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8. NMR.-Investigation of the Formaldehyde Addition and Oligomerisation Equilibria in the System Formaldehyde/ Water/Acetic Acid/Hydrochloric Acid

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(16. V. 72)

Summary. – An NMR. investigation of the state of formaldehyde in acidic solutions has been carried out. Solutions of $DCl/D_2O/CD_3COOD$ containing two sources of formaldehyde, i.e. para-formaldehyde (I) and trioxane (II), were used for this purpose. In systems I and II the effect of various D_2O/CD_3COOD ratios, at a constant DCl concentration, was studied, while for II the effect of changing DCl concentration was also investigated. The results show that in aqueous solution, formaldehyde exists primarily as the monomeric and linear oligomeric forms of methylene glycol. Reducing the amount of D_2O (at constant DCl concentration), while increasing the CD_3COOD content, results in an increase in the polymeric species and in trioxane. In addition, substitution of water by acetic acid results in systems that are catalytically more active than aqueous solutions of the same hydrochloric acid concentration. Along with the usual polymer-monomer equilibria which exist in such solutions, side reactions of methylene glycol with the hydrochloric acid present also occur to a small extent, e.g. acetylation, substitution of OH by Cl and the Cannizzaro reaction. It is suggested that these findings will result in a better understanding of the formaldehyde crosslinking reactions in cotton cellulose.

1. Introduction. – Since formaldehyde (1) is a very reactive electrophilic species, it is not surprising that, in aqueous solutions, the equilibrium (1) with water strongly favours the hydrate, methylene glycol (2). The equilibrium has been investigated by Bieber & Trümpler [1], Illiceto [2], Bell [3], and Schecker & Schulz [4] and an equilibrium constant K' of 4.1×10^{-4} at 25° [4] was obtained (equation (2)).
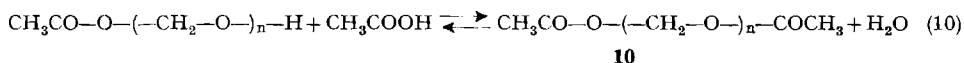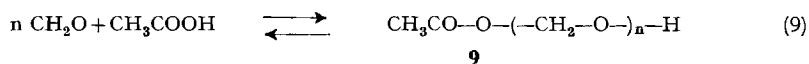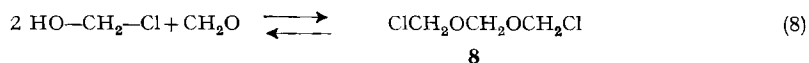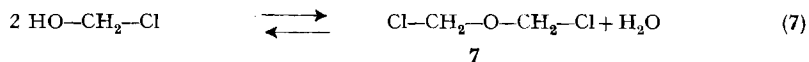
$$CH_2O + H_2O \underset{K}{\overset{K}{\rightleftarrows}} HO-CH_2-OH \tag{1}$$

1   2
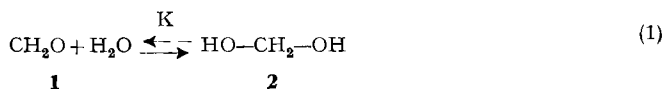
$$K' = \frac{K}{[H_2O]} = \frac{[CH_2O]}{[HO-CH_2-OH]} \tag{2}$$

In addition, the electrophile formaldehyde reacts with methylene glycol in aqueous solutions, forming dimer, trimer and higher oligomer hydrates [equation (3)], the formation of which is of course favoured by increasing formaldehyde concentration. *Walker* [5] has summarized studies on these equilibria.

$$(n-1) CH_2O + HO-CH_2-OH \rightleftarrows HO-(-CH_2-O-)_n-H \tag{3}$$

3
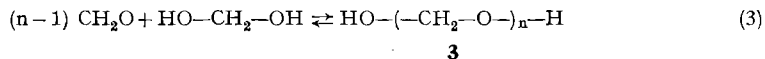
Furthermore, formaldehyde forms cyclic oligomers, in particular trioxane (4) and tetroxane (5) (4–5).

In the context of our investigations on cotton crosslinking with formaldehyde (see below), reactions of formaldehyde with hydrochloric acid (6–7) and acetic acid (8–9) may be particularly important.

$$3 CH_2O \qquad \rightleftarrows \qquad \tag{4}$$

4

$$4 CH_2O \qquad \rightleftarrows \qquad \tag{5}$$

5

$$CH_2O + H^{\oplus} + Cl^{\ominus} \qquad \rightleftarrows \qquad HO-CH_2-Cl \tag{6}$$

6

$$2 HO-CH_2-Cl \qquad \rightleftarrows \qquad Cl-CH_2-O-CH_2-Cl + H_2O \tag{7}$$

7

$$2 HO-CH_2-Cl + CH_2O \qquad \rightleftarrows \qquad ClCH_2OCH_2OCH_2Cl \tag{8}$$

8

$$n CH_2O + CH_3COOH \qquad \rightleftarrows \qquad CH_3CO-O-(-CH_2-O-)_n-H \tag{9}$$

9

$$CH_3CO-O-(-CH_2-O-)_n-H + CH_3COOH \rightleftarrows CH_3CO-O-(-CH_2-O-)_n-COCH_3 + H_2O \tag{10}$$

10
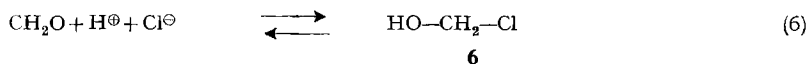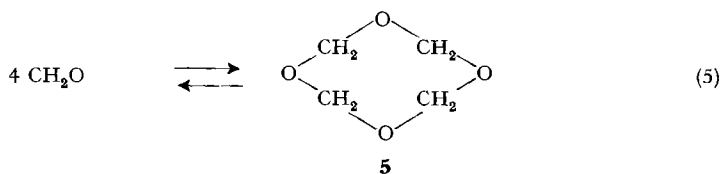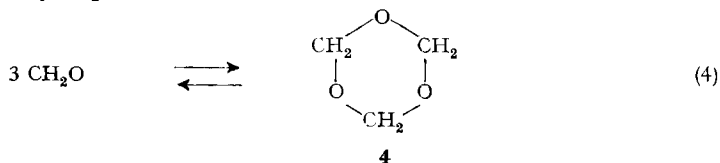
The purpose of this investigation was, therefore, to study the state of formaldehyde in $H_2O/CH_3COOH/HCl$ solutions of varying compositions. The advantages of using NMR. spectroscopy over the techniques used previously for the investigation of such equilibria has been shown [6–9]. *Skell & Suhr* [6] in an NMR. investigation

found good agreement between their results and the earlier results of *Auerbach &* *Barshall* [10] and those of *Illiceto & Bezzi* [2]. The more recent investigations of *Moedritzer & van Wazer* [8] have shown that the equilibrium between linear and cyclic species (trioxane) has to be considered although the amount of the latter species is small.
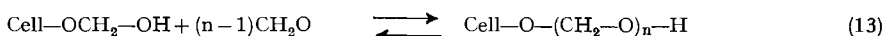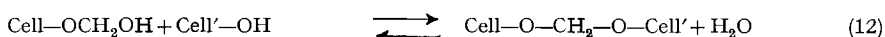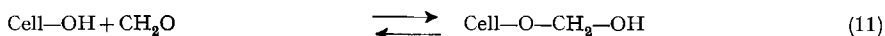
As a result of the inductive effect of oxygen on the adjacent methylene protons, it is possible to distinguish between three different types of methylene protons in the polyoxymethylene chain (due to the difference in the chemical shifts of these groups). The three types of methylene protons are

     a) methylene protons belonging to the monomeric hydrate methylene glycol,
     b) methylene protons at the ends of oligomeric chains (terminal methylenes), and
     c) all other methylene protons (central methylenes).

If the proportion of the three different methylene protons are known, the relative amounts of the different formaldehyde species present in these solutions can be estimated.

2. Related Investigations on Crosslinking of Cotton Cellulose with Formaldehyde. – Although this study is concerned only with the equilibria (1), (3), and (4) to (10), it seems appropriate to summarize briefly the problems occurring in reactions of $CH_2O/H_2O/CH_3COOH/HCl$ systems with cellulose hydroxyl groups, since these reactions are very important for so called easy-care treatments of cotton textile fabrics.

In previous investigations [11] we have shown how the structure of formaldehyde crosslinked cotton influences the mechanical properties of the resulting fabric. It was concluded that the average chain length (n) of the crosslinks introduced into the cellulose is greater than unity, regardless of whether the crosslinks are intra- or intermolecular. The average chain length was found to increase with reaction time, probably because of the existence of a grafting mechanism, expressed by the following scheme:

$$\text{Cell—OH} + CH_2O \quad \rightleftharpoons \quad \text{Cell—O—CH}_2\text{—OH} \tag{11}$$

$$\text{Cell—OCH}_2\text{OH} + \text{Cell'—OH} \quad \rightleftharpoons \quad \text{Cell—O—CH}_2\text{—O—Cell'} + H_2O \tag{12}$$

$$\text{Cell—OCH}_2\text{—OH} + (n-1)CH_2O \quad \rightleftharpoons \quad \text{Cell—O—(CH}_2\text{—O)}_n\text{—H} \tag{13}$$

$$\text{Cell—O—(CH}_2\text{—O)}_n\text{—H} + \text{Cell'—OH} \quad \longrightarrow \quad \text{Cell—O—(CH}_2\text{—O)}_n\text{—Cell'} + H_2O \tag{14}$$

It is clear that crosslinked products of chain-length n = 2 can also be formed by condensation of two O-methylol products from reaction (11).

The water content of the crosslinking solution has also been found to affect the chain length of the crosslinked cellulose, thus influencing the mechanical properties of the cotton fabrics. Other authors have concluded that while monomeric units most likely predominate in cotton cellulose that has been crosslinked by means of dilute formaldehyde solutions, longer crosslinks are introduced by more concentrated solutions [12]. We have shown that in a system of low water content crosslinks of shorter average chain length (n = 1.5) are formed, while in a system of higher water content longer crosslinks of average chain length (n = 2.5) are formed. These results for non-equilibrated systems indicate that a correlation exists between the chemical constitutions of crosslinked cellulose and the state of dissolved formaldehyde at the time of crosslinking.

In the treatment of cellulose with formaldehyde varying amonts of water, acetic acid and hydrochloric acid are used. For this reason the following related systems which are also suitable for NMR, studies were chosen:

System I   : Paraformaldehyde(3, n > 10)/D_2O/CD_3COOD/DCl

System II : Trioxane(4)/D_2O/CD_3COOD/DCl

System III: Model compounds/D_2O/CD_3COOD/DCl

In systems I and II the effect of varying the D_2O/CD_3COOD ratio was studied at a constant mineral acid concentration (14.6% by weight DCl). Also for system II the effect of changing the mineral acid concentration with respect to:

A) solutions containing varying amounts of CD_3COOD and constant amounts of D_2O (23.5% by weight) and

B) for aqueous systems without CD_3COOD
was investigated. In the technology of crosslinking cotton with formaldehyde, systems with varying water/acetic acid ratio are used for the so-called Form D and Form W processes [13].

3. Experimental Part. – 3.1. *Model Compounds for Methylene Peak Assignments.* – *Skell* & *Suhr* [6] made the first NMR. study of the state of formaldehyde in aqueous solutions and suggested the use of polyoxymethylene diacetates (chain length n = 1 to 6) as model compounds for different methylene peak assignments in formaldehyde oligomers. However, more recently, *Ihashi, Sawa* & *Morita* [7] showed the ambiguity of using acetates for such assignments, and used polyoxymethylene dimethyl ethers instead. We therefore decided to prepare and examine both of these models to confirm the peak assignments in our NMR. investigation.

Oligooxymethylene diacetates (**10**) (n = 1, 2 and 3): Compounds with n = 1 and 2 were prepared by the method of *Tomiska* & *Spoutsa* [14] starting with trioxane (**4**) and acetic anhydride in the presence of perchloric acid and subsequently fractionating the reaction mixture by distillation. However, since this method was not successful for the compound with n = 3, the latter was prepared from paraformaldehyde and acetic anhydride according to the method of *Staudinger* [15].

Oligooxymethylene dimethyl ethers CH_3O-$(CH_2$—$O)_n$-CH_3 (**15**) (n = 1, 2 and 3): Formaldehyde dimethyl acetal (n = 1) (*Fluka* purum) was used. The dimer and trimer (n = 2 and 3) were prepared [16] starting with 2 moles of monomer (n = 1), 0.5 moles of paraformaldehyde and 0.1% wt of sulphuric acid at 100° and 7 kg/cm² pressure for 1 h, and subsequently isolating the product by distillation.

Methylene chloride and dichlorodimethyl ether (both obtained from *Fluka*) and tetroxane (*Mitsui Toatsu Chem.*) were used as further model substances.

3.2 *Other chemicals used.* – Trioxane (**4**) and paraformaldehyde (**3**) (both *Fluka*) were used as formaldehyde sources without further purification. Acetic acid, acetic anhydride and hydrochloric acid (37% aqueous solution) were obtained from *Merck*.

All deuterated compounds, obtained from CIBA AG (now Ciba-Geigy AG), had the following reported isotopic purities (in atom % D):

Deuterium chloride (38% solution in D_2O)	99.5
Deuterium oxide	99.75
Acetic acid-d_4	99.5
Acetic anhydride-d_6	99

3.3. *Preparation of solutions.* – Solutions required for crosslinking cotton in a Form D or Form W process are usually prepared by dissolving paraformaldehyde in water/acetic acid/hydrochloric acid mixtures. The rate of dissolution of paraformaldehyde in water has been studied by *Wadano et al.* [17]. We measured the rate of dissolution of this polymer in acetic acid/water mixtures in the presence of hydrochloric acid by analysing the formaldehyde content of the solution (after the undissolved paraformaldehyde was separated from the solution) as a function of time using a standard procedure [18]. In all experiments, the maximum concentration of dissolved formaldehyde (sum of all equilibrium forms) was adjusted to 7.5%. Fig. 1 shows the con-
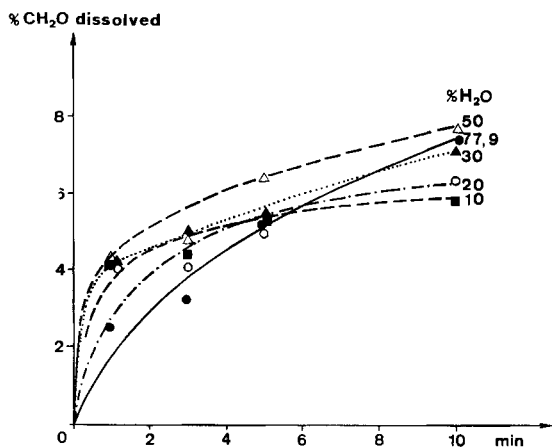
Fig. 1. *Rate of dissolution of paraformaldehyde in system I with varying water content*

centration of dissolved formaldehyde as a function of time and water content of the solvent. Although the initial rate of dissolution is slower for solutions of high water content, after 6 min. the rate is slower in systems with low water concentrations. Eventually (not shown in Fig. 1), all of the paraformaldehyde (7.5%) is dissolved at all water/acetic acid ratios investigated.

However, since the dissolution of paraformaldehyde in the systems used takes a relatively long time, this polymer cannot be used as a source of formaldehyde for any kinetic measurements. In later investigations we used trioxane which is very soluble in all solutions studied, while paraformaldehyde was only used to determine the equilibrium composition of a solution. As shown later, both of these formaldehyde sources gave the same equilibrium composition.

Systems I and II: The required amounts of D_2O, CD_3COOD and DCl were mixed at room temperature and either paraformaldehyde or trioxane was added. The mixture was shaken at room temperature until a clear solution was obtained and then allowed to stand for two days before running the spectra. In addition, in system II the acid concentration was varied while keeping the solvent composition constant, i.e., 23.5% D_2O with various amounts of CD_3COOD, or just deuterium oxide.

System III: The assignment of the NMR. signals for the spectra of formaldehyde solutions was achieved by the use of suitable model compounds. The spectra of 7.5% (w/w) methylene chloride, dichlorodimethyl ether or oligooxymethylene diacetates, oligooxymethylene dimethyl ethers, or tetroxane, were recorded and the decomposition of these compounds in the appropriate solutions was followed.

The composition of the solutions used for the two systems I and II are given in Tables I and II.

Table I: *Composition of System I and System II solutions*

D_2O %	Paraformaldehyde or trioxane %	DCl %	CD_3COOD %
13.2 [a])	7.5	14.6	64.7
19.7 [a])	7.5	14.6	58.2
23.5	7.5	14.6	54.4
29.6	7.5	14.6	48.3
50.0	7.5	14.6	27.9
77.9	7.5	14.6	–

[a]) These amounts were achieved by addition of appropriate amounts of acetic anhydride.

Talbe II: *Composition of System II A and B solutions*

D₂O %	Trioxane %	DCl %	CD₃COOD %
IIA 23.5	7.5	2	67
23.5	7.5	4	65
23.5	7.5	6	63
23.5	7.5	8	61
23.5	7.5	10	59
23.5	7.5	14.6	54.4
IIB 90.5	7.5	2	
88.5	7.5	4	–
86.5	7.5	6	–
82.5	7.5	10	–
77.9	7.5	14.6	–
57.5	7.5	35	–

3.4. *NMR. Measurements.* – Spectra reported in this work (if not otherwise stated in the text) were obtained with a *Varian* A-60 NMR. spectrometer at a probe temperature of $31 \pm 2°$ C. Chemical shifts are given in ppm with DSS as internal reference. For spectra recorded in CCl₄ TMS was used as internal reference. Since some signals overlapped, the NMR. integrator could not be used to obtain peak areas. In these cases evaluation of peak areas was carried out by resolving the peaks with a *Du Pont* 382 Curve Resolver, using standard *Lorentzian* curves. The individual peaks were integrated separately assuming a total methylene intensity of 100%. The results were then expressed as % methylenes involved in each species and are accurate to $\pm 5\%$.

In a NMR. investigation of this kind H/D exchange has to be considered when deuterated compounds are used. It has already been shown by *Skell & Suhr* [6] and by *Ihashi, Sawa & Morita* [7], that H/D exchange does not occur in aqueous formaldehyde solutions. Nevertheless, we measured the composition with respect to time of an aqueous solution obtained by mixing 14.6% DCl and 77.9% D₂O and subsequently adding 7.5% tetroxane. Tetroxane is easily soluble in this
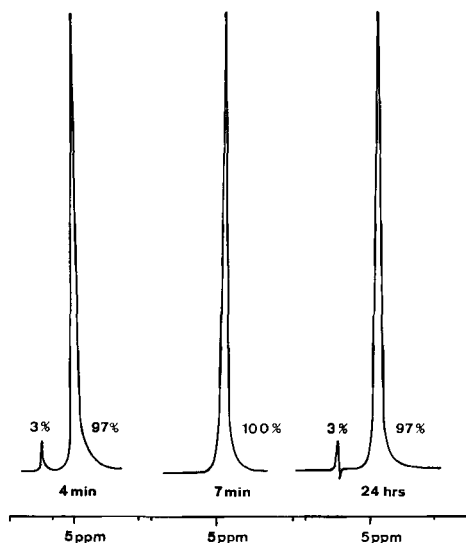

Fig. 2. *NMR. spectra taken during the decomposition of tetroxane in System III* (50% D₂O/27.9% CD₃COOD/14.6% DCl).

solution and equilibrates very quickly (see Fig. 2). The results are shown in Table III. Since the time investigated was long and no H/D exchange was observed for tetroxane, a similar result is expected for trioxane and paraformaldehyde.

Table III: *Composition of an equilibrated aqueous formaldehyde solution with time* (7.5% tetroxane/ 14.6% DCl/77.9% D_2O)

Time	Intensity ratio	
(hrs)	CH_2/OH	CH_2/DSS
0.5	85:15	82:18
17.75	86:14	82:18
25.0	86:14	83:17
41.5	86:14	83:17
48.0	86:14	83:17
65.75	86:14	83:17
330	84:16	82:18

4. Results. – 4.1 *Model Compounds.* – The NMR. signals for methylene groups of the various equilibrium forms of formaldehyde [equations (1), (3), (4), and (6) to (9)] in systems I to II were assigned with the use of model compounds, namely three oligooxymethylene diacetates [(**10**), n = 1,2 and 3] and three oligooxymethylene dimethyl ethers [(**15**), n = 1,2 and 3]. The NMR. chemical shifts of the methylene peaks, all singlets, of these compounds in CCl_4 are given in Table IV.

Table IV: *Chemical shifts* (ppm) *of the oligooxymethylene diacetates* (**10**) *and dimethyl ethers* (**15**); *methylene protons* (in CCl_4, internal reference TMS)

Compound	Chemical shifts			Intensity ratio
	Methylene glycol	Central methylene	Terminal methylene	
10 n = 1	5.61	–	–	–
n = 2	–	–	5.29	–
n = 3	–	4.84	5.24	1:2
mixtures of n = 1, 2 und 3	5.61	4.84	5.24	–
15 n = 1	4.45	–	–	–
n = 2	–	–	4.61	–
n = 3	–	4.75	4.61	1:2
mixtures of n = 1, 2 und 3	4.45	4.75	4.61	–

The data in Table IV demonstrate the influence of the acetoxy and methoxy substituents, respectively, on the adjacent methylene group: the chemical shift of the acetylated monomer (**10**, n = 1) as well as those of the terminal methylene groups of the dimer and trimer are shifted downfield by 1.2 and 0.6 ppm respectively, relative to the corresponding methyl ethers. The influence of the end group on the chemical shift of the central methylene group in the trimers of (**10**) and (**15**) is, however, small (as indicated by the similarity in their chemical shifts). Also, for a mixture of (**10**) and

(15) (both n = 1, 2, and 3) all 6 different methylenes could be clearly identified by the chemical shifts given in Table IV for the individual compounds (10) and (15).

In Table V the effects of hydroxy, methoxy and acetoxy substituents on the chemical shift of methylene groups in benzyl and ethyl derivatives are compared. The data demonstrate that of these substituents, an acetoxy group has the greatest effect on an adjacent methylene group (Table IV and V).

In our systems I and II we have to consider first of all the hydration equilibria (1) and (3). In agreement with *Ihashi, Sawa & Morita* [7] the data in Table V suggest that, for the assignment of methylene protons in mono and oligomeric formaldehyde hydrates, oxymethylene dimethyl ethers 11 are better models than the corresponding diacetates 10. On the other hand, equilibrium (10) yields products for which the diacetates are perfect models. Compounds 6 and 9 [equilibria (6) and (9)] are mixed hydrates and esters; therefore, these ethers and acetates may be regarded as acceptable model compounds for our study.

Table V: *Methylene chemical shifts* (ppm) *for benzyl and ethyl derivatives*

Compound	X	Methylene protons	Ref.
C_6H_5-CH_2-X	OH	4.58	[19]
	OCH_3	4.46	[20]
	O—$COCH_3$	5.08	[19]
CH_3-CH_2-X	OH	3.70	[19]
	OCH_3	3.40	[21]
	O—$COCH_3$	4.12	[19]

On this basis (Table IV and V) one expects the methylene protons of methylene glycol (2) at 4.5 to 4.8 ppm, followed by the terminal and central methylene groups of the oligomers ((3), n ≥ 2) at slightly lower field. As can be seen from Table VI this sequence of signals is obtained in acidic aqueous solution of formaldehyde in equilibrium (7.5% trioxane as the formaldehyde source) if the acid concentration is kept below 10%. For concentrations of DCl less than 6% the signals of methylene glycol (4.84 ppm), the terminal methylenes (4.90 ppm), and the central methylenes are well separated. The signals begin to overlap at 10% DCl, the methylene glycol signal shifting downfield from 4.84 to 4.87 ppm and, at 14.6% DCl, one unsymmetrical

Table VI: *Chemical shifts observed in an equilibrated, aqueous trioxane solution* (7.5% trioxane as starting concentration) *at different acid concentrations.*

% DCl in aqueous solution	Signals (singlets) in ppm				Additional signals (singlets) in ppm
	Trioxane	Polyoxymethylenes		Methylene glycol	
		Central	Terminal		
4.0	5.22	4.96	4.90	4.84	–
6.0	5.22	4.96	4.90	4.84	–
10.0	5.23	4.96	4.90	4.87	–
14.6	5.25	4.91*	4.89*	4.92*	–
34.8	5.29	5.05*	5.36*	5.27*	5.68 + 5.61

* Resolved with the curve analyser.

signal is obtained which could be resolved into three peaks with the curve resolver. The greatest downfield shift (5.27 ppm) and a broadened signal are observed for 34.8% DCl. As discussed later in this paper, this downfield shift is probably due to protonation of the ether and hydroxy oxygen atoms.

Moedritzer & van Wazer [8] have shown that trioxane is present in aqueous solutions. In CCl_4 trioxane and tetroxane give rise to singlets at 5.05 ppm and 4.93 ppm, respectively (Table VII). In aqueous formaldehyde solution, trioxane and tetroxane signals are observed at nearly the same position, i.e. 5.24 ppm and 5.19 ppm, respectively (Table VII). Tetroxane (as a source of formaldehyde) is very unstable in the presence of hydrochloric acid as it decomposes in a solution of 50% water/27.9% acetic acid/14.6% hydrochloric acid (Fig. 2) after 7 minutes. In this same solution trioxane is slowly formed, approx. 3% being present at equilibrium beside methylene glycol and oligomers. If solutions of higher acidity (for example with low amounts of water at a constant acid concentration) are used tetroxane decomposes immediately after addition. Thus one can assign the signal at 5.22–5.29 ppm in Table VI to trioxane (see also Fig. 2).

Table VII: *Methylene chemical shifts for cyclic formaldehyde oligomers* (n = 3 and 4)

Compound	Chemical shift (ppm)	
	CCl_4	50% D_2O/14.6% DCl 27.9% CD_3COOD
trioxane (n = 3)	5.05	5.22
tetroxane (n = 4)	4.93	5.19

4.2. *Interpretation of NMR. Spectra of Formaldehyde in Systems I and II.* – Typical NMR. spectra of solutions with extreme amounts of water (77.9% D_2O and 13.2% D_2O) in system I are shown in Fig. 3 and 4, respectively. At high D_2O content (Fig. 3),
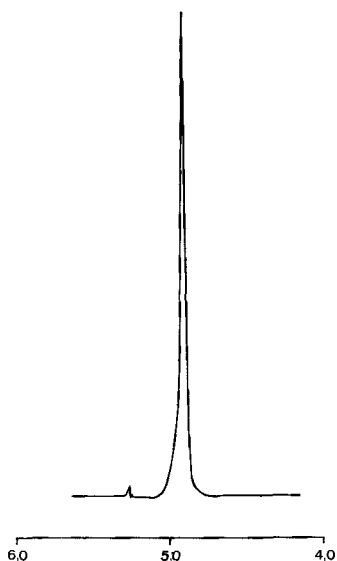

Fig. 3. *NMR. spectrum of an equilibrated paraformaldehyde solution* (system I: 77.9% D_2O/14.6% DCl).

6.0   5.0   4.0

a simple spectrum is observed with an intense sharp but unsymmetrical singlet at 4.90 ppm and a weak signal at 5.25 ppm. The spectrum of the system with low D_2O content is, however, more complex (Fig. 4), containing broad and overlapping signals.
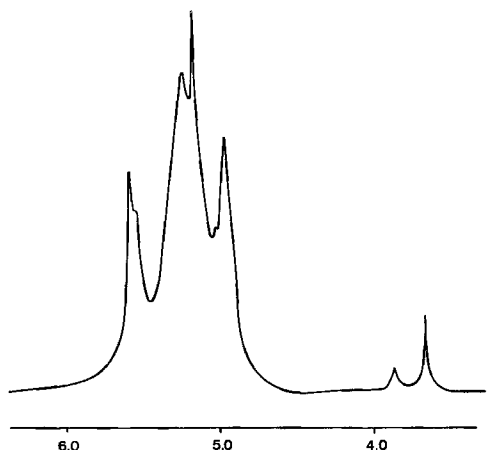

Fig. 4. *NMR. spectrum of an equilibrated paraformaldehyde solution*
(system I: 13.2% D_2O/14.6% DCl/64.7% CD_3COOD)

Therefore, all spectra were resolved by means of a curve analyser (see Exp. Part). In addition to the above methylene peaks one observes OH protons at 6.82–9.55 ppm, a small methyl signal appearing at 2.30 ppm which can be assigned to small amounts of undeuterated acetic acid, and small signals at 3.90 to 3.50 ppm. Only the latter signals, identified as those of methoxyl groups, were included in the calculation of the total methylene present.

It is evident that central methylene protons in an acid solution must appear in a comparable region (4.8 to 4.9 ppm) as in the case of ether or ester model compounds in an aprotic solvent. This is because the effect of protonating the corresponding terminal hydroxy groups is not transmitted to the methylene protons in a central position. However, terminal methylene protons and protons of methylene glycol are deshielded by protonation of the neighbouring hydroxy group; therefore, a downfield shift similar to that observed in the case of the corresponding ester model compounds is observed (Table VI). Thus, the position of methylene glycol and terminal methylenes in an NMR. spectrum of an acidic solution apparently depends on their degree of protonation, i.e. it is a function of the protonating power of the medium. In the solutions described in the present investigation, mineral acid concentrations of 1 to 10 moles/litre were used. Since the acidity function H_0 of H_2O/CH_3COOH/HCl mixtures increased with decreasing water content at a given (constant) molarity of mineral acid [11], the degree of protonation of formaldehyde hydrates (2) and (3) increases at lower water ratios. A downfield shift of methylene glycol protons and of the terminal methylene protons is expected in systems as the D_2O content is decreased or at low D_2O content (for example 23.5%) with increasing acid concentration.

Chemical shift assignments based on the foregoing discussion are presented in Table VIII and IX for systems II and I together with signal intensities calculated as

Table VIII. *Composition of acidic (14.6% DCl) equilibrated formaldehyde solutions from 7.5% trioxane*

D_2O %	OH protons ppm[a]	$ClCH_2(OCH_2)_{n+1}Cl$ ppm	%	$XO(CH_2O)_{n+2}X$ ($X = COCD_3$) ppm[d]	%	Trioxane ppm	%	Methylene glycol ppm[b]	%	Polyoxymethylene groups Terminal ppm[b]	%	Central ppm[b]	%	Methoxyl signal group (3.5–3.9 ppm) %[c]
77.9	6.80	–	–	–	–	5.22	tr.	4.92	70	4.89	20	4.91	10	–
50.0	7.54	–	–	5.40	0.5	5.22	6	4.94	65	5.04	20	4.96	8	0.5
29.6	8.64	5.64	8	5.40	3	5.25	7	5.12	54	5.07	15	4.96	12	1.0
23.5	8.79	5.63 5.60	11	5.34	2	5.25	11	5.08	52	5.10	10	4.96	13	1.0
19.7	8.75	5.64 5.60	11	5.40	3	5.24	6	5.04	54	5.10	9	4.96	15	2.0
13.2	9.59	5.64 5.60	16	5.38 5.34	17	5.20	8	5.08	29	5.16	8	5.02	29	2.0

a) Signals not included in the sum of all methylene protons
b) The intensity and chemical shift of these unresolved signals were calculated with a curve resolver
c) These intensities are calculated as methylene (instead of methyl)
d) n = 0, 1, 2 ...

Table IX. *Composition of acidic (14.6% DCl) equilibrated formaldehyde solutions from 7.5% paraformaldehyde*

| D_2O % | OH protons | $ClCH_2(OCH_2)_{n+1}Cl$ | | $XO(CH_2O)_{n+2}X$ $(X = COCD_3)$ | | Trioxane | | Methylene glycol | | Polyoxymethylene groups | | | | Methoxyl signal group (3.5–3.9 ppm) |
| | | d) | | d) | | | | b) | | Terminal b) | | Central b) | | c) |
	ppm a)	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	%
77.9	6.80	–	–	–	–	5.25	tr.	4.90	70	4.89	20	4.90	10	–
50.5	7.58	–	–	5.38	0.5	5.24	1	4.95	70	5.04	20	4.95	8	0.5
29.6	8.74	5.61	2	5.38	4.0	5.22	5	5.04	62	5.07	15	4.95	11	1.0
23.5	9.12	5.61 5.58	2	5.38	3.0	5.21	9	5.09	60	5.10	15	4.95	10	1.0
19.7	8.96	5.62 5.57	4	5.37	6.0	5.20	11	5.06	54	5.10	18	5.06	5	2.0
13.2	9.59	5.59 5.56	15	5.35	5.0	5.18	3	5.25	43	5.2	15	4.96	17	2.0

a) These are not included in the sum of all methylene protons

b) The intensity and chemical shift of these unresolved signals were calculated by using a curve resolver

c) These intensities are calculated as methylene (instead of methyl)

d) n = 0, 1, 2 ...

percent methylenes from the curve analyser integration. A comparison of Tables VIII and IX demonstrates that in the same system trioxane and paraformaldehyde yield the same products, as expected. Slight deviations in the % methylenes in Tables VIII and IX for solutions with low percentages of water may be due to experimental error and/or differences in the depolymerization of trioxane and paraformaldehyde based on the presence of end hydroxyl groups in the latter. This latter difficulty would only be important for paraformaldehyde oligomers where n ≤ 10, in which case the % D_2O reported in Table IX would only be larger by approximately 1%.

4.3. *Side Reactions.* – In addition to the equilibria of formaldehyde with trioxane and with its mono- and oligomeric hydrates (2) and (3) discussed previously, we must consider its equilibria with the acids DCl and CD_3COOD. In all systems there are two additional singlets of small intensity which sometimes overlap (Tables VI, VIII, IX). The positions of these signals are 5.64, 5.61, 5.40 and 5.38 ppm. As shown in Tables VIII and IX the two signals around 5.6 ppm are reported together, as are the two signals around 5.4 ppm; their areas increase with decreasing water concentration.

It is reasonable to assume that acetylation of methylene glycol or its oligomers occurs under the strong acid conditions used. Thus, one of these signal groups may originate from the products of such a reaction.

Another possibility based on earlier reports [23, 24] concerning equations (6) and (7) must also be considered, i.e. the reactions of methylene glycol with hydrochloric acid leading to dichloromethyl ether (7). Chloromethanol (6) has never been isolated and its stability is questionable under our reaction conditions [24], although fluoromethanol has been detected by *Olah & Pavlath* [25] as a reaction intermediate from paraformaldehyde and anhydrous hydrogen fluoride (fluoride ion being a better nucleophile than chloride). Dichlorodimethyl ether (7), however, might be stable and we therefore attempted to assign the unknown signals by following the kinetics of decomposition of model compounds (system III) by recording the disappearance or equilibration of the corresponding signals in the NMR. spectrum. The results of the acetylated model compounds are summarized in Table X. In solutions with low water content methylene glycol diacetate apparently is not stable (see Fig. 5), and, in addition no NMR. signal of the appropriate chemical shift (5.76 ppm) was observed in the spectra of our equilibrated formaldehyde solutions. If the dimer diacetate is decomposed in solutions of low or high water content, the decomposition can be followed at 5.42 ppm until equilibrium is reached. It is interesting to note that, at low concentrations of water, a signal at 5.02 ppm is obtained in addition to the central signal of methylene glycol oligomers at 4.98 ppm which may be due to the central methylene protons of the trimer diacetate. This trimer is also present in the formaldehyde solutions as shown by the appearance of a signal at 5.38 ppm which is observed when the trimer diacetate decomposes in a solution of 50% D_2O (Table XI). Additional proof for the existence of oligooxymethylene diacetates is obtained from the chemical shifts observed in the various solutions used in this investigation. The dimer derivative shows a chemical shift difference of 0.34 ppm from the monomeric derivative and of 0.04 ppm and 0.4 ppm from the terminal and central methylenes of the trimer derivative, respectively. These differences are in the same order as those reported in Table IV for the relative chemical shifts of the same compounds in CCl_4.
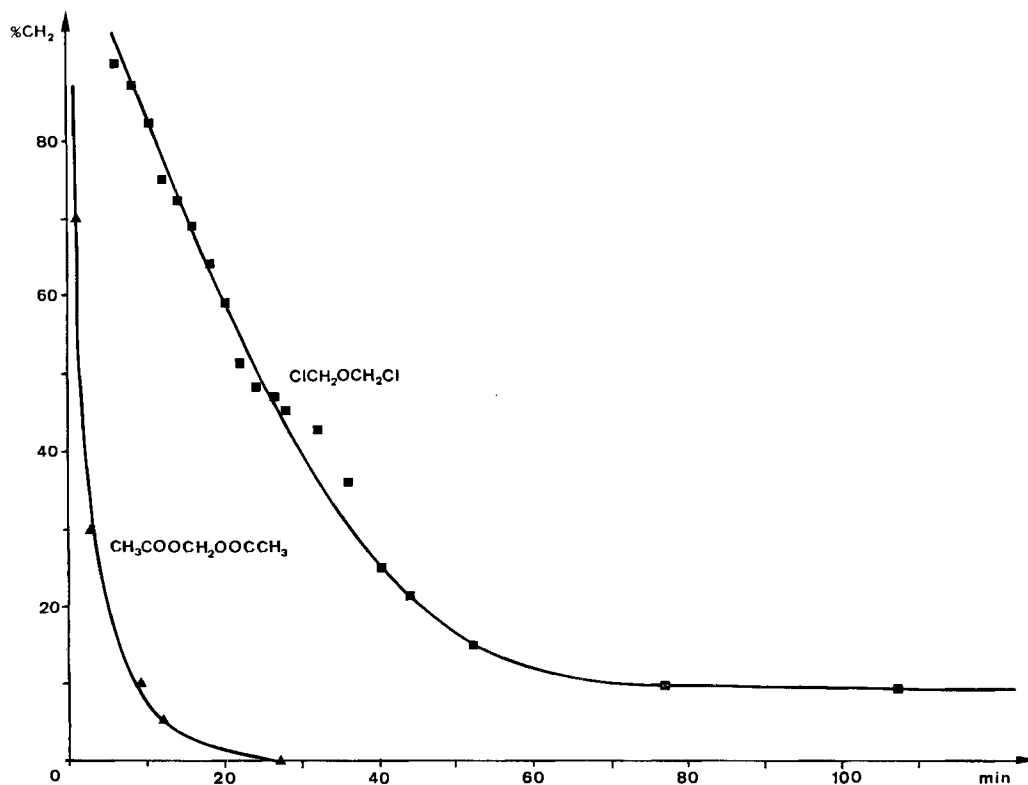
Fig. 5. *Decomposition of dichloro dimethyl ether* (**7**) *and methylene diacetate* (**10**), n = 1 in system III
with 14.6% DCl/23.5% D$_2$O/54.4% CD$_3$COOD

If these assignments are correct, one should not obtain a signal group at 5.4 ppm in
solutions which do not contain acetic acid. Indeed, as shown in Tables VIII and IX,
a signal at 5.4 ppm is not observed when acetic acid is not present. Also, if acetic
acid is replaced by dioxane as the cosolvent with water, no signal is found at 5.4 ppm
because acetylation is no longer possible.

The signal group at 5.6 ppm was assigned by following the decrease of the respec-
tive methylene signals of 7.5% solutions of dichlorodimethyl ether in a system
containing 23.5% D$_2$O, 54.4% CD$_3$COOD and 14.6% DCl. In comparison to the
acetylated compounds which disappear completely within 30 min. in this solvent,
the dichlorodimethyl ether decomposition reaches an equilibrium value of approxi-
mately 10% (relative to the initial concentration) after 70 minutes. This agrees within
the experimental limit of error with the area of the 5.60 ppm peak in the corresponding
system given in Tables VIII and IX.

Further results supporting the formation of dichlorodimethyl ether were obtained
from the NMR. spectrum of an equilibrated aqueous solution of trioxane (35%
DCl/57.5% D$_2$O). Two well separated signals at 5.68 and 5.61 ppm (Table VI) were
observed since no deuterioacetic acid was present in this system. These signals can

also be assigned to the oligooxymethylene dimethyl ether, substituted by two chloride ions according to equations (7) and (8). If, in system I, DCl is replaced by D_2SO_4 (CD_3COOD being present) only one signal at 5.40 ppm is observed which can be assigned to the diacetates discussed previously. No mono or disulfuric ester of methylene glycol is present. This was shown by decomposing the potassium salt of methylene glycol disulfuric acid $[CH_2(OSO_3K)_2]$ in an acidic medium when no signal at 5.40 ppm appeared. As can be seen from Tables VIII, IX and X, the existence of the dichloro derivatives depends on the DCl concentration. At low DCl concentration or low acidity of the medium, no chloro substitution occurs while substantial quantities of chloro derivatives can only be detected in an aqueous solution at high DCl concentration (35%). If acetic acid is replaced by dioxane as cosolvent, the chloro derivatives are also observed at 5.6 ppm.

To determine whether methylene dichloride exists in formaldehyde solutions, we added this compound to a solution containing 54.4% CD_3COOD/23.5% D_2O/14.6% DCl (System III). However, no decomposition of the compound (the methylene protons of which are recorded at 5.44 ppm) occurred during the measurements. Since methylene dichloride did not decompose under these reaction conditions, no substitution of methylene dichloride by this solvent system is possible. However, whether this compound exists as a transient intermediate in the presence of formaldehyde could not be determined.

Finally, the high field signals at 3.5 to 3.9 ppm can be attributed to the methoxyl groups of methanol, methylformate and methyl acetate, while the downfield signal 8.25 ppm is due to formic acid. These assignments are based on the observation of appropriate peak enhancements after addition of known amounts of these compounds to the reaction mixture. Methanol and formic acid can be formed via an acid catalyzed *Cannizzaro* reaction of formaldehyde. This reaction, although usually favoured under alkaline conditions [26], has been reported by *Prins* [27], *Dunlop* [28] and *Staudinger* [29] to occur also in acid solutions. According to our results (methoxyl group % in Table VIII and IX), the amount of products of this reaction increases with the acidity of the media. Methylacetate and methylformate are then formed by the esterification of acetic acid and formic acid with methanol. We have also confirmed the formation of large amounts of methanol and formic acid by the *Cannizzaro reaction*, in the reaction of paraformaldehyde + sulfuric acid [29].

5. Discussion of Results. – The results of Tables VIII and IX are represented in Fig. 6 and 7 as a function of the D_2O content of systems I and II. The results of Fig. 6 and 7 clearly demonstrate that, in systems with 77.9% D_2O, formaldehyde is present essentially in the form of linear oligomers of methylene glycol. If one compares the results (70% methylene glycol, 20% terminal, 10% central; in the case of equilibrated solutions originating from 7.5% trioxane in the presence of 14.6% DCl) in Table VIII with the results given in Table XII (where the composition of equilibrated aqueous trioxane solutions is shown as a function of the DCl concentration) it is evident that the degree of polymerisation increases slightly with increasing acid concentration. That is, the amount of central methylenes increases from 3–5% [8, 9] in the absence of acid to 10% with 14.6% DCl. It is difficult to explain this increase. The decrease in activity of D_2O molecules at higher acid concentration may result

Table X. *Decomposition of trioxane (7.5%) in D_2O/CD_3COOD mixtures in the presence of different amounts of DCl*

Reaction time	Composition of the solution			% Methylenes		$ClCH_2OCH_2Cl$ + $ClCH_2OCH_2OCH_2Cl$	$CH_3CO(CH_2O)_nCH_2OCH_3$ $n = 2$ and 3
	% DCl	% D_2O	% CD_3COOD	Methylene glycol + terminal + central polyoxy-methylene glycols	Trioxane		
Start	10	23.5	59	9	91	trace	0
24 hours				78	13	4.5	4.5
Start	8	23.5	61	2	98	0	0
24 hours				80	17	3	0
8.5 months				81	12	2	5
Start	6	23.5	63	0	100	0	0
24 hours				53	43	0	4
Start	4	23.5	65	0	100	0	0
24 hours				33	65	0	2
8.5 months				88	10	0	2
Start	2	23.5	67	0	100	0	0
24 hours				8	92	0	0
8.5 months				81	11	0	8

Table XI. *Decomposition of diacetates of different methylene glycol oligomers in various solutions containing 14.6% DCl*

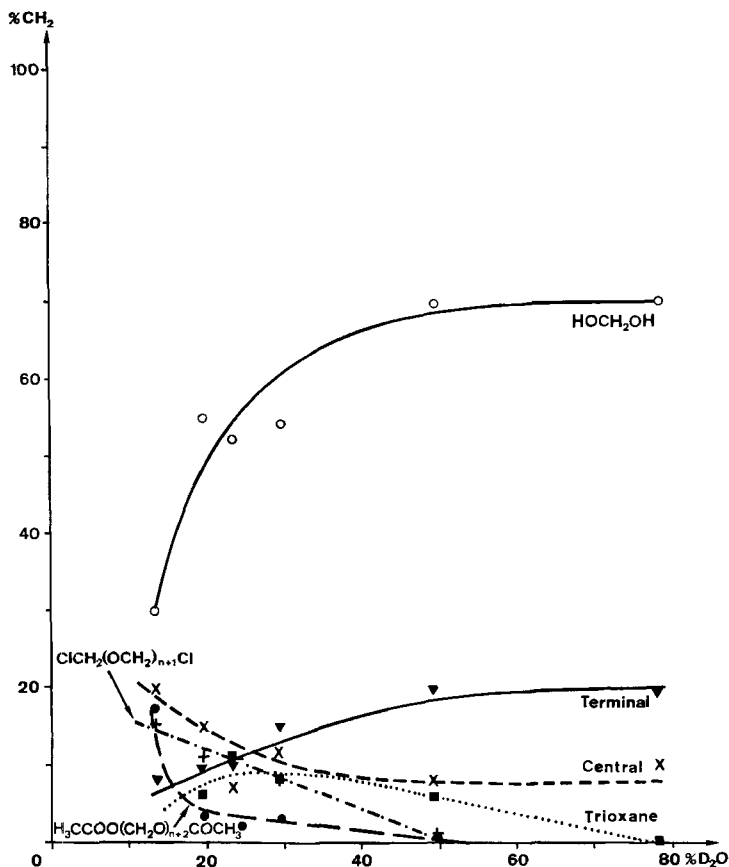| Model compounds $CH_3CO(CH_2O)_nCCH_3$	% D_2O	% CD_3COOD	Time hrs.	% Areas of observed signals								
				5.76 ppm	5.64 ppm	5.58 ppm	5.42 ppm	5.38 ppm	5.25 ppm (trioxane)	4.9–5.4 (oligoxymethylene glycol) ppm	5.02 ppm	4.98 ppm (central)
n = 1	23.5	54.4	Start	70	0					30		
			0.1	30	0					70		
			0.15	17	1					82		
			0.2	10	1					89		
			0.25	5	1					94		
			24	0	7.5	1.5	← 9 →		3	65	0	14
n = 2	50.0	27.9	Start	0	← 0.5 →		13	0	0	86	0	0
			5	0	← 0.5 →		1	0	5	93	0	0
			24	0	← 1 →		2	0	6	91	0	0
n = 2	77.9	0	Start	0	0	0	28	0	1	71	0	0
			5	0	0	0	0	0	1	99	0	0
n = 2	23.5	54.4	Start	0	12	8	7	2	12	45	1	13
			5	0	10	3	5	1	6	58	1	16
			24	0	10	4	5	1	3	55	2	20
n = 3	50.0	27.9	Start	0	0	0	0	1	1	98	0	0
			5	0	0	0	0	0.5	2	97.5	0	0
			24	0	0	0	0	0	4	96	0	0

Fig. 6. *Composition of equilibrated trioxane solutions* (system II) [a]) from Table VIII
a) n = 0,1, 2, 3...

in a shift of the polymerisation equilibria [n $HOCH_2OH \rightleftharpoons HO-(CH_2-O-)_n-H$ + (n–1) H_2O].

Since the NMR. peak contains contributions from all oligomers starting with the trimer (n = 3) and also 'counts' the tetramer twice (two central CH_2 groups in the tetramer), the pentamer three times etc., slight changes in these equilibria become magnified in the percent value for the central methylene group. A nonspecific solvent effect, however, cannot be excluded. Table X also shows the influence of the acid concentration on the rate of depolymerisation for a system with constant (low) water concentration, but increasing acid concentration. As long as the DCl concentration is kept below 6%, the equilibrium of the reaction is still not reached after 24 hours. Therefore, in such cases, the equilibrium concentration was recorded after 8.5 months. However, if one compares the rate of the depolymerisation at constant acid concentration (for example 10% DCl), but at different water concentration (82.5% D_2O in Table XII, 23.5% D_2O in Table X) it is evident that the depolymerisation is much faster at lower water concentrations, because the D_0 function of the acid
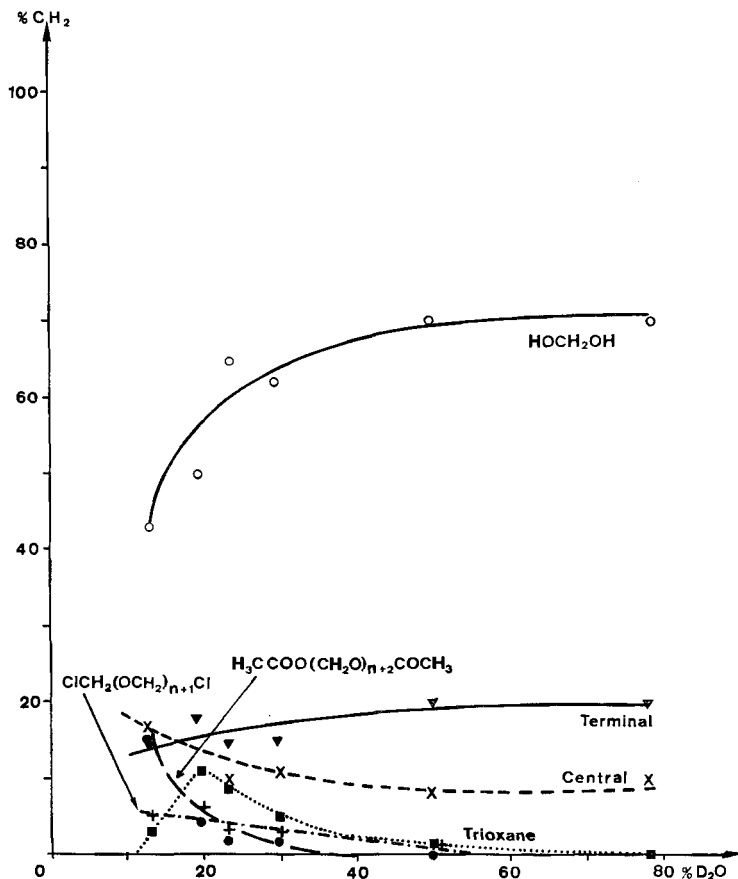
Fig. 7. *Composition of equilibrated paraformaldehyde solution* (system I) [a] from Table IX
a) n = 0, 1, 2, 3...

in this mixture is higher than in aqueous solution. In both types of solution, i.e. those originating from paraformaldehyde or trioxane, the amount of methylene glycol and of the terminal methylenes decreases with decreasing amount of water in the solution. At the same time, the percentage of central methylene protons and of trioxane increases. But diacetates and dichloro derivatives (5.4 ppm and 5.6 ppm) also start to appear, and their concentration increases with decreasing amounts of water. The minor differences in the composition of the solutions originating from paraformaldehyde or trioxane at low water content have been discussed earlier. Free formaldehyde is not detectable because of the unfavourable position of the equilibrium (1) [1–4]; these results are in agreement with *Illiceto & Bezzi's* observations [2] that formaldehyde is not stable in the free state because it is readily converted to methylene glycol in dilute solutions, and to linear polymers in concentrated solutions. The presence of trioxane at all D_2O contents confirms the *Moedritzer & van Wazer* [8] hypothesis that trioxane is in equilibrium with the linear oligomers of formaldehyde.

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Table XII: *Decomposition of trioxane (7.5%) in D_2O/DCl solutions*

| Reaction time | Composition of the solution | | | % Methylenes | | | |
| | % D_2O | % DCl | -H_0[a]) | Trioxane | Methylene glycol | Polyoxymethylene glycols | |
						Terminal	Central
Start	82.5	10	1.0	100	0	0	0
2.25 hours				100	0	0	0
22 hours				76	22	2	0
7.5 months				0.5	69	22	9
Start	86.5	6	0.58	100	0	0	0
2.25 hours				100	0	0	0
22 hours				92	8	0	0
7.5 months				1	68	26	5
b)	77.5	(15% D_2SO_4)	0.66	0	68	26	4.5
Start	88.5	4	0.30	100	0	0	0
2.25 hours				100	0	0	0
22 hours				100	trace	0	0
7.5 months				1.5	73	24	1.5
b)	82.5	(10% D_2SO_4)	0.31	0	71	26	3.0
b)	92.5	0	–	0	68	29	3.0
c)	92.5	0	–	0.2	71	22	5.0

a)   ref [22]
b)   ref [9], no time reported
c)   ref [8], no time reported

6. Conclusions. – From this investigation the following major conclusions can be drawn:

1) NMR. is a very useful technique for studying such complex problems as the equilibria of formaldehyde in different protic solvents.

2) The assignment of the peaks obtained in NMR. spectra of acidic solutions takes into account that protonation does not influence the chemical shift of the methylene protons of cyclic compounds, such as trioxane, and of the central methylene protons of linear formaldehyde species, such as trimers and higher oligomers, which contain acetyl, methoxyl or hydroxyl end groups. However, a downfield chemical shift is observed for methylene glycol protons and terminal methylene protons due to protonation of the neighbouring hydroxyl groups. Thus, the position of the latter methylene protons depends on the protonating power of the medium and is, therefore, different from that obtained for ester or ether model compounds in aprotic media.

3) Formaldehyde in acidic aqueous solutions is essentially present in the form of oligooxymethylene species. If one reduces the water content in this system by replacing it by acetic acid more oligomeric products appear together with trioxane and very small amounts of other products. The proportions of the products vary with the water/acetic acid ratio.

4) In addition to the oligomeric forms which are in equilibrium with methylene glycol in the presence of acetic acid, reactions such as acetylation and chloro substitution of methylene glycol take place.

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