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Studies of the Reaction between Chloral and Alcohols

VIII. A Study of the Formation of Chloral Hemiacetals of Aliphatic Tertiary Alcohols

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The kinetics of the uncatalyzed and the acetic acid catalyzed formation of chloral hemiacetals of some aliphatic tertiary alcohols and chloral in heptane have been studied by UV spectroscopy.

Investigations of the catalyzed formation of chloral hemiacetals of *tert*-butyl alcohol seem to indicate that tertiary aliphatic alcohols follow the same reaction mechanism as primary and secondary alcohols. The catalyzed chloral hemiacetal formation consists of at least three steps. The first step is the formation of a chloral acetic acid reaction complex, Chl···HA. This complex reacts in the second step with the alcohol, forming a second reaction complex, Chl···HA···ROH, which in a third step decomposes to hemiacetal and acetic acid. The reaction orders of the alcohols are found to be between 0.1 and 0.8, depending on the bulkiness and the initial concentration of the alcohol considered. Compared with primary and secondary alcohols these reaction orders are smaller than expected. From a rate expression derived from a steady state treatment of the catalyzed reaction, a steric constant, f, is determined which gives information about the bulkiness of the alcohols. The f values of different alcohols are discussed from a steric point of view.

In the uncatalyzed reaction the formation of a chloral-alcohol reaction complex is the slow step in all cases, which is also the case for sterically hindered primary and secondary alcohols.

The apparent stoichiometric equilibrium constants are determined, and it is found that they vary with the initial concentrations of the components. The degrees of association of the alcohols are examined by IR spectroscopy, and there seems to be a connection between the association and the low reaction orders and the variation in equilibrium constants.

As part of our study of the reaction between chloral and various alcohols,[1–7] we reported and discussed kinetic investigations of the uncatalyzed and acetic acid catalyzed formation of chloral hemiacetals in heptane solutions of a large number of aliphatic primary and aliphatic and alicyclic secondary alcohols (1).[5,7]

$$CCl_3CHO + ROH \rightleftharpoons CCl_3CH(OH)OR \qquad (1)$$

The observed catalyzed reaction was found to consist of two parellel reactions, *i.e.* a catalyzed and an uncatalyzed reaction. The contribution from the latter to the overall reaction could only be neglected when alcohols with a certain degree of bulkiness were used.

The reaction orders with respect to chloral, alcohol, and acetic acid were determined. This was done by measuring the initial rates at different initial concentrations of the component considered. A plot of the logarithm of the initial rates *versus* the logarithm of the initial concentrations yielded a straight line from whose slope the reaction order was obtained.

The initial rate, $\vec{v}_{0,k}$ of the real catalyzed reaction was calculated from the measured initial rates of the catalyzed and uncatalyzed reactions, $v_{0,K}$ and $\vec{v}_{0,UK}$, respectively (2).

$$\vec{v}_{0,k} = \vec{v}_{0,K} - \vec{v}_{0,UK} \tag{2}$$

The reaction orders of the catalyzed and uncatalyzed reactions referred to rate-expressions (3) and (4).

$$\vec{v}_{0,k} = \vec{k}_k[\mathrm{Chl}]_0^a[\mathrm{ROH}]_0^b[\mathrm{HA}]_{0,s}^c \tag{3}$$

$$\vec{v}_{0,UK} = \vec{k}_{UK}[\mathrm{Chl}]_0^{a'}[\mathrm{ROH}]_0^{b'} \tag{4}$$

In eqn. (3) and (4) the appropriate reaction orders were expressed by the letters a, b, and c in the catalyzed reaction, and by a′ and b′ in the uncatalyzed reaction. The indices s and 0 stand for stoichiometric and initial, respectively.

The reaction order, a, of chloral in the catalyzed reaction was found to be approximately 1.0. The reaction order, b, was found to be between 0.2 and 0.4 for straight chain primary alcohols, such as methanol, ethanol, and 1-butanol, and between 0.6 and 0.8 for straight chain secondary alcohols, such as 2-propanol, 2-butanol, and 3-pentanol. With β-disubstituted primary and secondary alcohols, such as 2,2-dimethyl-1-butanol and 3-methyl-2-butanol, reaction orders of approximately 1.0 were found. The influence of γ-branching was much less than that of β-branching.

The reaction order, c, of acetic acid was in all cases found to be close to 0.5. This was explained by the fact that carboxylic acids are almost completely dimerized in inert solvents (5).[8]

$$\mathrm{HA}\cdots\mathrm{HA} \rightleftharpoons 2\ \mathrm{HA} \tag{5}$$

These observations were explained by the following reaction mechanism (6), where Ha = hemiacetal.

$$\mathrm{Chl} + \mathrm{HA} \overset{1}{\rightleftharpoons} \mathrm{Chl}\cdots\mathrm{HA}$$

$$\mathrm{Chl}\cdots\mathrm{HA} + \mathrm{ROH} \overset{2}{\rightleftharpoons} \mathrm{Chl}\cdots\mathrm{HA}\cdots\mathrm{ROH} \overset{3}{\rightleftharpoons} \mathrm{Ha} + \mathrm{HA} \tag{6}$$

Since the reaction order of the alcohol was found to be between 0.2 and 1, step 1 can only be partially rate-determining. In this case the rate $\vec{v}_k$ of the forward reaction was described by eqn. (7).[7]

$$\vec{v}_k = \frac{\vec{k}_{1,k}[HA]_{0,s}^{\frac{1}{2}}\,[Chl][ROH]}{f+[ROH]} \tag{7}$$

$$\vec{k}_{1,k} = \vec{k}_1 \times (\tfrac{1}{2})^{\frac{1}{2}}\, K_{HA}^{-\frac{1}{2}}$$

$$f = \vec{k}_{1,k}/\vec{k}_{2,k}$$

K_{HA} refers to eqn. (5). The concentration of the monomeric acetic acid was nearly equal to $(\frac{1}{2})^{\frac{1}{2}}K_{HA}^{-\frac{1}{2}}\,[HA]_{0,s}^{\frac{1}{2}}$ and was assumed to be constant during the whole reaction. The factor f was, due to $\vec{k}_{2,k}$, a measure of the steric influence of the alcohol on the rate of the hemiacetal formation. Eqn. (7) also explained the observation that the reaction order of non-branched alcohols varied with $[ROH]_0$.

A reaction order for the alcohol of 1.0 would mean that either step 2 or 3 is rate-determining. In this case the forward reaction rate could be described by eqn. (8).

$$\vec{v}_k = \vec{k}_k\,[HA]_{0,s}^{\frac{1}{2}}\,[Chl][ROH] \tag{8}$$
$$\vec{k}_k = \vec{k}_{1,k}/f$$

This situation arose when bulky alcohols were used. Then $f \gg [ROH]$ and eqn. (7) was reduced to eqn. (8).

When $[Chl]=[ROH]$, and the contribution from the uncatalyzed reaction to the overall reaction was neglected, eqn. (8) could be treated as the expression for a pseudo-second-order reaction (9).

$$\vec{v}_k = \vec{k}_k\,[HA]_{0,s}^{\frac{1}{2}}\,[Chl]^2 \tag{9}$$

Plotting $1/[Chl]$ *versus* time yielded in this case a straight line in the first part of the reaction. If $[ROH]_0 \gg [Chl]_0$, and still neglecting the uncatalyzed reaction, eqn. (8) could be treated as a pseudo-first-order reaction (10).

$$\vec{v}_k = \vec{k}_k\,[HA]_{0,s}^{\frac{1}{2}}\,[ROH]_0\,[Chl] \tag{10}$$

Here, a plot of log [Chl] *versus* time yielded a straight line in the first part of the reaction.

In order to determine $\vec{k}_{1,k}$ and f, eqn. (7) was converted to eqn. (11).

$$[ROH]_0 = \frac{\vec{k}_{1,k}\,[HA]_{0,s}^{\frac{1}{2}}\,[Chl]_0\,[ROH]_0}{\vec{v}_{0,k}} - f \tag{11}$$

By measuring $\vec{v}_{0,k}$ at various $[ROH]_0$, keeping $[Chl]_0$ and $[HA]_{0,s}$ constant $\vec{k}_{1,k}$ and f can be obtained from a plot of $[ROH]_0$ *versus* $[HA_{0,s}^{\frac{1}{2}}\,[Chl]_0[ROH]_0\vec{v}_{0,k}$. This was done for 1-propanol and 2-propanol (Table 1). Table 1 shows that the values of $\vec{k}_{1,k}$ for the two alcohols are almost identical. This was taken as evidence for the conclusion that the reaction mechanism of hemiacetal formation for primary and secondary alcohols is the same. The values of f were found to be much dependent of the bulkiness of the alcohols (Tables 1 and 2). (In case of bulky alcohols, the initial rate $\vec{v}_{0,k}$ and f would be inversely

Table 1. $\vec{k}_{1,k}$ and f values for 1-propanol, 2-propanol, and 2-methyl-2-propanol.

	$\vec{k}_{1,k}$	f
	$mol^{-\frac{1}{2}} \times l^{\frac{1}{2}} \times sec^{-1} \times 10^2$	$mol \times l^{-1} \times 10^2$
$CH_3CH_2CH_2OH$	4.9	0.40
$CH_3CHOHCH_3$	4.5	2.4
$(CH_3)_3COH$	1.0	3.0

Table 2. The dependence of f on the bulkiness of the alcohols.

	f $mol \times l^{-1} \times 10^2$		f $mol \times l^{-1} \times 10^2$
$CH_3(CH_2)_3OH$	0.54	$CH_3CHOHCH_2C(CH_3)_3$	6.5
$CH_3C(CH_3)_2CH_2CH_2OH$	0.94	$CH_3CHOHCH(CH_3)_2$	7.2
$CH_3CH_2C(CH_3)_2CH_2OH$	5.8	$CH_3CHOHC(CH_3)_3$	33
$CH_3CHOHCH_2CH_3$	3.4	$(CH_3)_2CHCH_2CHOHCH_2CH(CH_3)_2$	9.1
$CH_3CHOHCH_2CH(CH_3)_2$	4.3	$(CH_3)_2CHCHOHCH(CH_3)_2$	99

proportional). This fact, together with observation of epimerization of hemiacetals made from optically active alcohols led us to assume that one of the possible structures of Chl···HA···ROH was cyclic (Fig. 1).

The initial rate of the uncatalyzed reaction was 10 – 30 times less than that of the corresponding catalyzed reaction. This was explained by the fact that acetic acid is a better hydrogen bonder than the alcohols. Increased branching in β-position was found to decrease the initial rate markedly as in the catalyzed reaction. In the uncatalyzed reaction the reaction order was found to change characteristically when going from straight chain to increasingly branched (especially β-branched) alcohols. When straight chain alcohols were used, the reaction orders of chloral and alcohol, a′ and b′, were about 1.8 and 2.3, respectively, indicating that more than one molecule of each component reacts before or during the rate-determining step. These reaction orders indicated a mixture of reaction complexes having the general composition $(Chl)_m \cdots (ROH)_n$ with $n \geq m$. In the case of β,β-branched primary and secondary alcohols the reaction orders of chloral and alcohols were both found to be 1.0. This means that the rate-determining step now is the reaction between one molecule of chloral and one molecule of alcohol. On the basis of these results for the uncatalyzed formation of chloral hemiacetals we suggest the following reaction mechanism (12),[1-4,6]

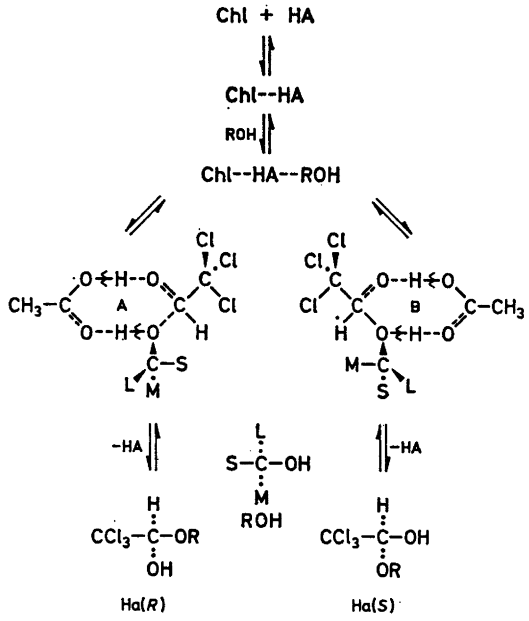


Fig. 1. Possible reaction paths in the catalyzed formation of chloral hemiacetal showing the cyclic structure of Chl···HA···ROH.

$$m\ Chl + n\ ROH \rightleftharpoons (Chl)_m\cdots(ROH)_n \begin{matrix} \nearrow \\ \searrow \end{matrix} \begin{matrix} Ha(R) + (m-1)\ Chl + (n-1)\ ROH \\ Ha(S) + (m-1)\ Chl + (n-1)\ ROH \end{matrix} \quad (12)$$

$m = 1,2 \qquad n = 1,2,3$

The epimerization was, of course, only observed when optically active alcohols were used. The structures of some of these reaction complexes are believed to be cyclic (Fig. 2a and b). Bell [9] also has proposed similar cyclic structures.

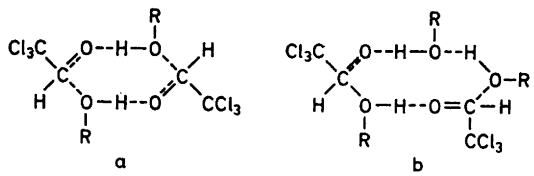


Fig. 2a and b. Possible models of two cyclic reaction complexes $(Chl)_2\cdots(ROH)_2$ and $(Chl)_2\cdots(ROH)_3$

The investigations reported in this paper consist of determinations of equilibrium constants and initial rates of both the uncatalyzed and the catalyzed formation of chloral hemiacetals of aliphatic tertiary alcohols. From these determinations the reaction orders for chloral, alcohol, and acetic acid are calculated. The rate constant $\vec{k}_{1,k}$ and f in the catalyzed reaction are estimated and compared with those found for primary and secondary alcohols. The influence of branching in the alcohols on the initial rate is examined.

The idea of using kinetics in this kind of problems is not a new one. Herz and Kuntze [10] and Willcox and Brunel [11,12] have used polarimetry and Herold *et al.*[13–16] and Cantacuzéne [17] have used UV-spectroscopy. These authors, however, proposed a simpler mechanism for the hemiacetal formation.

RESULTS AND DISCUSSION

The reactions were all carried out at 25.0°C. The chloral concentrations were determined by UV-spectroscopy. The concentrations of the alcohol and hemiacetal were deduced from the stoichiometry of eqn. (1). The tertiary alcohols have been investigated in the same manner as the primary and secondary ones.[7] A direct comparison of the initial rates for the tertiary alcohols with those for the primary and secondary alcohols is not possible since it was necessary to use much higher concentrations of tertiary alcohols in order to get measurable rates.

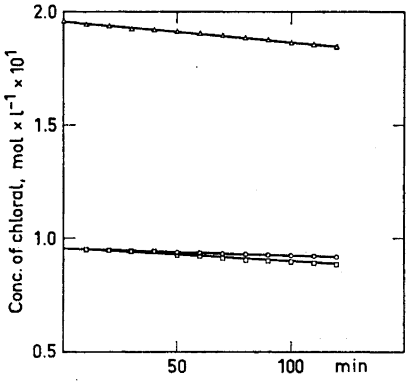


Fig. 3. The course of the uncatalyzed formation of chloral hemiacetals of 2-methyl-2-propanol, illustrated by a plot of the chloral concentration *versus* time at various initial concentrations. △: Conc. of chloral and alcohol are 2×10^{-1} M and 10^{-1} M, respectively. ○: Conc. of chloral and alcohol are both 10^{-1} M and □: Conc. of chloral and alcohol are 10^{-1} M and 2×10^{-1} M, respectively.

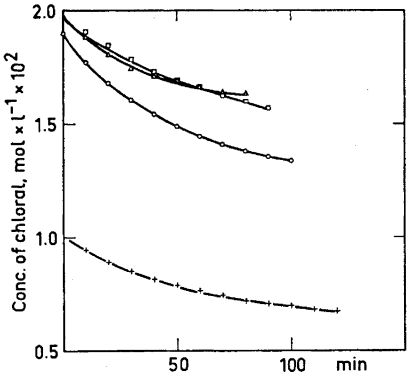


Fig. 4. The course of the catalyzed formation of chloral hemiacetals of 2-methyl-2-propanol illustrated by a plot of the chloral concentration *versus* time at various initial concentrations of chloral, alcohol, and acetic acid. ○: Conc. of the components in the above mentioned order 2×10^{-2} M, 2×10^{-2} M, and 10^{-3} M, respectively. +: 10^{-2} M, 2×10^{-2} M, and 10^{-3} M, respectively. △: 2×10^{-2} M, 10^{-2} M, and 10^{-3} M, respectively, and □: 2×10^{-2} M, 2×10^{-2} M, and 4×10^{-4} M, respectively.

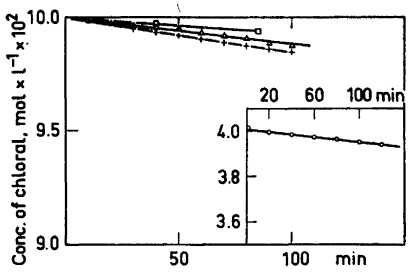


Fig. 5. The course of the catalyzed formation of chloral hemiacetals of 2-methyl-2-pentanol illustrated by a plot of the chloral concentration *versus* time at various initial concentrations of chloral, alcohol, and acetic acid. ○: Conc. of chloral, alcohol, and acetic acid 4.0×10^{-2} M, 10^{-1} M, and 10^{-3} M, respectively. △: Conc. of chloral, alcohol, and acetic acid 10^{-1} M, 10^{-1} M, and 10^{-3} M, respectively. □: Conc. of chloral, alcohol, and acetic acid 10^{-1} M, 4×10^{-2} M, and 10^{-3} M, respectively. +: Conc. of chloral, alcohol, and acetic acid 10^{-1} M, 10^{-1} M, and 2×10^{-3} M, respectively.

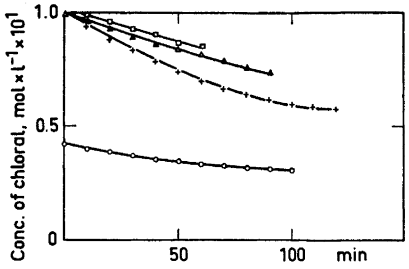


Fig. 6. The course of the catalyzed formation of chloral hemiacetals of 2,3,4-trimethyl-3-pentanol illustrated by a plot of the chloral concentration *versus* time at various initial concentrations of chloral, alcohol, and acetic acid: ○: Conc. of chloral, alcohol, and acetic acid 4.0×10^{-2} M, 10^{-1} M, and 10^{-3} M, respectively. △: Conc. of chloral, alcohol, and acetic acid 10^{-1} M, 10^{-1} M, and 10^{-3} M, respectively. □: Conc. of chloral, alcohol, and acetic acid 10^{-1} M, 4×10^{-2} M, and 10^{-3} M, respectively +: Conc. of chloral, alcohol, and acetic acid 10^{-1} M, 10^{-1} M, and 2×10^{-3} M, respectively.

The course of the uncatalyzed hemiacetal formation from 2-methyl-2-propanol is shown in Fig. 3. The catalyzed reaction course is shown in Figs. 4, 5, and 6, and is illustrated by 2-methyl-2-propanol, 2-methyl-2-pentanol, and 2,3,4-trimethyl-3-pentanol, respectively. The initial rates, equilibrium constants, and the reaction orders of the components for the following reaction (13), where R = alkyl, are listed in Table 3:

$$CCl_3CHO + R_3COH \overset{HA}{\rightleftharpoons} Cl_3CH(OH)OC(R)_3 \qquad (13)$$

The rate of the uncatalyzed reaction is about 1/10 of the rate of the catalyzed reaction when the concentration of the catalyst is about 1 % of the concentration of chloral or alcohol.*

The reaction orders for chloral and alcohol in the uncatalyzed reaction are both approximately 1, which means that a molecule of each component reacts in the rate-determining step, *i.e.* a second-order addition reaction.

No reaction order for tertiary alcohols greater than 1 was found even at high concentration of the alcohol in contrast to the results found for most of the primary and secondary alcohols.[7] This difference is probably steric in origin since the tendency to association is reduced with the bulkier tertiary alcohols. Examples of primary and secondary alcohols which also have reaction orders of about 1 in the uncatalyzed reaction are

* 4-Propyl-4-heptanol is an exception since the rate of the uncatalyzed reaction is of the same magnitude as the rate of the catalyzed reaction. The alcohol used may have contained catalytic impurities even after purification (b.p. 82–84°C, 14 mmHg).

2,2-dimethyl-1-butanol	$CH_3CH_2C(CH_3)_2CH_2OH$
2,4-dimethyl-3-pentanol	$(CH_3)_2CHCHOHCH(CH_3)_2$
3-methyl-2-butanol	$CH_3CH(OH)CH(CH_3)_2$

and the alcohols in the menthol-series.

In the catalyzed reaction the reaction orders of chloral and acetic acid are approximately 1 and 0.5, respectively, indicating that one molecule of chloral and one molecule of acetic acid enter the reaction before or during the rate-determining step. The reaction orders of the various alcohols lie in the interval from 0.1 to 1. Table 3 shows that the reaction order of 2-methyl-2-propanol (which has been examined most thoroughly) decreases with increasing concentration of the alcohol. Thus a plot of log $\tilde{v}_{0,k}$ *versus* log[2-methyl-2-propanol]$_0$ yields a curve with steadily decreasing slope instead of a straight line. The reason for this could be association of the alcohol molecules at higher concentrations. The mol % of monomeric 2-methyl-2-propanol and 3-ethyl-3-pentanol at different stoichiometric concentrations have been determined *via* IR-spectroscopy [5,8] by measuring the optical density of the free O–H stretching band near 3620 and 3630 cm^{-1}, respectively, see Figs. 7 and 8 and Table 4.

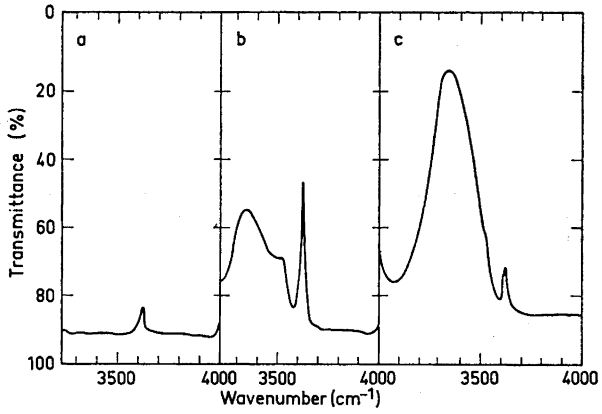


Fig. 7. IR-spectra of a) 10^{-2} M (l = 1.0 mm), b) 10^{-1} M (l = 1.0 mm) and c) 1 M (l = 0.1 mm) solutions of 2-methyl-2-propanol in heptane.

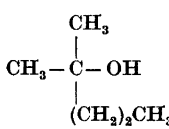
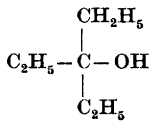
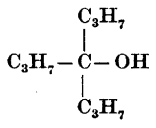
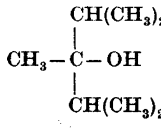
It can be seen that association of 3-ethyl-3-pentanol is unimportant at stoichiometric concentrations at or below 10^{-1} M. Therefore association cannot account for the reaction order of this alcohol. The association (dimerization) of 2-methyl-2-propanol is more pronounced and is partially responsible for the low reaction order and the decrease in the reaction order with increasing alcohol concentration.

The reaction mechanism (6) proposed for primary and secondary alcohols gives rise to the rate expression (7) for the forward reaction using the steady state treatment on Chl···HA.[7] According to this expression the reaction order of the alcohol should be between 0 and 1, depending upon the relative

Table 3. Initial rates of a) measured uncatalyzed reaction b) measured catalyzed and c) calculated real catalyzed formation of chloral hemiacetals made from tertiary alcohols, the reaction orders for chloral, alcohol, and acetic acid, and equilibrium constants.

	Initial concentrations mol × l^{-1} × 10^3			Initial rates of hemiacetal formation mol l^{-1} sec^{-1} × 10^6			Reaction orders					Equilibrium constant K_s mol^{-1} l
							Uncatalyzed reaction		Catalyzed reaction			
	chloral	alcohol	acetic acid	$\bar{v}_{0,K}$	$\bar{v}_{0,UK}$	$\bar{v}_{0,k}$	chloral	alcohol	chloral	alcohol	acetic acid	
$CH_3-C(CH_3)(CH_3)-OH$	0.40	2.00	0.100	0.35		0.35						
	1.00	2.00	0.100	1.10	0.04	1.1			1.1			
	2.00	2.00	0.100	2.30	0.16	2.1						49
	4.00	2.00	0.100	4.50	0.28	4.2						50
	2.00	0.50	0.100	0.75		0.75						
	2.00	1.00	0.100	1.50	0.04	1.50				0.5		
	2.00	5.0	0.100	3.10	0.60	2.5						47
	2.00	2.00	0.020	0.86	0.16	0.70						
	2.00	2.00	0.040	1.25	0.16	1.1					0.6	46
	2.00	2.00	0.200	3.30	0.16	3.1						
	4.00	10.0			0.27							
	10.0	10.0			0.65		1.1					
	20.0	10.0			1.43							
	10.0	4.00			0.31							

Table 3. Continued.

	10.0	20.0			1.0			0.75				
	4.00	10.0	0.100	2.2	0.10	2.1	1.0		1.0			21
	10.0	10.0	0.100	5.4	0.25	5.1						
	10.0	4.00	0.100	5.0	0.12	4.9		0.8		0.1		
	10.0	10.0	0.200	0.9	0.25	8.7					0.7	17
	4.0	10.0	0.200	0.60		0.60			0.9			
	10.0	10.0	0.200	1.25		1.25						
	10.0	5.0	0.200	1.15		1.15				0.15		
	10.0	10.0	0.100	9.00		0.90					0.5	
	4.0	10.0	0.100	2.8					0.8			7.0
	10.0	10.0	0.100	5.5								5.0
	10.0	4.0	0.100	3.8						0.4		6.0
	10.0	10.0	0.200	6.8							0.4	5.0
	4.0	10.0	0.100	0.09		0.09			0.9			
	10.0	10.0	0.100	0.21		0.21						
	10.0	4.00	0.100	0.10		0.10				0.8		
	10.0	10.0	0.200	0.28		0.28					0.4	

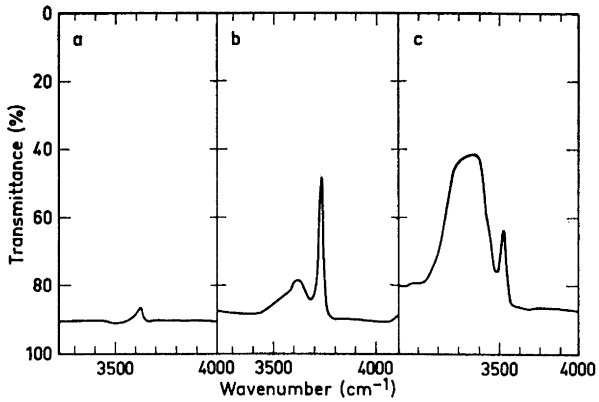


Fig. 8. IR-spectra of a) 10^{-2} M ($l = 1.0$ mm), b) 10^{-1} M ($l = 1.0$ mm) and c) 1 M ($l = 0.1$ mm) solutions of 3-ethyl-3-pentanol in heptane.

Table 4. Mol % of monomeric 2-methyl-2-propanol and 3-ethyl-3-pentanol in heptane solution at different stoichiometric concentrations of the alcohols.

	Path length l (mm)	Concentration (mol × l^{-1})	Extinction coefficient ε	Mol %[a] of monomer
	1.0	1.00×10^{-2}	38.6	100
	0.1	1.00×10^{-1}	24.9	65
$(CH_3)_3COH$	1.0	1.00×10^{-1}	27.8	72
	0.1	1.00	7.68	20
	1.0	1.00×10^{-2}	25.9	100
	0.1	1.00×10^{-1}	24.5	94
$(C_2H_5)_3COH$	1.0	1.00×10^{-1}	25.2	97
	0.1	1.00	13.5	52

[a] The mol % fraction of monomeric 2-methyl-2-propanol and 3-ethyl-3-pentanol are $\varepsilon/38.6$ and $\varepsilon/25.9$, respectively.

magnitude of f and [ROH]. It can also be seen that the reaction order of a certain alcohol should vary with its concentration in the above mentioned manner. Therefore it seems likely that the formation of chloral hemiacetals of tertiary alcohols follows the same reaction mechanism as that for primary and secondary alcohols (6).

As mentioned in the introduction, $\vec{k}_{1,k}$ and f can be determined according to eqn. (11) from a plot of $[ROH]_0$ *versus* $[ROH]_0/\vec{v}_{0,k}$. In Fig. 9 this plot

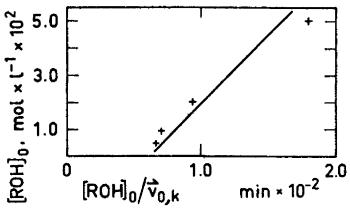


Fig. 9. Determination of $\vec{k}_{1,k}$ and f for 2-methyl-2-propanol chloral hemiacetal. from a plot of $[ROH]_0$ *versus* $[ROH]_0/\vec{v}_{0,k}$

is shown for 2-methyl-2-propanol and values of $\vec{k}_{1,k}$ and f are listed in Table 1 together with the corresponding values for 1-propanol and 2-propanol. The rather large deviation between the $\vec{k}_{1,k}$ values may be explained by the usual experimental uncertainty. It can be seen that Fig. 9 is a curve rather than a straight line, due to the association of the alcohol (Table 4), which makes this method very uncertain.

The f values for the other tertiary alcohols can be found using eqn. (7) if $\vec{k}_{1,k}$ is known. In Table 5 this determination is made using the $\vec{k}_{1,k}$ values from Table 1 in addition to the appropriate initial rates from Table 3.

Table 5. f values of different tertiary alcohols determined from eqn. (7) and the value of $\vec{k}_{1,k}$ from Table 1.

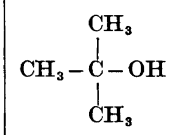
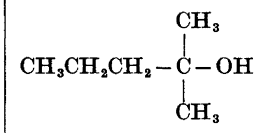
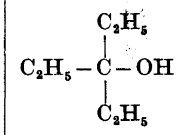
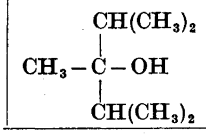
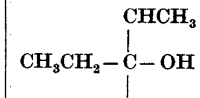
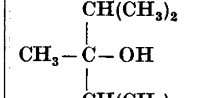
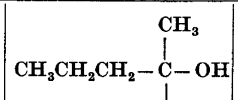
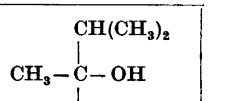
	Initial concentrations mol × l^{-1} × 10^2			f (mol/l × 10^2)
	Chloral	Alcohol	Acetic acid	$\vec{k}_{1,k} = 1.0 \times 10^{-3}$
	2.00	2.00	0.100	4.0
	10.0	10.0	0.100	52
	10.0	10.0	0.100	350
	10.0	10.0	0.100	1500

Table 6. Determinations of k_k by means of pseudo-first-order, pseudo-second-order and initial rate treatment for 3-ethyl-3-pentanol and 2,3,4-trimethyl-3-pentanol.

	Initial concentrations mol × l^{-1} × 10^{-2}			$\vec{k}_k$ (mol$^{-3/2}$ × l$^{3/2}$ × sec^{-1})		
	chloral	alcohol	acetic acid	pseudo-first-order treatment [a]	pseudo-second-order treatment [b]	initial rate treatment [c]
	10.0	10.0	0.100		2.3×10^{-3}	2.9×10^{-3}
	4.0	10.0	0.200	2.9×10^{-3}		3.4×10^{-3}
	10.0	10.0	0.200		2.6×10^{-3}	2.8×10^{-3}
	10.0	10.0	0.100		6.8×10^{-4}	6.7×10^{-4}
	4.0	10.0	0.100	7.5×10^{-4}		7.2×10^{-4}
	10.0	10.0	0.200		6.0×10^{-4}	6.3×10^{-4}

[a] See eqn. (10).
[b] See eqn. (9).
[c] See eqn. (8).

Table 7. Experimental and calculated reaction orders of tertiary alcohols.

	$(CH_3)_3COH$		$(CH_3CH_2)_3COH$	$(CH_3CH_2CH_2)_3COH$	
Experimental	0.15	0.10	0.15	0.40	0.80
Calculated [7]	0.40	0.80	0.98	1.0	1.0

If $f \gg [ROH]_0$ the rate-expression (7) becomes (8) which means that step 2 or 3 in (6) is now rate-determining and the reaction is first-order with respect to alcohol.

According to Table 5 this should be the case for 3-ethyl-3-pentanol and 2,3,4-trimethyl-3-pentanol. For these two alcohols $\vec{k}_k$ has been determined by the two methods mentioned in the introduction (*cf.* p. 2896).

The $\vec{k}_k$ values are listed in Table 6 together with the values deduced from initial rates and concentrations (see eqn. (8)).

The table shows that the different $\vec{k}_k$ values for 3-ethyl-3-pentanol lie within a factor 1.5 and for 2,3,4-trimethyl-3-pentanol this factor is 1.25. The average value of the graphically determined $\vec{k}_k$ values are 2.6×10^{-3} and 6.8×10^{-4} $(l/mol)^{3/2}$ sec^{-1}, respectively. The f values deduced from these values ($\vec{k}_k = \vec{k}_{1,k}/f$) using $\vec{k}_{1,k}$ equal to 10^{-2} are 3.80 and 14.50 (mol/l). For comparison the values from Table 5 are 3.50 and 15.00 (mol/l).

Using the f-values from Table 5 and the $\vec{k}_{1,k}$ value for 2-methyl-2-propanol (Table 1) it is possible to deduce a "theoretical" reaction order of the alcohols using eqn. (7).[7] A comparison of the theoretical and the experimentally determined values (Table 3) is made in Table 7. The agreement is not very good but the deviation is, as mentioned before, partly due to dimerization of the alcohols. There is, however, still a large experimental uncertainty left if the proposed mechanism is correct, but it does not seem possible to propose another mechanism consistent with the experimental data.

The stoichiometric equilibrium constant, K_s, for the hemiacetal formation is calculated from the measured chloral concentration, and the concentrations of alcohol and hemiacetal are deduced from eqn. (1). In the experiments reported earlier [5] it was found that K_s was not a true equilibrium constant because it varied with the initial concentrations of alcohol and chloral. The K_s values from Table 3 are almost constant for 2-methyl-2-propanol (about 50 l/mol). The K_s values are about 1000 and 600 l/mol for 1-propanol and 2-propanol, respectively.[7] The magnitude of these values is in agreement with that expected from steric considerations. The crowding in the hemiacetals of tertiary alcohols lowers their stability compared with the hemiacetals of straight chain primary and secondary alcohols. The equilibrium constant drops another factor of 10 for 4-propyl-4-heptanol ($K_s \sim 6$). IR-spectroscopic measurements have shown that there exists association between the hemiacetal and the alcohol (Ha···ROH) at concentrations where neither dimeric alcohol (ROH···ROH) or dimeric hemiacetal (Ha···Ha) exist. These measurements can explain the variation in the equilibrium constant as will be discussed further in following papers. The variation is not so pronounced for tertiary alcohols, which is consistent with the lowered tendency for association.

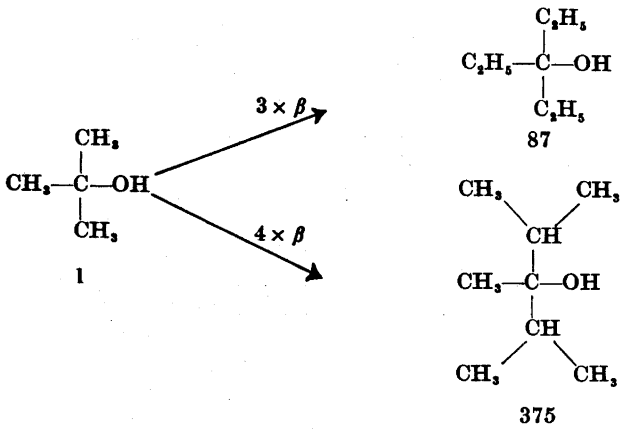
The f values provide information about how the steric properties of the alcohols influence their reactivity in the formation of the Chl···HA···ROH complex, while the $\vec{v}_{0\,k}$ values give similar information for the over-all reaction (of the same stoichiometry). Since the step in which the alcohol enters the reaction is only rate-determining in those cases where $[ROH]_0$ is small or when it involves a very bulky alcohol, the f values are more informative.

Another advantage is the independence of f on the initial concentrations. Relative f values for different series of alcohols are listed below.[7]

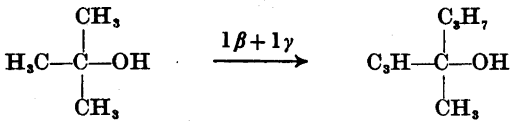
α-Branching

$$\underset{1}{CH_3OH} \xrightarrow{\alpha} \underset{1.2}{CH_3CH_2OH} \xrightarrow{\alpha} \underset{6}{CH_3CHOHCH_3} \xrightarrow{\alpha} \underset{67}{(CH_3)_3COH}*$$

β-Branching



γ-Branching



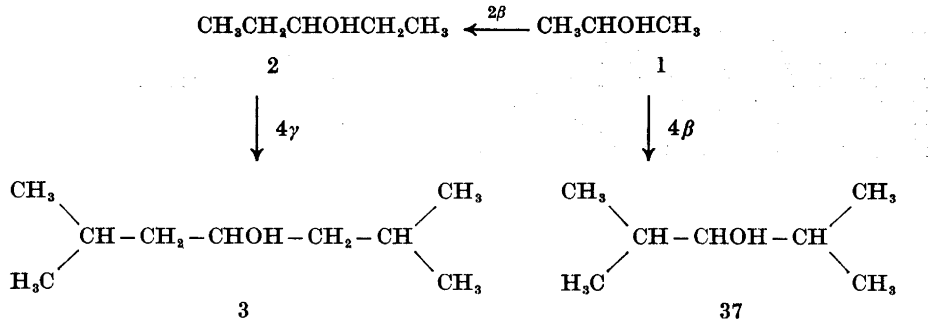
In this connection 4-propyl-4-heptanol should be compared with 3-ethyl-3-pentanol. However, as mentioned before the experiments with the former cannot be treated (see footnote p. 2900).

Any ponderal effect in these comparisons is unimportant as can be seen from the following relative f values:

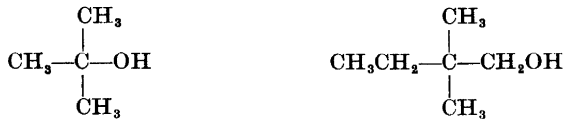
CH_3OH	C_2H_5OH	C_3H_7OH	C_4H_9OH
1.0	1.2	1.4	1.2

The influence of α- and β-branching is great and of the same magnitude. In addition it can be seen that the introduction of a methyl group has a greater influence when several groups are already present. Earlier experiments [7] with primary and secondary alcohols showed that the effect of γ-branching is much less than that of α- and β-branching:

* This f value is calculated from $\vec{v}_{0,k}$ using $k_{1,k} = 4.5 \times 10^{-3}$.[7]



For a comparison of α- and β-branching the following example is illustrative.



In order to present a more detailed description of the reaction between chloral and alcohols in heptane, it is necessary to make a number of precise IR-spectroscopic measurements in order to determine the different degrees of association of the components. We intend to make some investigations on this in the future.

EXPERIMENTAL

The UV-measurements were made on a Pye-Unicam-Philips spectrophotometer model 800 and the IR-measurements on a Perkin-Elmer infrared grating spectrophotometer model 337. The alcohols used were dried and redistilled.

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