

Studies of the Reaction between Chloral and Alcohols

IX. A Study of the Dissociation of Chloral Hemiacetals of some Aliphatic Primary and Secondary Alcohols

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The kinetics of the uncatalyzed and the acetic acid catalyzed dissociation of chloral hemiacetals of methanol, ethanol, and 2-propanol into chloral and the corresponding alcohols in heptane have been studied by UV and IR spectroscopy. In conjunction with this study the formation of 2-propanol chloral hemiacetal has also been investigated in a more detailed manner than previously.

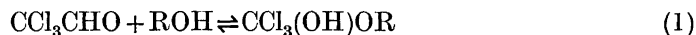
As was the case with the forward reaction, the catalyzed dissociation is shown to consist of two parallel reactions, one of which is catalyzed by acetic acid. The uncatalyzed dissociation seems to be in some way autocatalytic and it is shown that the catalyst is the alcohol arising from the dissociation. The other component, chloral, does not show any catalytic effect.

All these observations with respect to the catalyzed as well as to the uncatalyzed dissociation establish the reaction mechanism and confirm the rate expression proposed in previous papers for the forward reaction.

The variations in the equilibrium constants for the formation of 2-propanol chloral hemiacetal determined at different concentrations of chloral, 2-propanol, and hemiacetal are discussed on the basis of association between hemiacetal and alcohol molecules and between the alcohol molecules themselves. The degree of association is determined by IR spectroscopy. It is also shown that the magnitude of the equilibrium constants decreases with increasing steric bulk of the alcohol used.

The equilibrium constants for the formation of chloral hemiacetals of methanol, ethanol, and 2-propanol are determined at various temperatures. From these determinations ΔH° , ΔG° , and ΔS° , at 25°C are calculated for the hemiacetal formation.

As part of our study of the reaction between chloral and various primary, secondary, and tertiary alcohols,¹⁻⁸ we reported and discussed kinetic investigations of the uncatalyzed and acetic acid catalyzed formation in heptane solutions of the chloral hemiacetals of these alcohols (1).⁶⁻⁸



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

The reaction orders of the chloral, alcohol, and acetic acid were determined. The initial rate $\hat{v}_{0,k}$ of the catalyzed reaction was calculated as shown in eqn. (2).

$$\hat{v}_{0,k} = \hat{v}_{0,K} - \hat{v}_{0,UK} \quad (2)$$

$\hat{v}_{0,k}$: Forward initial rate of the catalyzed reaction;

$\hat{v}_{0,K}$: » » » » » observed catalyzed reaction;

$\hat{v}_{0,UK}$: » » » » » » uncatalyzed reaction;

0 refer to initial.

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 (3) and (4).

$$\hat{v}_{0,k} = \hat{k}_k [\text{Chl}]_0^a [\text{ROH}]_0^b [\text{HA}]_{0,s}^c \quad (3)$$

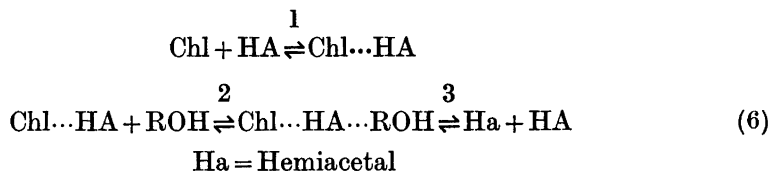
$$\hat{v}_{0,UK} = \hat{k}_{UK} [\text{Chl}]_0^{a'} [\text{ROH}]_0^{b'} \quad (4)$$

Chl = chloral, HA = acetic acid, s = stoichiometric.

In the catalyzed reaction the reaction order of chloral was found to be about 1.0 and independent of the alcohol. The reaction orders of primary and secondary straight chain alcohols⁷ were found to be between 0.2 and 0.6. The reaction orders were also found to be dependent of the initial concentration of the alcohol. Using bulky alcohols, especially β -disubstituted ones, the reaction orders were found to be 1.0. In the case of tertiary alcohols,⁸ the reaction orders were found to be much lower than 1 in spite of the very high degree of bulkiness. The reaction order of acetic acid was always found to be about 0.5. This was explained by the fact that carboxylic acids are almost completely dimerized in inert solvents (5)⁶



On the basis of these observations we suggested the following reaction mechanism for the formation of chloral hemiacetals (6).



Using a steady state treatment⁷ on $\text{Chl} \cdots \text{HA}$ in eqn. (6) the following rate-equation including the forward reaction as well as the reverse reaction was obtained (7)

$$v_k = \vec{v}_k - \hat{v}_k = \frac{[\text{HA}]_{0,s}^{\frac{1}{2}} (\vec{k}_{1,k} [\text{Chl}][\text{ROH}] - f \hat{k}_{2,k} [\text{Ha}])}{f + [\text{ROH}]} \quad (7)$$

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

$$\vec{k}_{1,k} = \vec{k}_1 K_{\text{HA}}^{-\frac{1}{2}} \left(\frac{1}{2}\right)^{\frac{1}{2}}$$

$$\hat{k}_{2,k} = \hat{k}_2 K_{\text{HA}}^{-\frac{1}{2}} \left(\frac{1}{2}\right)^{\frac{1}{2}}$$

Excluding terms connected with the reverse reaction we obtained the following rate equation describing the forward reaction (8)

$$v_k = \vec{v}_k = \frac{\vec{k}_{1,k} [\text{HA}]_{0,s}^{\frac{1}{2}} [\text{Chl}][\text{ROH}]}{f + [\text{ROH}]} \quad (8)$$

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. Tertiary alcohols (α -disubstituted), such as 2-methyl-2-propanol, and β -disubstituted primary and secondary alcohols, such as 2,2-dimethyl-1-butanol and 2,4-dimethyl-3-pentanol, yield large f values compared with unbranched primary and secondary alcohols, such as 1-propanol and 2-propanol (Table 1). When $f \gg [\text{ROH}]$ eqn. (8) was converted to eqn. (9)

$$\vec{v}_k = (\vec{k}_{1,k}/f) [\text{HA}]_{0,s}^{\frac{1}{2}} [\text{Chl}][\text{ROH}] \quad (9)$$

In order to determine $\vec{k}_{1,k}$ and f eqn. (8) was transformed to eqn. (10)

$$[\text{ROH}]_0 = \frac{\vec{k}_{1,k} [\text{HA}]_{0,s}^{\frac{1}{2}} [\text{Chl}]_0 [\text{ROH}]_0}{\vec{v}_{0,k}} - f \quad (10)$$

By measuring $\vec{v}_{0,k}$ at various $[\text{ROH}]_0$, keeping $[\text{Chl}]_0$ and $[\text{HA}]_{0,s}$ constant, $\vec{k}_{1,k}$ and f were obtained from a plot of $[\text{ROH}]_0$ versus $[\text{HA}]_{0,s}^{\frac{1}{2}} [\text{Chl}]_0 [\text{ROH}]_0 / \vec{v}_{0,k}$. This has been done for 1-propanol, 2-propanol, and 2-methyl-2-propanol (Table 2). The table indicates that the reaction mechanism proposed in (6) for the formation of chloral hemiacetals is applicable to primary and secondary alcohols, and presumable to tertiary alcohols also.

The initial rate of the uncatalyzed reaction was 10–30 times slower than that of the corresponding catalyzed reaction (with 1 mol % of catalyst). This was explained by the fact that acetic acid is a better hydrogen bond donor than the alcohols and, therefore, a better catalyst⁷ (see Pimentel and McClellan⁹).

In the uncatalyzed reaction the reaction orders of chloral and alcohol were found to be about 1.8 and 2.3, respectively, when straight chain primary alcohols were used. This showed that more than one molecule of each component reacted before or in the rate-determining step. This indicates a mixture of reaction complexes having the general composition $(\text{Chl})_m \cdots (\text{ROH})_n$ with $n \geq m$. With straight chain secondary alcohols, such as 2-propanol, reaction orders of chloral and alcohols of about 1.2 and 2, respectively, were found. In the case of tertiary and very bulky primary and secondary alcohols the reaction orders of chloral and alcohol were both found to be about 1.0 which means that the rate determining step is a reaction between one molecule of chloral and one molecule of alcohol.

Table 1. The variation of f values in the formation of chloral hemiacetals of alcohols with α , β , and γ branching computed by means of eqn. (10). The value of $\tilde{k}_{1,k}$ is $4.85 \text{ mol}^{-1} \text{ h}^{-1} \text{ sec}^{-1} \times 10^2$.

	f (absolute) $\text{mol l}^{-1} \times 10^2$	f (relative)		f (absolute) $\text{mol l}^{-1} \times 10^2$	f (relative)
$(\text{CH}_3)_3\text{COH}$	27	67	$\text{CH}_3\text{CHOHCH}_3$	3.4	8.5
$\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$	5.8	14	$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OH}$	0.94	2.3
$(\text{CH}_3)_2\text{CHCHOHCH}(\text{CH}_3)_2$	31	77	$(\text{CH}_3)_2\text{CHCH}_2\text{CHOHCH}_2\text{CH}(\text{CH}_3)_2$	9.1	23
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	0.4	1.0			

Table 2. Determination of $\vec{k}_{1,k}$ and f for 1-propanol, 2-propanol, and 2-methyl-2-propanol, eqn. (10).

	$\vec{k}_{1,k}$	$f = \vec{k}_{1,k} / \vec{k}_{2,k}$
	$\text{mol}^{-1/2} \text{l}^{1/2} \text{sec}^{-1} \times 10^3$	$\text{mol l}^{-1} \times 10^3$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ⁷	4.85	0.40
$\text{CH}_3\text{CHOHCH}_3$ ⁷	4.51	2.40
$(\text{CH}_3)_3\text{COH}$ ⁸	1.0	4.0 ^a

^a In Table 1 f has been calculated using $\vec{k}_{1,k} = 4.85 \times 10^{-2}$ from that of 1-propanol instead of $\vec{k}_{1,k} = 1.0 \times 10^{-2}$.

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 ^{5,7,8} it was found that K_s was not a true constant, especially for chloral hemiacetals of primary and secondary alcohols, because it varied with the initial concentrations of chloral and alcohol. Similar observations were made by Herold *et al.* ¹⁰⁻¹³ and Cantacuzéne. ¹⁴ This dependence was explained by association between the hemiacetal and alcohol molecules. At higher alcohol concentrations the association between the alcohol molecules must also be taken into account. That such an association took place was shown by IR measurements. ^{5,7,8} A similar association between the hemiacetal and chloral did not occur.

The investigations reported in this paper consist of determinations of the initial rates of both the uncatalyzed and catalyzed dissociation of chloral hemiacetals of 2-propanol, ethanol, and methanol. From these determinations the reaction orders of hemiacetal, alcohol, chloral, and acetic acid are calculated. These determinations are also made for the formation of the hemiacetal of 2-propanol in a more detailed way than given earlier. ⁷ The values of the equilibrium constants of 2-propanol chloral hemiacetal are determined using different initial concentrations of chloral, alcohol, and hemiacetal. The difference of these values are discussed on the basis of association between hemiacetal and alcohol molecules and between the alcohol molecules themselves. The equilibrium constants for the hemiacetal formation of methanol, ethanol, and 2-propanol are determined at various temperatures. They are used for calculation of ΔH° , ΔG° , and ΔS° for the reaction.

RESULTS AND DISCUSSION

Unless stated otherwise, the reactions were all carried out at 25°C in heptane with acetic acid as catalyst. The concentration of chloral was determined by UV spectroscopy. The initial rate of the reverse catalyzed reaction

was calculated in a manner similar to that for the forward reaction (eqn. 2) as shown in eqn. (11).^{5,7,8}

$$\tilde{v}_{0,k} = \tilde{v}_{0,K} - \tilde{v}_{0,UK} \quad (11)$$

$\tilde{v}_{0,k}$: Initial rate of the reverse reaction
 $\tilde{v}_{0,K}$: » » » » » catalyzed reaction
 $\tilde{v}_{0,UK}$: » » » » » uncatalyzed reaction

In the rate expressions (12) and (13) the appropriate reaction orders (see eqns. (3) and (4)) are expressed by the letters d and g in the catalyzed reaction and by d' in the uncatalyzed reaction.

$$\tilde{v}_{0,k} = \tilde{k}_k [\text{Ha}]^d [\text{HA}]^g \quad (12)$$

$$\tilde{v}_{0,UK} = \tilde{k}_{UK} [\text{Ha}]^{d'} \quad (13)$$

Formation of 2-propanol chloral hemiacetal. The course of the catalyzed and the uncatalyzed formation of 2-propanol chloral hemiacetal at different initial concentrations of chloral, 2-propanol, and acetic acid are shown in Fig. 1a and b. The initial rates, reaction orders of chloral, 2-propanol, and acetic acid, together with equilibrium constants are listed in Table 3.

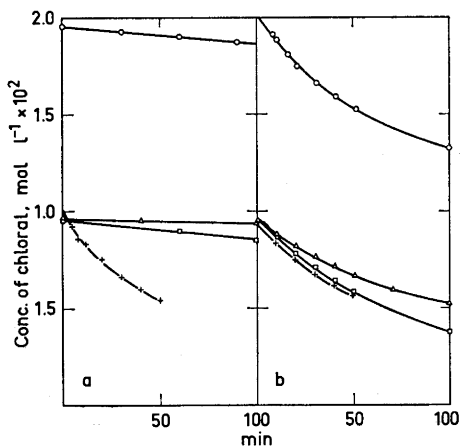


Fig. 1a and b. a. The course of the uncatalyzed formation of chloral hemiacetal of 2-propanol, illustrated by a plot of the chloral concentration *versus* time at various initial concentrations of chloral and 2-propanol. Δ : Conc. of chloral and alcohol are 10^{-2} M. \square : Conc. of chloral and 2-propanol are 10^{-2} and 2×10^{-2} M, respectively. $+$: Conc. of chloral and 2-propanol are 10^{-2} and 5×10^{-2} M, respectively. \circ : Conc. of chloral and 2-propanol are 2×10^{-2} and 10^{-2} M, respectively. b. The course of the catalyzed formation of the chloral hemiacetal of 2-propanol, illustrated by a plot of the chloral concentration *versus* time at various initial concentrations of chloral, 2-propanol, and acetic acid. Δ : Conc. of chloral, 2-propanol, and acetic acid are 10^{-2} , 10^{-2} , and 10^{-4} M, respectively. \circ : Conc. of chloral, 2-propanol, and acetic acid are 2×10^{-2} , 10^{-2} , and 10^{-4} M, respectively. \square : Conc. of chloral, 2-propanol, and acetic acid are 10^{-2} , 2×10^{-2} , and 10^{-4} M, respectively. $+$: Conc. of chloral, 2-propanol, and acetic acid are 10^{-2} , 10^{-2} , and 2×10^{-4} M, respectively.

Table 3 shows that the reaction order of chloral and of 2-propanol is about 1.2 and 2, respectively, in the uncatalyzed reaction, which means that one molecule of chloral and two molecules of 2-propanol react before or in the rate-determining step. This may indicate the existence of a well-defined reaction complex of the composition $\text{Chl} \cdots (\text{ROH})_2$. The structure of such a com-

Table 3. Initial rates of a) measured uncatalyzed, b) measured catalyzed and calculated real catalyzed formation of chloral hemiacetal of 2-propanol, together with the reaction orders of chloral, 2-propanol, and acetic acid, and equilibrium constants.

Initial concentrations mol l ⁻¹ × 10 ³			Initial rates of the hemiacetal of formation mol l ⁻¹ sec ⁻¹ × 10 ⁶			Reaction orders for				K _s l mol ⁻¹	
chloral	2-propanol	acetic acid	$\bar{v}_{0,K}$	$\bar{v}_{0,UK}$	$\bar{v}_{0,k}$	uncatalyzed reaction		catalyzed reaction			
						Chl	ROH	Chl	ROH	HA	
0.50	1.00	0.0100	0.70	~0	0.70						600
1.00	1.00	0.0100	1.27	0.06	1.21			0.90			650
2.00	1.00	0.0100	2.45	0.14	2.31	1.2					580
1.00	0.25	0.0100	0.43	~0	0.43						
1.00	0.50	0.0100	0.83	~0	0.83		~2		~0.60		620
1.00	2.00	0.0100	1.90	0.17	1.76						610
1.00	5.00	0.0100	6.00	2.70	3.3						
1.00	1.00	0.0050	0.80	0.06	0.74					0.60	570
1.00	1.00	0.0200	1.85	0.06	1.79						620
0.50	0.50	0.0100	0.40								600
4.00	4.00	0.0200	13								380

plex may be cyclic, see Fig. 2. On the other hand the reaction order of the alcohol increases with increasing alcohol concentration indicating that there might be a special solvent effect caused by the alcohol. Therefore, the explanation of the reaction orders may be that the molecules associate by dipole-dipole attraction, and in these associates the molecules may form more or less well-defined reaction complexes $(\text{Chl})_n \cdots (\text{ROH})_m$ with n and m being whole numbers.

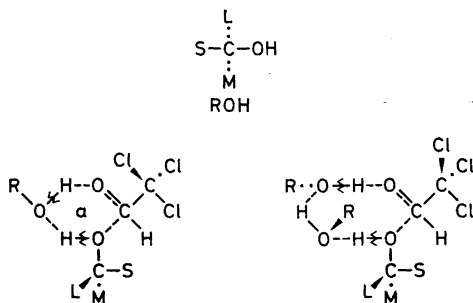


Fig. 2. Possible cyclic models of $\text{Chl} \cdots (\text{ROH})_2$, and $\text{Chl} \cdots (\text{ROH})_3$ intermediates. The symbols L, M, and S in the alcohol part refer to large, medium, and small with respect to steric bulk.

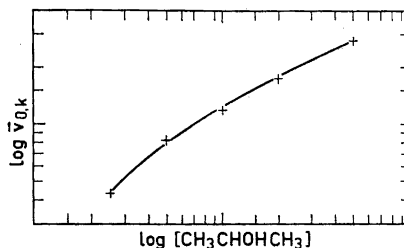


Fig. 3. A plot of the logarithm of $\bar{v}_{0,k}$ versus the logarithm of the initial concentration of 2-propanol, illustrating the variation of the reaction order of alcohol with its initial concentration.

In the catalyzed reaction the reaction order of chloral and of acetic acid are found to be about 1.0 and 0.5, respectively, as found in all cases investigated previously.^{5,7,8} The reaction order of 2-propanol is found to be about 0.6, on an average, varying with the initial concentration of 2-propanol, which is demonstrated by a plot of $\log \bar{v}_{0,k}$ versus $\log [2\text{-propanol}]_0$, Fig. 3. As indicated earlier,^{5,8} the reason for this decrease in reaction order with increasing alcohol concentration may be that the alcohol molecules associate (dimerize) at higher concentrations. The mol % of monomeric 2-propanol at different stoichiometric concentrations has been determined by means of IR-spectroscopy as shown in the first part of Table 4 and Figs. 4a, b, c, and d. It can be seen that the mol % of monomeric 2-propanol is between 100 % and 75 % in the concentration range from 1×10^{-2} to 5×10^{-2} M. If it is assumed that the reaction order is 1.0 for monomeric 2-propanol the initial rate can be expressed by eqn. (14), (cf. eqn. (3)).

$$\bar{v}_{0,k} = \bar{k}_k [\text{Chl}]_0^1 [\text{ROH}]_{\text{monomeric}}^1 [\text{HA}]_{0,s}^{0.5} \quad (14)$$

If this equation is valid the association would only be able to reduce the stoichiometric reaction order of 2-propanol to 0.8. This shows that association cannot be the only factor determining the reaction order, which also was shown by previous investigations⁷ where reaction orders between 0.2 and 1.0 were found. The reaction mechanism (6) proposed earlier,⁷ gives rise to a rate expression (8) for the forward reaction using a steady state treatment on

Table 4. The mol % of monomeric 2-propanol and 2-propanol chloral hemiacetal at different stoichiometric concentrations, different mol to mol mixtures of 2-propanol chloral hemiacetal and 2-propanol and different mol to mol mixture of 2-propanol chloral hemiacetal and chloral. The mol %'s are determined in heptane by IR spectroscopy. (See Figs. 4a, b, c, and d).

Concentration (mol l ⁻¹)			Extinction coefficient ϵ		mol % of monomer of	
2-propanol	2-propanol chloral hemiacetal	chloral	2-propanol ^a	hemi-acetal ^b	2-propanol	hemi-acetal
0.0100			34.8		100	
0.040			26.8		77	
0.100			23.5		68	
1.00			5.72		16.5	
	0.020			108.2		100
	0.040			109.4		100
	0.20			69		63
0.020	0.020		24.5	87.9	70.5	81
0.040	0.040		25.6	88	73.5	81
	0.040	0.040		109		100

^a At 3615 cm⁻¹.

^b At 3565 cm⁻¹.

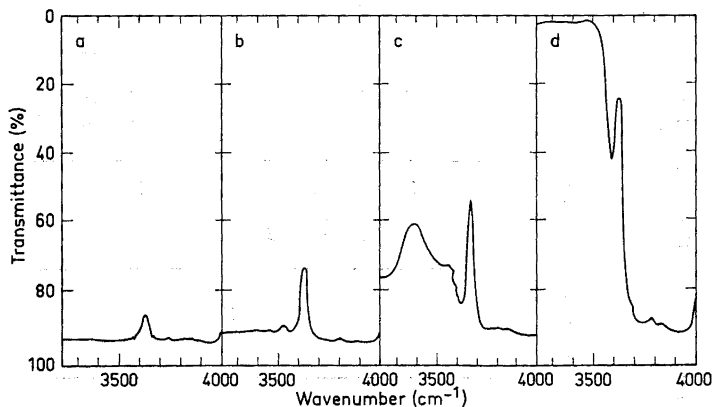


Fig. 4a, b, c, and d. IR-spectra of heptane solutions of 2-propanol. The concentration of 2-propanol is a: 10⁻² M, b: 4 × 10⁻² M, c: 10⁻¹ M, and d: 1 M. The cell path is 1 mm.

Table 5. Initial rates of the measured uncatalyzed, measured catalyzed, and calculated catalyzed dissociation of 2-propanol chloral hemiacetal, together with reaction orders and equilibrium constants.

Initial concentrations mol l ⁻¹ × 10 ²				Initial rate of dissociation of the hemiacetal mol l ⁻¹ sec ⁻¹ × 10 ⁶			Reaction orders for			Equilibrium constants K _s l mol ⁻¹	
Chl	ROH	HA	Ha	$\bar{v}_{0,K}$	$\bar{v}_{0,UK}$	$\bar{v}_{0,k}$	uncatalyzed reaction		catalyzed reaction		
				$\bar{v}_{0,K}$	$\bar{v}_{0,UK}$	$\bar{v}_{0,k}$	Ha	HA	Ha	HA	
		0.0100	1.00	0.27	0.040	0.23					
		0.010	2.00	0.55	0.077	0.47		0.95	1.04		560
		0.040	2.00	1.24	0.077	1.16				0.60	560
	1.00	0.0100	2.00	0.32	0.035	0.28					
	2.00		2.00		0.075						
	4.00		2.00		0.078						
1.00		0.0100	2.00	0.28	0.050	0.23					650
2.00			2.00		0.023						
4.00			2.00		~ 0						

$\text{Chl} \cdots \text{HA}$. It can be seen from this rate expression that the reaction order of alcohol must be between 0 and 1, depending on the relative magnitude of f and $[\text{ROH}]$. It can also be seen that the reaction order of a certain alcohol has to vary with its concentration in the above mentioned manner. This mechanism thus agrees well with the experimental data for the forward reaction and, as will be shown later, also with those for the reverse reaction. The equilibrium constants listed in Table 3 will be discussed after the treatment of the dissociation of the chloral hemiacetals of 2-propanol, ethanol, and methanol.

Dissociation of the chloral hemiacetal of 2-propanol. In Table 5 the initial rates, reaction orders of the hemiacetal and acetic acid together with equilibrium constants of the catalyzed and uncatalyzed dissociation (the reverse reaction) of 2-propanol chloral hemiacetal are listed. The course of the uncatalyzed and the catalyzed reaction are shown in Fig. 5 and 6, respectively.

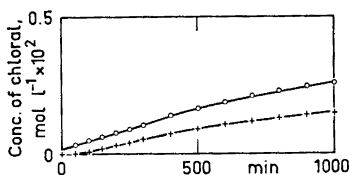


Fig. 5. The course of the uncatalyzed dissociation of chloral hemiacetal of 2-propanol illustrated by a plot of the chloral concentration *versus* time at various initial concentrations of hemiacetal. +: 10^{-2} ; O: 2×10^{-2} M.

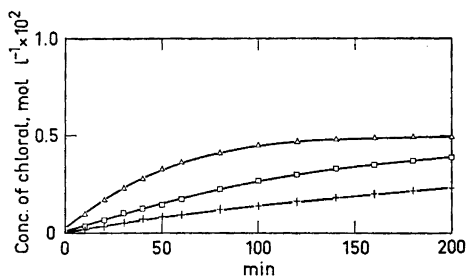


Fig. 6. The course of the acetic acid catalyzed dissociation of chloral hemiacetal of 2-propanol, illustrated by a plot of the chloral concentrations *versus* time at various initial concentrations of hemiacetal and acetic acid. +: Conc. of hemiacetal and of acetic acid are 10^{-2} and 10^{-4} M, respectively. □: Conc. of hemiacetal and acetic acid are 2×10^{-2} and 10^{-4} M, respectively. Δ: Conc. of hemiacetal and acetic acid are 2×10^{-2} and 4×10^{-4} M, respectively.

The table shows, as expected, that the reaction order of hemiacetal is about 1.0. In the catalyzed case the reaction order of hemiacetal and acetic acid are 1.04 and 0.60, respectively, which also agrees with the proposed reaction mechanism (6). The experiments with added chloral or alcohol were made in order to determine the influence of these two components on the initial rates of the catalyzed and uncatalyzed dissociation. However, when the chosen initial concentrations of chloral and alcohol are high compared with that of hemiacetal, the rate contribution from the forward reaction is large relative to that of the reverse reaction. Therefore the measured rate may differ considerably from the initial rate of the reverse reaction. This difference is especially apparent in the experiments with high chloral concentrations.

Table 6. Initial rates of measured uncatalyzed, measured catalyzed, and calculated catalyzed dissociation of chloral hemiacetals of methanol, ethanol, and 2-propanol, respectively, with and without the presence of chloral and alcohol. In addition reaction orders are listed.

	Initial concentrations mol l ⁻¹ × 10 ²				Initial rate of dissociation of hemiacetals mol l ⁻¹ sec ⁻¹ × 10 ⁶						Reaction orders for uncatalyzed reaction			
	Chl	ROH	HA	Ha	$\tilde{v}_{0,K}^a$	$\tilde{v}_{0,UK}^b$	$\tilde{v}_{0,UK}^c$	$\tilde{v}_{0,K}^d$	$\tilde{v}_{0,UK}^e - \tilde{v}_{0,UK}^f$	HA	Ha	Chl	ROH	
														catalyzed reaction
Methanol chloral hemiacetal				10.0		0.18	0.18							
				2.00		0.036	0.036				1.0			
			0.0100	1.00		0.018	0.018	2.5						
			0.040	10.0	2.7	0.18	0.18	5.8		0.57				
				10.0	6.0	0.18	0.18							
		1.00		10.0		1.8	0.18		1.6					
		0.50		10.0		1.0	0.18		0.8					
		0.25		10.0		0.6	0.18		0.4				1.0	
		1.00		10.0		0.13	0.18		-0.05					
		2.00		10.0		0.15	0.18		-0.03				~0	

Table 6. Continued.

Ethanol chloral hemiacetal	10.0	0.15	0.15	0.15	2.2	1.12	0.58	1.0	0.89
	2.0	0.30	0.30	0.30					
	10.0	0.15	0.15	0.15	4.9	0.54			
	10.0	0.15	0.15	0.15		0.28			
	10.0	1.27	0.15	0.15		-0.07		~0	
	10.0	0.69	0.15	0.15					
	10.0	0.43	0.15	0.15					
	10.0	0.08	0.15	0.15					
	10.0	0.20	0.20	0.20					
	10.0	0.95	0.20	0.20		0.75			
2-propanol chloral hemiacetal	10.0	0.42	0.20	0.20		0.22			
	10.0	2.00							
	10.0	1.00							

^a $\bar{v}_{0,K}$ refers to the measured initial rate of the acetic acid catalyzed dissociation of chloral hemiacetals.

^b $\bar{v}_{0,UK}$ refers to the measured initial rate of the uncatalyzed dissociation of chloral hemiacetals.

^c When the uncatalyzed dissociation of chloral hemiacetals is carried out in the presence of chloral or alcohol, the rate term $\bar{v}_{0,UK}$ is used, and refers to that contribution to the rate which is only caused by the concentration of hemiacetal.

^d $\bar{v}_{0,K}$ refers to the calculated initial rate of the catalyzed dissociation of chloral hemiacetals and equals $\bar{v}_{0,K} - \bar{v}_{0,UK}$.

^e The rate term $\bar{v}_{0,UK} - \bar{v}_{0,UK}$ is only used when the uncatalyzed dissociation is carried out in the presence of chloral or alcohol and refers, contrary to ^c, to the contribution to the rate which is only caused by the presence of chloral or alcohol.

In the catalyzed reaction the presence of alcohol seems to cause a small decrease in the initial rate, while the presence of chloral does not seem to have any influence at all. These observations confirm reaction mechanism (6) for the catalyzed reaction and the following rate expression (15), (see eqn. 7).

$$\bar{v}_k = \frac{f\bar{k}_{2,k} [\text{HA}]_{0,s}^{\ddagger} [\text{Ha}]}{f + [\text{ROH}]} \quad (15)$$

In order to minimize the contribution from the forward reaction mentioned above the initial concentration of hemiacetal was increased by a factor 10. These investigations were mainly carried out with the hemiacetal of methanol and ethanol. The results are listed in Table 6. The table shows initial rates and reaction orders of the catalyzed and uncatalyzed dissociation of methanol, ethanol, and 2-propanol chloral hemiacetals with and without the presence of chloral and the corresponding alcohol.

Table 7. $\bar{k}_{2,k}$ values determined from the catalyzed dissociation of chloral hemiacetals of methanol, ethanol, and 2-propanol, together with f values determined from initial rates of catalyzed dissociation of ethanol chloral hemiacetal in the presence of ethanol. The f value thus found is compared with that calculated from the forward reaction.

	$\bar{k}_{2,k}$	f (mol ⁻¹) of the	
	mol ⁻¹ l ^{1/2} sec ⁻¹	reverse reaction ^a	forward reaction ^b
CH ₃ OH	2.5 × 10 ⁻³		
CH ₃ CH ₂ OH	2.2 × 10 ⁻³	0.42 × 10 ⁻³	0.54 × 10 ⁻²
CH ₃ CHOHCH ₃	2.3 × 10 ⁻³		

^a This value is the intercept of the line in Fig. 9, which is a plot of [ROH]₀ versus 1/ $\bar{v}_{0,k}$, see eqn. (15).

^b This value is taken from Table 4, paper 7.

It can be seen from Table 6 that the initial rates of both the catalyzed and the uncatalyzed reaction are of nearly the same magnitude for methanol-, ethanol-, and 2-propanol chloral hemiacetal. In Table 7 the $\bar{k}_{2,k}$ values are listed. These values are found according to eqn. (16)

$$\bar{v}_{0,k} = \bar{k}_{2,k} [\text{Ha}]_0 [\text{HA}]_{0,s}^{\ddagger} \quad (16)$$

for the case where [ROH]₀ = [Chl]₀ = 0.

In the uncatalyzed reactions the reaction orders of the hemiacetals are found to be about 1.0. The presence of chloral does not have any influence on the initial rate in contrast to the presence of alcohol which causes an increase in the initial rate. This catalytic effect from the alcohols in the uncatalyzed dissociation of chloral hemiacetals is in agreement with what has already been observed for the forward reactions.⁷ The reaction orders of the alcohols are determined in Fig. 7 and are found to be about 1.0.

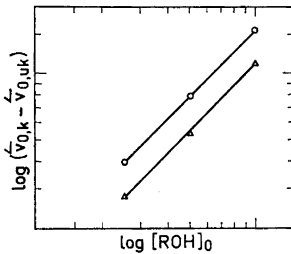


Fig. 7. A plot of $\log(\hat{v}_{0,K} - \hat{v}_{0,UK})$ for the methanol and ethanol catalyzed dissociation of the corresponding chloral hemiacetals versus the logarithm of the initial concentrations of methanol (O) and ethanol (Δ) respectively.

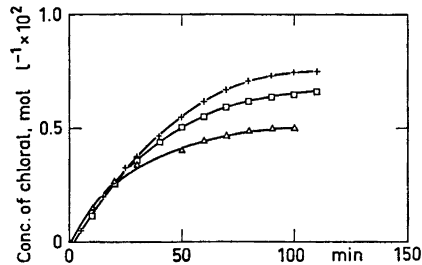


Fig. 8. The course of the acetic acid catalyzed dissociation of the chloral hemiacetal of ethanol, illustrated by a plot of the chloral concentrations versus time at various initial concentrations of ethanol. Δ : Conc. of hemiacetal, acetic acid, and ethanol are 10×10^{-2} , 10^{-4} , and 1.00×10^{-2} M, respectively. \square : Conc. of hemiacetal, acetic acid, and ethanol are 10×10^{-2} , 10^{-4} and 0.50×10^{-2} M, respectively. $+$: Conc. of hemiacetal, acetic acid, and ethanol are 10×10^{-2} , 10^{-4} , and 0.25×10^{-2} M, respectively.

In the catalyzed reaction, the presence of alcohol seems to cause a small decrease in the calculated initial rate which further confirms the rate expression (15) and the general reaction mechanism (6). In Table 8 the initial rates of the catalyzed dissociation of ethanol chloral hemiacetal in the presence of ethanol are listed and the courses of these reactions are shown in Fig. 8. From the rate expression (15) f can be determined in a similar way, as shown

Table 8. Initial rates of measured uncatalyzed, measured catalyzed, and calculated catalyzed dissociation of ethanol chloral hemiacetal at different initial concentrations of ethanol.

Initial concentrations $\text{mol l}^{-1} \times 10^2$			Initial rate of dissociation of hemiacetals $\text{mol l}^{-1} \text{sec}^{-1} \times 10^6$				
ROH	Ha	HA	$\hat{v}_{0,K}^a$	$\hat{v}_{0,UK}$	$\hat{v}_{0,uk}$	$\hat{v}_{0,k}$	$\hat{v}_{0,UK} - \hat{v}_{0,uk}$
1.00	10.0	0.0100	2.64	1.78	0.62	0.86	1.16 ^b
0.50	10.0	0.0100	2.49	1.20	0.62	1.29	0.58
0.25	10.0	0.0100	2.62	0.90	0.62	1.72	0.28

^a Definition of $\hat{v}_{0,K}$, $\hat{v}_{0,UK}$, $\hat{v}_{0,uk}$, $\hat{v}_{0,k}$ and $\hat{v}_{0,UK} - \hat{v}_{0,uk}$, see Table 6.

^b Compare these values with corresponding values in Table 6. These values arise from another series of experiments.

earlier,⁷ from a plot of $[\text{ROH}]_0$ versus $1/\bar{v}_{0,k}$ according to eqn. (17) derived from eqn. (15)

$$[\text{ROH}]_0 = \frac{f \bar{k}_{2,k} [\text{Ha}]_0 [\text{HA}]_{0,s}^\dagger}{\bar{v}_{0,k}} - f \quad (17)$$

f is found to be about 0.4×10^{-2} (mol/l), see Fig. 9. For comparison f was found to be 0.5×10^{-2} (mol/l) for the forward reaction. A better agreement is not expected because the line in Fig. 9 is only based on three points.

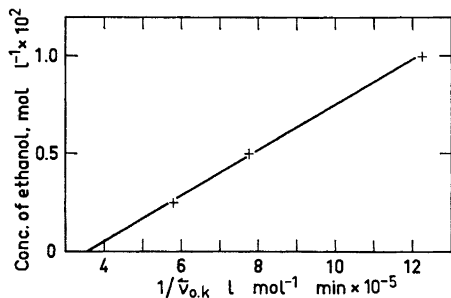
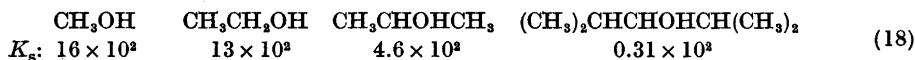


Fig. 9. A plot of the initial concentration of ethanol versus $1/\bar{v}_{0,k}$ of the acetic acid catalyzed dissociation of the ethanol chloral hemiacetal in the presence of ethanol, in order to determine f .

The equilibrium constants at 25°C (Tables 3 and 5) show a considerable decrease in magnitude with increasing bulkiness of the alcohols (20)



Increased steric bulk in the alcohols also leads to increased crowding in the corresponding chloral hemiacetals.

It can be seen from Table 3 that the K_s values vary with the initial concentrations of the reacting components. The reason for this variation is assumed to be association of the different species in the solutions. The existence of an alcohol hemiacetal associate, $\text{ROH}\cdots\text{Ha}$, is demonstrated by IR measurements shown in Figs. 10 and 11 and listed in the last part of Table 4. From the table and figures it is seen that the mol % of monomeric 2-propanol is about 70 % and the mol % of monomeric hemiacetal is about 81 % in a mixture of these two components each having a stoichiometric concentration of 2×10^{-2} M. In the concentration range from 2×10^{-2} to 10^{-1} M the hemiacetal exists almost entirely as a monomer.

In the same concentration range chloral exists entirely as a monomer and the same is true for both chloral and hemiacetal in a mixture of the two. The only important associations in the experiments therefore seem to be $\text{ROH}\cdots\text{ROH}$ and $\text{ROH}\cdots\text{Ha}$. Therefore, when K_s is determined from the stoichiometry, the deduced concentrations for alcohol and hemiacetal are too high since the true equilibrium constant refers to monomeric species. For example the constant is found to be 650 (mol l⁻¹) with $[\text{ROH}]_0 = [\text{Chl}]_0 = 10^{-2}$ M but 380 (mol l⁻¹) with $[\text{ROH}]_0 = [\text{Chl}]_0 = 4 \times 10^{-2}$ M. In the first case association cannot be important because of the low concentrations, but in the second

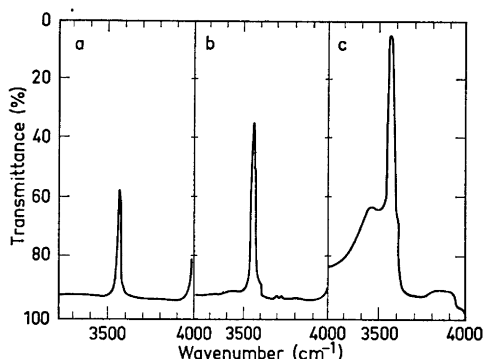


Fig. 10a, b, and c. IR spectra of heptane solutions of 2-propanol chloral hemiacetal. The concentration is, a: 2×10^{-2} M, b: 4×10^{-2} M, and c: 2×10^{-1} M. The cell path is 1 mm.

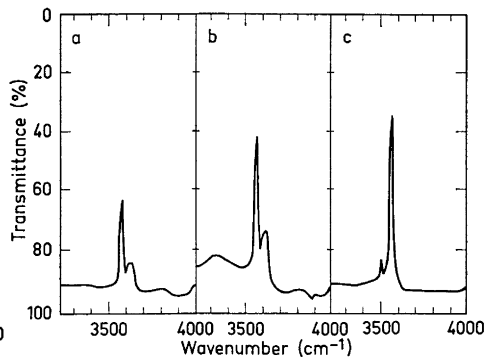


Fig. 11a, b, and c. IR spectra of heptane solutions of 2-propanol chloral hemiacetal together with 2-propanol and chloral, respectively. The concentrations are, a: Conc. of hemiacetal and 2-propanol are both 2×10^{-2} M. b: Conc. of hemiacetal and 2-propanol are both 4×10^{-2} M. c: Conc. of hemiacetal and chloral are both 4×10^{-2} M.

case $[\text{Chl}]_e \sim [\text{ROH}]_e \sim 0.9 \times 10^{-2}$ M and $[\text{Ha}]_e \sim 3.1 \times 10^{-2}$ M, (where e denotes equilibrium) and therefore it is likely that some of the alcohol molecules associate with the hemiacetal in a 1:1 complex. Because $[\text{ROH}]_e$ is much smaller than $[\text{Ha}]_e$ it is seen that the true constant must be considerably larger than 380 (mol l^{-1}). To confirm this explanation it is necessary to carry out more experiments on this different kind of association by precise IR measurements.

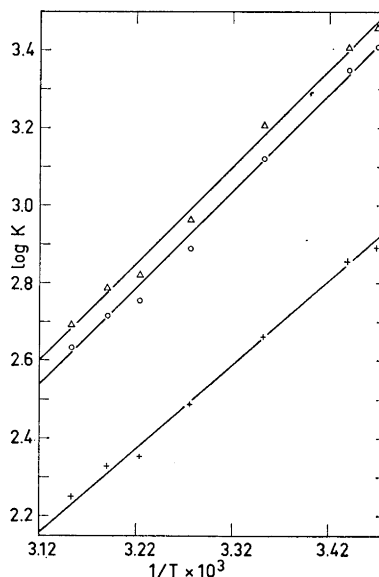


Fig. 12. A plot of the logarithm of the equilibrium constant for the formation of chloral hemiacetals versus $1/T$ in order to determine ΔH° , ΔS° , and ΔG° . Δ : Methanol, \circ : ethanol, and $+$: 2-propanol.

Table 9. Determination of equilibrium constants of the formation of chloral hemiacetals of methanol, ethanol, and 2-propanol at different temperatures. The initial concentrations were always: $[\text{Chl}]_0 = [\text{ROH}]_0 = 1.00 \times 10^{-2}$ mol/l and $[\text{HA}]_0 = 1.00 \times 10^{-4}$ mol/l.

	Concentrations at equilibrium mol l ⁻¹ × 10 ²			Equilibrium constant K_s l/mol	Temperature $t(^{\circ}\text{C})$
	Chl	ROH	Ha		
Methanol	0.17	0.17	0.83	2870	15.0
	0.18	0.18	0.82	2550	18.0
	0.22	0.22	0.78	1610	25.0
	0.28	0.28	0.72	920	32.2
	0.32	0.32	0.68	665	37.2
	0.32	0.32	0.68	615	40.6
	0.36	0.36	0.64	495	44.2
Ethanol	0.18	0.18	0.82	2550	15.0
	0.19	0.19	0.81	2240	18.0
	0.24	0.24	0.76	1320	25.2
	0.30	0.30	0.70	780	32.2
	0.34	0.34	0.66	570	37.2
	0.35	0.35	0.65	530	40.6
	0.38	0.38	0.62	430	44.2
2-Propanol	0.30	0.30	0.70	780	15.0
	0.31	0.31	0.69	720	18.0
	0.37	0.37	0.63	460	25.2
	0.43	0.43	0.57	310	32.2
	0.48	0.48	0.52	226	37.2
	0.49	0.49	0.51	213	40.6
	0.52	0.52	0.48	178	44.2

The temperature dependence of the equilibrium constants for the formation of hemiacetals of methanol, ethanol, and 2-propanol are listed in Table 9. From these values ΔH° and ΔS° were determined by a plot of $\log K$ versus $1/T$ as shown in Fig. 12. From ΔH° and ΔS° , ΔG° is determined at 25°C. The results

are listed in Table 10. The table shows that the hemiacetal formation is followed by a substantial loss of entropy. The corresponding values of ΔH° (kcal mol⁻¹), ΔS° (cal K⁻¹ mol⁻¹), and ΔG° (kcal mol⁻¹) for the hydration of chloral in aqueous solution at 25°C are -12.7, -30.2, and -3.68, respectively, and are of the same order of magnitude as the values given in Table 10, even though a quite different solvent has been used (see the review of Schallinger and Long¹⁵). That the effect of the solvent change on the equilibrium involving non-ionic species is small agrees with the small variation in thermodynamic quantities at 25°C determined for the formation of acetone cyanohydrin, Table 11.¹⁵

EXPERIMENTAL

The UV-measurements were made on a Pye-Unicam-Philips spectrophotometer SP 800 and the IR-measurements were made on a Perkin-Elmer grating infrared spectrophotometer 337.

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Table 10. ΔH° , ΔG° , and ΔS° for the formation of chloral hemiacetals of methanol, ethanol, and 2-propanol at 25.0°C.

	ΔH° kcal mol ⁻¹	ΔS° cal K ⁻¹ mol ⁻¹	ΔG° kcal mol ⁻¹
Methanol	-11.5	-23.8	-4.35
Ethanol	-11.3	-23.6	-4.27
2-Propanol	-9.95	-21.4	-3.56

Table 11. Thermodynamic quantities at 25°C for the reaction $(\text{CH}_3)_2\text{C}=\text{O} + \text{HCN} = (\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$ taken from Schallinger and Lang.¹⁵

Solvent	$-\Delta G^\circ$ kcal mol ⁻¹	$-\Delta H^\circ$ kcal mol ⁻¹	ΔS° cal K ⁻¹ mol ⁻¹
Water	23.8	26.7	-9.6
Ethanol	24.6	28.1	-10.4
Benzene	21.4	24.2	-8.4
Chloroform	25.1	28.1	-9.1

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