alcohols, the simplest assumption, in view of the affinity of hydrogen for oxygen, would be that the difference in affinity is controlled by the difference in the number and position of the hydrogen atoms in the molecule. A consideration of the results will be seen to justify this point of view.

The position of the hydrogen atoms will be designated by their relation to the carbon atom united with the hydroxyl or chloral group. Some scale must be adopted which expresses the relative influence of hydrogen atoms in different positions upon the affinity of the radical. According to van't Hoff[1] the total influence which two atoms in a molecule have on each other can be separated into two effects, the indirect action exerted along the carbon chain and the direct action exerted through space. Michael,[2] not discriminating between these two effects, uses a scale which represents the sum of the direct and indirect influences of all the atoms of a normal organic compound upon any given atom. The following scale represents the order of decreasing influence: 1–2–3–5–6–4–7–(9–10–11)–8. The carbon atom joined to the —OH radical is taken as 1 and the other atoms are numbered according to their degree of removal from carbon atom 1; thus, for example, in methylisobutylcarbinol,



$$\begin{array}{l}(\overset{5}{H}_3\overset{4}{C})_2\overset{4}{H}\overset{3}{C}.\overset{3}{H}_2\overset{2}{C}\diagdown \\ \qquad\qquad\qquad\qquad \rangle \overset{1}{C}\overset{2}{H}OH. \\ \qquad\qquad\quad \overset{3}{H}_3\overset{2}{C}\diagup\end{array}$$

It is to be noticed that according to this scale the atoms in Position 4 have relatively less effect than those in Positions 5 and 6. This assumption, among others, is tested by the results obtained in this investigation.

The alcohols were all purified with care and an examination of the results seems to indicate that none of the differences in the amounts of active alcohol displaced can be the result of impurities.[3] As will be seen, all the important conclusions are based on comparatively large differences.

(*a*) Within the first five positions the replacement of hydrogen by methyl, which introduces three hydrogen atoms into the position next further removed, always increases the positive character of the radical, so that less active alcohol is displaced. Since, *however, the primary, secondary,*

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[1] *Ansichten über organische Chemie*, 1, 284; **2**, 252 (1878).

[2] *J. prakt. Chem.*, N. S., **60**, 331 (1899); *Ber.*, **39**, 2139 (1906).

[3] The smallest difference could be accounted for only by over 1% of impurity, which is entirely improbable, although further work on some of the alcohols is now in progress.

and tertiary alcohols fall in three separate groups, it appears that the replacement of a hydrogen atom in Position 2, $\overset{2}{\mathrm{H}}$, by a methyl group in Position 2–3, $\overset{2\ 3}{\mathrm{CH_3}}$, is much more effective in increasing the positive character of the alkyl radicals than any alteration in their structure and composition which leads to the replacement of $\overset{3}{\mathrm{H}}$ by $\overset{3\ 4}{\mathrm{CH_3}}$, or of $\overset{4}{\mathrm{H}}$ by $\overset{4\ 5}{\mathrm{CH_3}}$.

(*b*) *Three hydrogen atoms in Position 4 are more effective than one in Position 3, although Position 4 is relatively weak according to the scale adopted.* Whenever $\overset{3}{\mathrm{H}}$ is replaced by $\overset{3\ 4}{\mathrm{CH_3}}$ there is an increase in the positive character of the radical, less active alcohol being displaced. Examples of this are, ethyl and *n*-propyl alcohols; isopropyl and *s*-butyl alcohols; methylisopropyl- and methyl-*t*-butylcarbinols; and *t*-butyl and *t*-amyl alcohols. The differences between the end points are considerably greater in the butylchloral than in the chloral series, which is a result of the relatively greater importance of Position 4 in the former.

(*c*) *The relatively small influence of atoms in Position 4 as compared with those in Position 5, as predicted by Michael, can be clearly seen in the chloral series.* In the first place, the replacement of $\overset{4}{\mathrm{H}}$ by $\overset{4\ 5}{\mathrm{CH_3}}$ is much more effective than the replacement of $\overset{3}{\mathrm{H}}$ by $\overset{3\ 4}{\mathrm{CH_3}}$. For example, the change in passing from *n*-propyl to *n*-butyl alcohol is greater than that in passing from *n*-propyl to isobutyl alcohol; from *s*-butyl alcohol to methyl-*n*-propylcarbinol greater than from *s*-butyl alcohol to diethylcarbinol; and from *t*-amyl alcohol to dimethyl-*n*-propylcarbinol greater than from *t*-amyl alcohol to diethylmethylcarbinol. Still more striking evidence of the influence of Position 5 is the fact that methyl-*n*-propyl- lies below methyl-*t*-butylcarbinol, as well as the fact that methyl-*n*-propyl- and methylisobutylcarbinols lie below methylisopropyl- and methyl-*t*-butylcarbinols, respectively. It is apparent that the position of the hydrogen atoms has a marked influence upon the positive character of these radicals and that it even outweighs the effect of difference in number of hydrogen atoms in the case of methyl-*n*-propyl- and methyl-*t*-butylcarbinols.

(*d*) Turning to the *butylchloral series, the relative effects of atoms in Positions 4 and 5 appear in most cases to be reversed*, which accounts for the most important differences in the two series. In the butylchloral series, *n*-butyl alcohol lies above *n*-propyl and isobutyl alcohols; methyl-*n*-propyl- and methylisobutylcarbinols lie above diethyl- and methylisopropylcarbinols; and dimethyl-*n*-propyl- and dimethylisobutylcarbinols lie above diethylmethylcarbinol. Evidently the spatial arrangement comes into play in some way not accounted for in the scale of influence given above. More definite conclusions can only be reached after other series of equilibria have been investigated.

(*e*) Looking again at Michael's scale of influence, 1–2–3–5–6–4–7–9–10–11–8–, it *will be seen that atoms in Position 8 have much less influence than those in Position 7*, so that $3\overset{8}{H}$ may be less influential than $\overset{7}{H}$. This would account for the fact that *n*-heptyl alcohol lies above *n*-hexyl alcohol in both series. It is also evident that both Positions 7 and 8 are less effective than Positions 4 and 5 and this may partly explain why *n*-heptyl and *n*-hexyl alcohols lie higher up in both series than would be expected from their comparatively large molecular weights.

(*f*) *Isomeric compounds have quite different end points except when they have the same number of hydrogen atoms in the same positions.* The fact that isomeric compounds usually displace different amounts of active alcohol is explained by the fact that their hydrogen atoms are differently situated, as in several of the cases cited under (*c*) and (*d*). The resulting differences in the positive character of the radicals is slight, however, in the case of diethyl- and methylisopropylcarbinols, which have the same number of hydrogen atoms in the same positions. In both series the difference between the end points reached with these two alcohols is clearly less than the difference between the end point of either and that of their common isomer, methylisopropylcarbinol, whose hydrogen atoms occupy different positions. It will be noticed, however, that in the chloral series diethylcarbinol lies above methylisopropylcarbinol, whereas the order is reversed in the butylchloral series. Here, again, is evidence of spatial influences not accounted for in the scale adopted.

(*g*) *Whether or not some specific influence of the carbon atoms comes into play can hardly be determined from the results obtained with the alcohols used in this investigation.* If, however, carbon has a negative influence, it is doubtless weak as compared with the positive influence of hydrogen. Rather strong evidence of this is furnished by the fact that the replacement of $\overset{3}{H}$ by $\overset{3}{C}\overset{4}{H}_3$ increases the positive character of the radical even in the chloral series where Position 4 is weaker than Positions 3 and 5. If the positive character of the radical is still increased, in spite of the fact that the positive $\overset{3}{H}$ has been replaced by negative $\overset{3}{C}$ and three hydrogen atoms introduced into the relatively weak Position 4 it is evident that any negative influence due to the carbon must be slight as compared with the positive influence of hydrogen. Michael has considered the effect of the carbon somewhat in detail, but the results given here do not justify any further discussion.

The results may thus be to a considerable extent coördinated on the basis adopted—that the affinity of the aliphatic radicals for negative groups is governed chiefly by the number and position of the hydrogen atoms. It is possible to construct a scale which represents the relative influence of all the atoms in the molecule, although the scale cannot be exactly the same for the two series.

As stated above, it is concluded that the affinity of the alkyl radicals for hydroxyl increases more than does that for the chloral radical as we pass downward in the table. Obviously, however, since the order of the alcohols is not the same in the two series, neither of them can be assumed to represent the relative affinity of the alkyl radicals for hydroxyl. Nevertheless it is possible that this is represented approximately by the order in either of the series. The order in which these radicals would fall as regards their affinity for the chloral and butylchloral radicals, respectively, is evidently not the same.

If we consider that this increase in the affinity of the alkyl radicals for "negative" radicals is due to increasing "positive" character of the former, it is evident that the degree of this "positive" character is not an absolute property or characteristic of any given radical, but depends upon the structure of the group to which it is joined. This is quite in keeping with the assumption that the affinity for the negative radical is controlled to a considerable extent by attractive forces between the hydrogen atoms and the oxygen or other atoms of the negative group. The position of these hydrogen atoms relative to the carbon by which the alkyl group is united to other groups—the factor chiefly considered above—may thus be in some cases of less significance than their position relative to various other atoms of the molecule. The spatial relationships involved here, as well as the other questions raised above, obviously require much further investigation. The problem, however, appears to be more fundamental and is probably simpler than that of the relation between constitution and reaction velocity.

IV. Molecular-weight Determinations with Chloralethylalcoholate.

Since chloralethylalcoholate was found by Beckmann[1] to be dissociated in benzene solutions, it was considered desirable to carry out further molecular-weight determinations at various concentrations in benzene, in order to gain information regarding the condition of the alcoholate at the concentrations at which the foregoing experiments were carried out. At the same time it appeared to be a good opportunity to investigate the behavior of such a nonelectrolytic dissociation in a variety of solvents. Brunner's[2] statement that no dissociation was to be found in any solvent was open to doubt in view of the dissociation known to occur in benzene.

The customary Beckmann apparatus was used, except that the stirrer was provided with a mercury seal to prevent the entrance of moisture and the evaporation of solvent. Without this it was found impossible to obtain accurate results, especially when the solutions were left standing

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[1] *Z. physik. Chem.*, **2**, 724 (1888).

[2] *Z. physik. Chem. R.*, 45, 380 (1903).

for several hours or often for a day or more. The freezing point and dielectric constants were taken from Landolt, Börnstein, and Roth Tabellen (1912).

The molecular weight of chloral itself was first determined in benzene. In a 2.5% solution by weight, the molecular weight of chloral was found to be 164 (calculate 147.4); therefore, chloral is somewhat associated in benzene solution. Since the freezing point did not alter on standing for two days, it is evident that chloral does not react with benzene in any way.

TABLE III.

Chloralethylalcoholate in benzene. Calculated molecular weight 193.4. Freezing point constant 4.9. Dielectric constant 2.288^{18°.

G. solute per 100 g. solvent.	Δ.	Molecular weight.	Percentage dissociation.	$K \times 10^{-4}$.
0.15	0.044°	167	15.74%	1.99
0.37	0.109	173	11.99	2.75
0.49	0.142	174	11.15	2.79
0.59	0.166	176	9.61	2.74
0.73	0.206	178	8.41	2.56
1.07	0.295	182	6.38	2.11
1.22	0.331	186	4.21	1.13
2.04	0.543	189	2.30	0.50
5.01	1.276	197	...	....
7.90	1.974	199	...	....
9.23	2.218	208	...	....
13.46	3.026	222	...	....

It was found that the dissociation does not occur instantaneously since, in the more dilute solutions where dissociation was greatest, equilibrium was reached only after several hours, the change in the molecular weight amounting to 10% in some cases. In the solutions where association occurred equilibrium was usually reached immediately; although the value here was sometimes high at first, indicating, as would be expected, that part of the molecules were undergoing dissociation.

For solutions of concentrations 0.37, 0.44 and 0.59%, the dissociation is evidently taking place in accordance with the law of mass action. The values of the dissociation constant $K = \frac{[CCl_3.CHO][C_2H_5OH]}{[CCl_3.CH(OH)O—C_2H_5]}$, are in fairly good agreement, 2.74, 2.79 and 2.74×10^{-4}. For more concentrated solutions the value of the dissociation constant gradually decreases, which is readily accounted for by the fact that association has already begun to take place to an appreciable degree. In solutions of the concentration 5.01% association predominates. The concentrations of alcoholate in the equilibrium determinations was always considerably greater than this.

There seems to be, in general, no evidence of any definite relation between association and optical rotation,[1] but, in any case, since the re-

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[1] Turner, "Molecular Association," p. 104 (1915).

sulting rotations were referred to an empirical curve any disturbance from this cause would be eliminated.

Table IV.

Chloralethylalcoholate in bromoform.

Freezing-point constant = 14.4. Dielectric constant = 4.51^{20°.

G. solute per 100 g. solvent.	Δ.	Molecular weight.	G. solute per 100 g. solvent.	Δ.	Molecular weight.
0.42	0.332°	182.6	1.54	1.072°	208
0.44	0.351	183.1	5.14	3.016	246
1.04	0.761	198	5.55	3.193	250

Chloralethylalcoholate in nitrobenzene.

Freezing-point constant = 7.05. Dielectric constant = 36.45^{18°.

G. solute per 100 g. solvent.	Δ.	Molecular weight.
2.05	0.700°	205

Chloralethylalcoholate in ethylene bromide.

Freezing-point constant = 11.8. Dielectric constant = 4.86^{18°.

G. solute per 100 g. solvent.	Δ.	Molecular weight.
0.38	0.231°	179

In Fig. 3 the molecular weight of chloralethylalcoholate is plotted against the concentration of the solution. When extended to more concentrated solutions the curve for benzene bends upward.

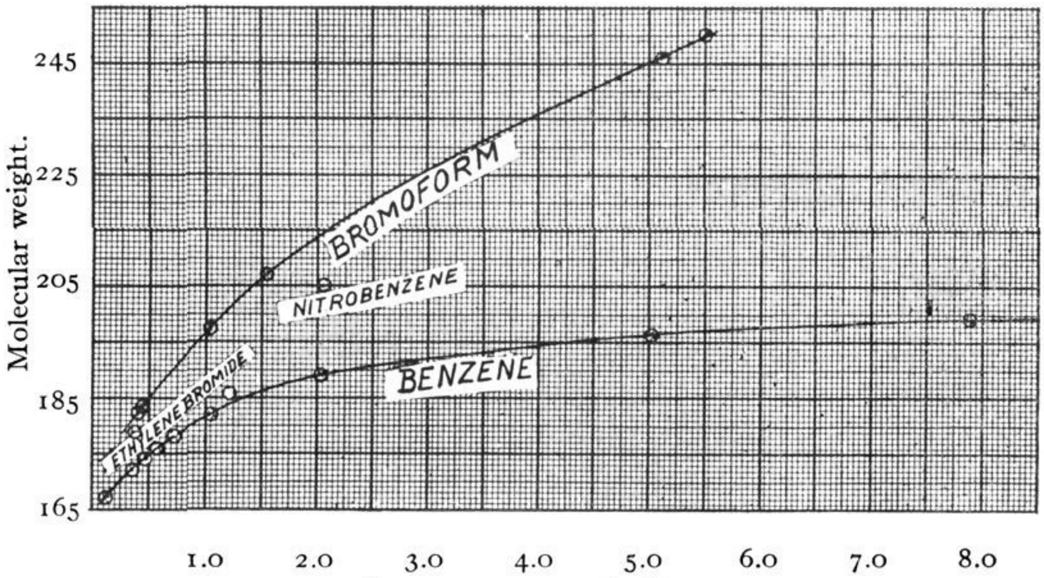

Fig. 3.

It will be seen that the values of the molecular weight in bromoform are higher throughout than in benzene, although the former has a somewhat larger dielectric constant. In a 5.01% benzene solution the molecular weight is 197, whereas in a 5.14% bromoform solution it is 246. The effect of the dielectric constant is more conclusively tested by the determination of the molecular weight in nitrobenzene. It was found that chloralethylalcoholate is no more dissociated in nitrobenzene of high dielectric constant than in the solvents whose dielectric constants are comparatively low. Table V gives a comparison of the values of the molecular weight of chloralethylalcoholate in the various solvents with their dielectric constants, the values being read from the curve in the case of bromoform.

TABLE V.

Solvent.	D. E.	Conc.	Mol. wt.	Conc.	Mol. wt.
Benzene	2.288	2.04	189	0.37	173
Nitrobenzene	36.450	2.05	205	....	...
Bromoform	4.510	2.05	215	0.38	182
Ethylene bromide	4.860	....	...	0.38	179

V. Experimental.

l-**Amyl Alcohol.**—*l*-Amyl alcohol was dried by boiling with lime for two days and was carefully fractionated with a column of beads. B. p. 128–128.05° (760 mm.). $\alpha_D^{25°} = -4.43°$, $d_{4°}^{25°} = 0.8152$, $[\alpha_D^{25°}] = -5.428°$; $\alpha_D^{20°} = -4.49°$, $d_{4°}^{20°} = 0.8169$, $[\alpha_D^{20°}] = -5.496°$. The rotation of the pure alcohol given by Marckwald[1] is $[\alpha_D^{20°}] = -5.90°$. The alcohol used here is 93.15% pure, and the impurity is doubtless isoamyl alcohol as discussed above.

d-**Sec.butyl Alcohol.**—*dl*-Sec.butyl alcohol was prepared by the reduction of methylethyl ketone by hydrogen according to Ipatiew's method. The reduction occurred at 180–200° with nickel oxide as catalyst. *d*-Sec.butyl alcohol was obtained by the method recently described by Pickard and Kenyon[2] and the separation was carried out in most respects according to their description. It was found, however, (a point not noted by them) that the solubility of the brucine *s*-butyl phthalate in acetone was greatly influenced by the amount of water present. It was found necessary to add 30–50 cc. of water to a liter of acetone to bring about solution in the proportion specified by them. The brucine salt was recrystallized from methyl alcohol seven or eight times until a constant rotation was obtained for a sample containing 1 g. salt in 50 cc. absolute ethyl alcohol. The specific rotation of the salt usually obtained was $[\alpha_D] = -4.62°$. The value given by Pickard and Kenyon is $[\alpha_D] = -2.93°$. Since the *d*-sec.butyl alcohol proved to have a lower rotation than that obtained by Pickard and Kenyon, it is evident that a complete separation was not obtained, although the rotation of the brucine salt did not change on further recrystallization. It appears possible that the brucine used contained other alkaloids which interfered with the separation. The *d*-sec.butyl alcohol was dried with fused potassium carbonate and by boiling with lime for three days, and was then carefully fractionated with a column of beads. B. p. 98.7–99.1° (760 mm.). $\alpha_D^{25°} = +10.53°$; $d_{4°}^{25°} = 0.8034$; $[\alpha_D^{25°}] = +13.11°$. The value given by Pickard and Kenyon (obtained by interpolation between the values given for 21°

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[1] *Ber.*, 34, 485 (1901).

[2] *J. Chem. Soc.*, 103, 1923 (1913).

and 27°) is $[\alpha_D^{25°}] = +13.63°$. The impurity in the alcohol is probably the *l*-isomer.

Chloral was obtained by distilling pure chloral twice from sulfuric acid, care being taken to protect it from moisture. B. p. 97.3–97.8° (760 mm.).

Butylchloral was prepared from butylchloral hydrate, which was dehydrated by shaking with sulfuric acid in a separating funnel. The upper layer, consisting of the butylchloral, was removed and treated with powdered lime to remove any sulfuric acid which might be present, and carefully protected from moisture during the subsequent fractionation. B. p. 164.5–165.5° (760 mm.).

Chloral-*l*-amylalcoholate and **butylchloral-*d*-sec.butylalcoholate** are colorless liquids, prepared by mixing equimolecular quantities of the active alcohol and the aldehyde. Since the union is accompanied by a large evolution of heat, the liquids were cooled in ice and salt and protected from moisture as much as possible while they were being mixed.

Chloralethylalcoholate was recrystallized twice from benzene and dried in a desiccator. It was introduced into the solvent in the form of pellets. M. p. 50°.

The primary alcohols were all good commercial products, carefully dried by boiling with lime and fractionated with a column of beads.[1]

Methyl alcohol.	B. p. 64.7°.	*n-Butyl alcohol.*	B. p. 117.55–117.95°.
Ethyl alcohol.	B. p. 78.0°.	*n-Hexyl alcohol.*	B. p. 155.2–155.7°.
n-Propyl alcohol.	B. p. 97.1–97.4°.	*n-Heptyl alcohol.*	B. p. 172.5–173.5°.
Isobutyl alcohol.	B. p. 107.85–107.95°.		

Isoamyl alcohol, from a commercial product containing 15% of active amyl alcohol, was obtained nearly pure by Marckwald's urethane process.[2] The alcohol was converted into its urethane which was recrystallized from ligroin. Isoamyl urethane which, is much the less soluble, was obtained very nearly free from active amyl urethane after one recrystallization. The alcohol so obtained had a specific rotation of $[\alpha_D] = -0.048°$, thus containing about 0.81% of active amyl alcohol. B. p. 131.2–131.6°.

The secondary alcohols, with the exception of diethylcarbinol, were all obtained by the reduction of ketones according to Ipatiew's method. Alcohols prepared in this way always contain some ketone which can be detected by the sodium nitroprusside test. This test is sensitive to one part of acetone in 1000, but is somewhat less sensitive to the other ketones. The alcohols can be freed from ketone in either of the two following ways: by treatment with phenylhydrazine according to Michael's[3] method or by treatment with *p*-nitrophenylhydrazine, which has the great advantage of remaining behind during the subsequent distillation. The alcohols

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[1] The boiling points of all the alcohols are corrected to 760 mm.

[2] *Ber.*, **37**, 1040 (1904).

[3] *Ibid.*, **42**, 3157 (1909).

were all carefully dried by boiling with lime and fractionated with a column of beads.

Isopropyl alcohol was prepared by the reduction of acetone. It was treated with *p*-nitrophenylhydrazine and gave no test for ketone. B. p. 82.5–82.7°.

***s*-Butyl alcohol** was prepared by the reduction of methylethyl ketone and treated with phenylhydrazine. It gave no test for ketone. B. p. 98.4–99.0°.

Methylisopropylcarbinol was prepared by the reduction of methylisopropyl ketone. The alcohol was fractionated repeatedly and gave only a slight test for ketone. B. p. 112.9–113.9°.

Methylpropylcarbinol was prepared by the reduction of methylpropyl ketone, obtained from acetacetic ester. The alcohol was given the phenylhydrazine treatment. B. p. 118.9°.

Methylisobutylcarbinol was prepared by the reduction of mesityl oxide, which was obtained by boiling diacetone alcohol with a trace of iodine as described by Hibbert.[1] The alcohol was treated with phenylhydrazine. B. p. 130–131°.

Methyl-*t*-butylcarbinol was prepared by the reduction of pinacoline. The alcohol was purified by freezing out twice and gave no test for ketone. B. p. 120–120.6°.

Di-*n*-propylcarbinol was prepared by the reduction of di-*n*-propyl ketone. The di-*n*-propyl ketone was obtained from *n*-butyric acid by the method of Senderens[2] by passage over thorium oxide at 400–420°. The alcohol was well fractionated and gave no test for ketone. B. p. 154–155°.

Diisobutylcarbinol was prepared by the reduction of diisobutyl ketone. The latter was obtained from isovaleric acid catalytically as above. The alcohol was treated with *p*-nitrophenylhydrazine. B. p. 171.4–173.4°.

Diethylcarbinol was prepared by the Grignard reaction from ethyl formate and ethyl bromide. B. p. 114.8–115.2°.

***t*-Butyl alcohol.** Kahlbaum's *t*-butyl alcohol was purified by freezing out twice, and then dried and fractionated.[3] B. p. 81.7–82.1°.

***t*-Amyl alcohol** was prepared from amylene by Wyschnegradsky's[4] method. B. p. 101.7–102.1°.

Diethylmethylcarbinol was prepared by the Grignard reaction from ethyl bromide and ethyl acetate. B. p. 122.1–122.9°.

Dimethylpropylcarbinol was prepared by the Grignard reaction from methyl iodide and ethyl butyrate. B. p. 122.1–122.6°.

Dimethylisobutylcarbinol was prepared by the Grignard reaction from acetone and isobutyl iodide. B. p. 132–133°.

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[1] THIS JOURNAL, **37**, 1748 (1915).

[2] *Ann. chim. phys.*, [8] **28**, 243 (1913).

[3] This alcohol was probably not thoroughly dried.

[4] *Ann.*, **190**, 332 (1878).

OBSERVED ROTATIONS OF THE MIXTURES OF CHLORAL-*l*-AMYLALCOHOLATE AND *l*-AMYL ALCOHOL FROM WHICH THE CURVE IN FIG. 1 WAS CONSTRUCTED.

Molar pct. alcoholate.	Molar pct. alcohol.	Observed rotations.	
0%	100%	—1.130°	—1.130°
20	80	0.645	...
30	70	0.420	0.420
40	60	0.200	...
50	50	0.000	0.000
60	40	+0.160	...
80	20	0.455	+0.455
100	0	0.720	0.720

OBSERVED ROTATIONS OF THE MIXTURES OF BUTYLCHLORAL-*d*-SEC.BUTYLALCOHOLATE AND *d*-SEC.BUTYL ALCOHOL FROM WHICH THE CURVE GIVEN IN FIG. 2 WAS CONSTRUCTED.

Molar pct. alcoholate.	Molar pct. alcohol.	Observed rotations.	
0%	100%	+2.600°	+2.600°
25	75	4.700	4.700
50	50	6.700	...
75	25	8.550	8.550
100	0	10.200	10.200

DETERMINATIONS MADE WITH CHLORAL-*l*-AMYLALCOHOLATE.

Inactive alcohol.	α.		Average.	Pct. act. alcohol.
n-Heptyl alcohol	—0.025°	...	—0.025°	51.2%
n-Hexyl alcohol	0.020	...	0.020	50.9
Ethyl alcohol	+0.060	+0.070°	+0.065	45.9
n-Propyl alcohol	0.075	0.075	0.075	45.3
Isobutyl alcohol	0.085	0.085	0.085	44.7
n-Butyl alcohol	0.090	0.100	0.095	44.1
Methyl alcohol	0.120	0.120	0.120	42.6
Isoamyl alcohol	0.190	0.190	0.190	38.1
Isopropyl alcohol	0.290	0.290	0.290	31.7
s-Butyl alcohol	0.300	0.300	0.300	30.9
Diethylcarbinol	0.365	0.365	0.365	26.5
Methylisopropylcarbinol	0.370	0.370	0.370	26.0
Methyl-*t*-butylcarbinol	0.380	0.380	0.380	25.2
Methyl-*n*-propylcarbinol	0.395	0.405	0.400	23.9
Methylisobutylcarbinol	0.410	0.410	0.410	23.1
Di-*n*-propylcarbinol	0.420	0.420	0.420	22.5
Diisobutylcarbinol	0.445	0.455	0.450	20.3
t-Butyl alcohol	0.620	0.620	0.620	7.7
t-Amyl alcohol	0.630	0.630	0.630	6.9
Diethylmethylcarbinol	0.635	0.635	0.635	6.6
Dimethyl-*n*-propylcarbinol	0.640	0.640	0.640	6.0
Dimethylisobutylcarbinol	0.650	0.660	0.655	4.9

DETERMINATIONS MADE WITH BUTYLCHLORAL-*d*-SEC.BUTYLALCOHOLATE.

Inactive alcohol.	α.		Average.	Pct. act. alcohol.
Ethyl alcohol	+5.200°	+5.200°	+5.200°	68.8%
n-Butyl alcohol	5.240	5.240	5.240	68.4
n-Propyl alcohol	5.280	...	5.280	67.8
n-Heptyl alcohol	5.290	...	5.290	67.7
n-Hexyl alcohol	5.300	...	5.300	67.6
Isobutyl alcohol	5.335	5.325	5.330	67.3
Isopropyl alcohol	6.230	6.230	6.230	56.0
s-Butyl alcohol	6.420	...	6.420	53.6
Methyl-*n*-propylcarbinol	6.440	6.440	6.440	53.2
Methylisobutylcarbinol	6.460	6.460	6.460	52.9
Methylisopropylcarbinol	6.495	6.505	6.500	52.4
Diethylcarbinol	6.530	...	6.530	52.0
Methyl-*t*-butylcarbinol	6.740	6.740	6.740	49.6
Di-*n*-propylcarbinol	6.860	...	6.860	47.8
Diisobutylcarbinol	7.270	...	7.270	42.5
t-Butyl alcohol	8.405	8.415	8.410	26.8
t-Amyl alcohol	8.530	...	8.530	25.2
Dimethyl-*n*-propylcarbinol	8.680	...	8.680	23.1
Dimethylisobutylcarbinol	8.750	...	8.750	22.0
Diethylmethylcarbinol	8.860	8.860	8.860	20.6

Purification of Solvents.

Benzene was frozen out six times, dried with calcium chloride and phosphorus pentoxide, and fractionated. B. p. 79.4°.

Nitrobenzene was frozen out eight times, dried with calcium chloride, and fractionated. B. p. 210.6–210.8°.

Bromoform was frozen out six times, dried with calcium chloride, and fractionated. B. p. 146.6–147.5°.

Ethylene bromide was frozen out four times, dried with phosphorus pentoxide, and fractionated. B. p. 131.2–131.4°.

Summary.

The equilibrium point has here been determined for the reversible reaction of chloral-*l*-amyl alcoholate and butylchloral-*d*-sec.butylalcoholate, respectively, with an extended series of aliphatic alcohols, the optically active alcohol being in each case partially displaced from its combination with the aldehyde by the other alcohol. The equilibrium point of the reaction varies with the alcohol taking part in the reaction, and the order in which the alcohols fall is not the same, although nearly so, in the two series.

The significance of the results as regards the affinities between the radicals concerned is discussed, and an attempt is made to establish a relationship between the constitution of the alcohol radicals and the end point attained in the above reactions.

The degree of dissociation of chloralethylalcoholate into its constituents has been determined in benzene for a wide range of concentrations, and in bromoform, ethylene bromide, and nitrobenzene in fewer concentrations. It is dissociated in dilute solutions, associated in more concentrated ones. There appears to be no relation between the degree of dissociation and the dielectric constant of the solvent.

We take pleasure in acknowledging our indebtedness to the Warren Fund of the American Academy of Arts and Sciences for the excellent polarimeter and spectroscope which were placed at our disposal for this work.

BRYN MAWR, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

ON THE REACTIONS OF THE FORMAMIDINES. VI. SOME THIAZOLE DERIVATIVES.

BY F. B. DAINS AND A. E. STEPHENSON.

Received June 24, 1916.

Owing to the inability of one of the authors to continue this investigation, it has been deemed best to publish the results already obtained as a preliminary paper in this special field.

It has already been pointed out[1] that compounds containing a methylene grouping react with ease with the substituted formamidines, giving a primary amine and the complex CHNHR in place of the H_2 of the methylene group, as follows:

$$>CH_2 + RN=CHNHR = >C=CHNHR + RNH_2$$

This occurs not only in the malonic ester, acetoacetic ester and benzyl cyanide type, but also with ring compounds like the pyrazolones and isoxazolones.

In the isothiohydantoins (ketotetrahydro-thiazoles), there is found the complex $-CO-CH_2-S-$, which exhibits the general reactions characteristic of an acid methylene grouping, such as aldehyde, phthalic anhydride, nitroso derivatives, etc.

Such compounds should by analogy react with the formamidines; a supposition confirmed by the following experiments:

Diphenyl-isothiohydantoin (2-phenylimido-3-phenyl-4-keto-tetra-hydrothiazole) was readily obtained by heating in alcohol solution thiocarbanilide and chloroacetic acid. Small amounts of phenyl mustard oil glycollide and phenyl thiourethan were also formed.

Molar quantities of the isothiohydantoin and diphenylformamidine were heated at 140–50° for five hours. The reaction product contained

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[1] *Ber.*, **35**, 2509 (1902); THIS JOURNAL, **31**, 1148 (1909); **35**, 959, 970 (1913).