

838. *Acetals and Oligoacetals. Part I. Preparation and Properties of Reactive Oligoformals.**

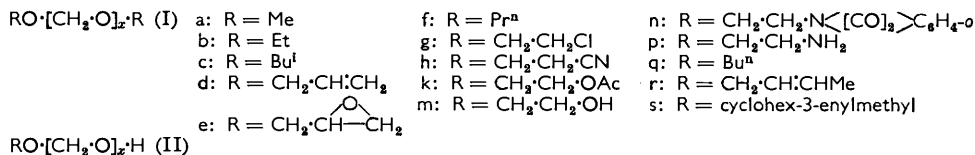
By R. F. WEBB, A. J. DUKE, and L. S. A. SMITH.

Convenient preparative procedures have been developed for compounds of the general formula $\text{RO} \cdot [\text{CH}_2 \cdot \text{O}]_x \cdot \text{R}$ containing reactive end-groups, which are potential intermediates for the synthesis of new classes of polymers. The chemical and thermal stabilities of such compounds have been examined, and their spectral properties are described.

DIETHERS of oxymethylene glycols were first obtained, during Staudinger's classical investigations into the structure of formaldehyde polymers, by acid-catalysed etherification of α -polyoxymethylene by lower aliphatic alcohols with concomitant partial chain degradation. Low yields of the lower members of the methyl-terminated series (Ia; $x = 1-4$) were isolated by distillation, and fractions of higher members were

* The trivial term oligoformal will be used for compounds of formula (I) as a class, and the terms diformal, tri-, tetra-, penta-formal, etc., for members of the subclasses wherein x is 2, 3, 4, 5, etc., respectively. They will also be used for the corresponding bivalent groupings $\cdot \text{O} \cdot [\text{CH}_2 \cdot \text{O}]_x \cdot$, as in "dimethyl diformal" (Ia; $x = 2$). The term monoformal is used where necessary to distinguish the similar compounds or groupings with $x = 1$. This nomenclature is more convenient than the "bis-, tris-, tetrakis-, and pentakis-oxymethylene glycol diethers" sometimes used previously.

obtained by crystallisation.¹ The only subsequent general investigation of diethers of oxymethylene glycols of low molecular weight (for which compounds we propose the use of the generic term "oligoformals"*) describes the acid-catalysed reaction of dialkyl monoformals with small molar quantities of formaldehyde donors to produce the related oligoformals (Ia, $x = 2-4$; Ib, $x = 2$ and 3 ; Ic, $x = 2$ and 3).² Certain diformals (I; $x = 2$) have been prepared by condensations of the Williamson type between alkoxides or phenoxides and bishalogenomethyl ethers;³ this method is clearly inapplicable to the production of higher oligoformals.



The occurrence of oligoformal groupings in more complex molecules has occasionally been postulated,⁴ but in the absence of any selective method for their identification in the presence of monoformal groups, these proposals have remained unsupported by definitive experimental evidence.

We wished to compare polymer systems containing oligoformal units with those derived from the corresponding monoformals, and also with end-blocked formaldehyde polymers of high molecular weight which are of great current technical interest.⁵ We also hoped to correlate the physical, chemical, and particularly the thermal properties of oligoformal-based systems with the corresponding systems based on oligoethylene ([CH₂·CH₂]_x) and oligoethyleneoxy ([CH₂·CH₂·O]_x) units in the absence of effects due to crystallinity, such as are observed with the compounds comprising the corresponding chains of high molecular weight.

Our first requirement was the development of preparative methods giving acceptable yields of the lower functionally substituted oligoformals, avoiding side reactions of the functional group, and preferably proceeding directly from the parent alcohol without requiring isolation of the monoformal. The best procedure found involved the use of paraformaldehyde, and removal of the water formed by codistillation with a water-immiscible solvent, usually benzene. Other sources of formaldehyde gave poorer results. Trioxan reacts more slowly, presumably owing to its lower rates of acid-catalysed hydrolysis⁶ and thermal decomposition,⁷ and accordingly yields more by-products. The use of more than one mole of aqueous formaldehyde per two moles of alcohol results in considerable loss of formaldehyde in the aqueous phases removed, in contrast to the results in similar production of monoformals.⁸

The reaction requires catalysis by a strong acid or Lewis acid, or by certain salts not

* See note on p. 4307.

¹ Staudinger and Johner, *Annalen*, 1929, **474**, 205; Staudinger, Johner, and Signer, *ibid.*, p. 216; Kern, in "Die Hochmolekularen Organischen Verbindungen; Kautschuk und Cellulose," ed. Staudinger, Springer Verlag, Berlin, 1932, p. 224.

² Gresham and Brooks, U.S.P. 2,449,469 (to Du Pont).

³ Descude, *Compt. rend.*, 1904, **138**, 1704; Mamedov and Kulibekov, *Zhur. obshchei Khim.*, 1957, **27**, 1206; Kohama and Fukugawa, *Kagaku to Kogyo (Osaka)*, 1959, **33**, 351; Britton and Slagh, U.S.P. 2,201,074 (to Dow Chemical Co.); Ali-Zade, Kosheleva, and Aliyeva, *Zhur. obshchei Khim.*, 1949, **19**, 1475; Reiche and Gross, *Chem. Ber.*, 1960, **93**, 259.

⁴ Gresham and Bell, U.S.P. 2,475,610 (to Du Pont); Wegler, *Angew. Chem.*, 1948, **60**, 88; *Compt. rend.*, 1959, **249**, 2076; Shell International Research Maatschappij, South African Patent Appl. 60/3019 (by Fischer and Smith); Gruntfest and Gagliardi, *Textile Res. J.*, 1948, No. 11, 18; Gresham, U.S.P. 2,350,350 (to Du Pont).

⁵ Schweitzer, MacDonald, and Punderson, *J. Appl. Polymer Sci.*, 1959, **1**, 158, and four subsequent papers, and references there cited; Barrett, *Plastics*, 1960, April, 136; and many patents.

⁶ Walker and Chadwick, *Ind. Eng. Chem.*, 1947, **39**, 974; Brice and Lindsay, *J. Amer. Chem. Soc.*, 1960, **80**, 3538.

⁷ Burnett and Bell, *Trans. Faraday Soc.*, 1938, **34**, 420.

⁸ Vinokurov, *Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Technol.*, 1960, **3**, No. 1, 190; *Chem. Abs.*, 1960, **54**, 17255b.

generally regarded as Lewis acids, such as lithium, calcium, and magnesium chloride. The activity of the salts is not due to traces of acid, since comparable results were obtained with calcium chloride in the presence of up to five mol. of carbonate. Possible catalysts⁹ were surveyed by using infrared analysis to determine the composition of the product (see below), and with propan-1-ol as alcoholic component, in order to avoid side-reactions and interfering absorption in the analytical region of the spectrum. The results are displayed in Fig. 1, in which the solid line indicates the limit corresponding to conversion into monoformal only. Wide ranges of both salt and acid catalysts give good yields of

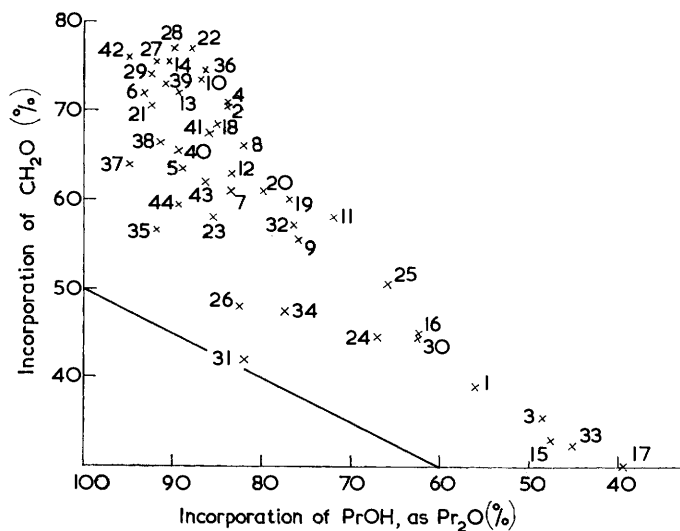


FIG. 1. Incorporation of propan-1-ol and formaldehyde into oligoformals under the influence of various catalysts.

Catalyst: 1, $\text{HO-CH}_2\text{-CO}_2\text{H}$; 2, HCl ; 3, $\text{H}_2\text{C}_2\text{O}_4$; 4, $p\text{-Me-C}_6\text{H}_4\text{-SO}_3\text{H}$; 5, AlBr_3 ; 6, AlCl_3 ; 7, $\text{Al}_2(\text{SO}_4)_3$; 8, NH_4Br ; 9, NH_4Cl ; 10, NH_4I ; 11, NH_4NO_3 ; 12, BeCl_2 ; 13, BCl_3 ; 14, $\text{BF}_3\text{-Et}_2\text{O}$; 15, $\text{CaCl}_2\text{-CaCO}_3$; 16, CaCl_2 ; 17, $\text{Ca}(\text{NO}_3)_2$; 18, CoCl_2 ; 19, CrCl_3 ; 20, CuCl_2 ; 21, FeBr_2 ; 22, FeCl_2 ; 23, FeCl_3 ; 24, $\text{FeCl}_3\text{-pyridine}$; 25, $\text{Fe}(\text{NO}_3)_3$; 26, $\text{Fe}_2(\text{SO}_4)_3$; 27, GaCl_3 ; 28, GeCl_4 ; 29, iodine; 30, LiCl ; 31, $\text{Mg}(\text{ClO}_4)_2$; 32, MgCl_2 ; 33, MnCl_2 ; 34, HgCl_2 ; 35, NiCl_2 ; 36, SiCl_4 ; 37, NaHSO_4 ; 38, SnBr_2 ; 39, SnCl_2 ; 40, SnCl_4 ; 41, ThCl_4 ; 42, TiCl_4 ; 43, VOCl_3 ; 44, Amberlite IR-120(H^+).

product mixtures containing a high proportion of di- and higher oligo-formals. A suitable catalyst for a particular preparation may therefore be chosen, according to the expected lability of the functional substituent, the rate of reaction required, and in some cases the acceptability of using a toxic catalyst. It is noteworthy that ferrous and stannous chloride are superior to ferric and stannic chloride.

Certain specificities have been encountered. Diallyl triformal (Id; $x = 3$) is stable at *ca.* 105° in the presence of calcium chloride alone, but is converted into a mixture of diallyl oligoformals (Id; $x = 1$ to at least 4) by similar treatment in the presence of a trace of allyl alcohol: ferric chloride effects similar interconversion in the absence of added alcohol. Further, ferric chloride catalyses incorporation of additional formaldehyde residues into diallyl monoformal (cf. ref. 2), whereas calcium chloride does not.

The diallyl series of oligoformals was examined first, since these were expected later to afford cross-linked polymers and diepoxides (Ie), which are of interest for epoxy-resins and textile treatment. Attention has been concentrated in preparative work on the use of formaldehyde: alcohol ratios of 1.5 or less, since the use of higher ratios gives only

⁹ Adkins and Nissen, *J. Amer. Chem. Soc.*, 1922, **44**, 2749; Adams and Adkins, *ibid.*, 1925, **47**, 1358.

slightly greater yields of the higher members of a series and results in large losses of both components in the form of base- and heat-labile compounds, presumably of general formula (II) (" hemioligoformals "). The first five diallyl oligoformals (Id; $x = 2-6$) were obtained analytically pure by fractional distillation of the product of a reaction catalysed by calcium chloride; Lewis acid catalysts (such as ferric chloride or stannic chloride) cause contamination of members with $x > 2$ by inseparable formals of polyols, formed by Prins reactions at the double bonds.¹⁰ Other completely separated series of oligoformals (If, $x = 2-5$; Ig, $x = 2-4$; Ih, $x = 2$ and 3; Ik, $x = 2-4$) were produced similarly; their properties are summarised in Table 1. In the last case the use of the milder salt catalysts is again advantageous, an acid catalyst causing acyl interchange which produces glycol diacetate, an undistillable residue of glycol polyoligoformals (III; $y > 1$), and possibly also acetates (IV).



Oligoformals have been prepared from other alcohols (see Table 1 and Experimental section), but series of pure individual members produced directly by such reaction have been isolated only in the five cases above. Removal of protecting groups, under basic conditions, gives oligoformals whose terminal groups would react with formaldehyde donors. Di-(2-acetoxyethyl) oligoformals (Ik; $x = 2$ and 3) thus give di-(2-hydroxyethyl) oligoformals (Im; $x = 2$ and 3), and mixed di-(2-phthalimidoethyl) oligoformals (In) similarly give di-(2-aminoethyl) oligoformals (Ip): these are the required intermediates for polycondensation polymers containing oligoformal groups.

The oligoformals show the expected variation of physical properties. The densities and refractive indices tend towards common limits on ascending the series, at about 1.27 and 1.456, respectively, corresponding to the values for the infinite polyoxymethylene chain in the liquid phase.

Comparison of the 1200—900 cm^{-1} region of the infrared spectra of the pure oligoformals showed that, for $x > 1$ in formula (I), the complex absorption pattern that depends on the end-group of monoformals¹¹ is resolved into two strong bands only; the position of the higher-frequency band (near 1120 cm^{-1}) is relatively independent of the value of x , while that of the lower-frequency band is characteristic of the value of x and essentially independent of the nature of the end-group R (formula I). Thus, diformals absorb at 991—1003, triformals at 968—979, tetraformals at 954—956, pentaformals at 946—948 cm^{-1} , etc. (see Table 2). This series tends towards the value of 932 cm^{-1} found for formaldehyde polymers of high molecular weight,¹² and the assignments for the two bands of oligoformals are made by analogy with those of their infinite-chain analogue, polyoxymethylene.¹²

Notes to Table 1

* $t = 25^\circ$ unless otherwise indicated. † Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 936. ‡ C:C and AcO in equiv./kg.

Literature: (a) b. p. 138—139°, Trillat and Cambier, *Bull. Soc. chim. France*, 1894, **11**, 757; (b) b. p. 66°/8 mm., n_D^{25} 1.472, d_{25}^{20} 0.946, Britton *et al.*, ref. 3; (c) b. p. 137.2—137.6°/760 mm., $n_D^{18.5}$ 1.3936—1.3939, d_{25}^{20} 0.8334—0.8338, Ghysels, *Bull. Soc. chim. belges*, 1924, **33**, 57; b. p. 136.5°/751 mm., n_D 1.39261, d_{25}^{20} 0.8338, Vogel, *J.*, 1948, 623; (d) b. p. 68—69°/12 mm., n_D^{20} 1.4021, Reiche *et al.*, ref. 3; (e) b. p. 98°/11 mm., $n_D^{19.5}$ 1.4082, Reiche *et al.*, ref. 3; (f) b. p. 105°/14 mm., Anker and Cook, *J.*, 1948, 808; b. p. 93—94°/11 mm., Freudenberg and Acker, *Ber.*, 1941, **74**, 1404; b. p. 218.1°/760 mm., d_{25}^{20} 1.2339, McClure, *Chem. Eng. News*, 1944, **22**, 421; (g) b. p. 124.5—128°/4 mm., b. p. 108°/1 mm., n_D^{20} 1.4475, d_{25}^{20} 1.1502, Gresham, ref. 4; (h) b. p. 181.8°/760 mm., n_D^{17} 1.4072, d_{25}^{20} 0.8340, Ghysels, *loc. cit.*; b. p. 180.5°/760 mm., n_D 1.40573, d_{25}^{20} 0.8354, Vogel, *loc. cit.*; (j) b. p. 102—103°/13 mm., n_D^{19} 1.4123, Reiche *et al.*, ref. 3; b. p. 72—79°/6 mm., n_D^{20} 1.4080, d_{25}^{20} 0.8619, Ali-Zade *et al.*, ref. 3.

¹⁰ Arundale and Mikeska, *Chem. Rev.*, 1952, **51**, 505.

¹¹ Nukada, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80**, 1112, A89; Nukada, *Reports Govt. Chem. Ind. Res. Inst., Tokyo*, 1960, **55**, 11, 92; cf. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 116.

¹² Novak and Whalley, *Trans. Faraday Soc.*, 1959, **55**, 1484; Tadokoro, Kobayashi, Kawaguchi, Sobajima, Murahashi, and Matsui, *J. Chem. Phys.*, 1961, **35**, 369.

These bands are sharper in solution spectra, particularly in mineral oil, in which they obey Beer's law and provide a convenient method for the analysis of mixed oligoformals up to pentaformals: monoformals do not absorb in the 930—1000 cm^{-1} region.

TABLE 2.

Strong infrared peaks of oligoformals in the 1200—900 cm^{-1} region.

No.	α	Phase *					
Id	1	MO (& C)	1178, 1146,	1122, 1109,		1056 ,	990, 963, 921
Id	2	MO (& C)		1125 , 1111 ,		1003 ,	988, 966, 924
Id	3	MO (& C)		1125 ,		979 ,	963 , 936
Id	4	MO (& C)		1115 , (1041),		954	
Id	5	MO (& C)		1113 ,		946	
Id	6	MO (& C)		1113 ,		938	
If	1	MO (& C)	(1148),	1120 , (1098, 1064),		1042 ,	(955)
If	2	MO (& C)		1120 , (1030),		996 ,	(935)
If	3	MO (& C)		1115 , (1025),		971 ,	(935)
If	4	MO (& C)		1118 , (1035),		956	
If	5	MO (& C)		1115 ,		948	
Ig	1	MO (& S)	1155,	1124 , 1084 ,		1029 ,	1004, (959)
Ig	2	MO (& S)		1126 , (1072),		995	
Ig	3	MO		1118 ,		969	
Ig	4	MO		1116 ,		954	
Ih	1	C (& S)	1165,	1125 , 1085 ,		1041 ,	1012 , (992, 923)
Ih	2	C (& S)	1136,	1120 , (1070, 1020),		991	
Ih	3	C (& S)		1118 ,		974	
Ik	1	S		1120 ,		1030	
Ik	2	S (& C)		1130 , 1058,		992 ,	(950)
Ik	3	S		1125, 1060,		970	
Im	1	C	1166,	1132 , 1100 , 1074 ,		1032 ,	(977)
Im	2	C		1123 ,		1069 ,	993
Im	3	C		1118 ,		1070 ,	970
Ip	1	C (& S)		1118 ,		1032 ,	(974)
Ip	2	C (& S)		1118 ,		995	
Ip	3	C (& S)		1116 ,		968	
Iq	1	S	1178, (1144),	1114 , 1068 ,		1047 ,	1017 , (989, 935)
Iq	2	S		1112 ,		997 ,	(936)
Ir	1	S	1168,	1103 , (1082),		1034 ,	977
Ir	2	S		1105 , (1025?),		998 ,	975
Is	1	S	1162,	1118 , 1048 ,		1036 ,	(961, 938, 908)
Is	2	S		1121 , (1046?, 1035?),		996	

* MO = 1.5—3% in mineral oil; C = 2—5% in chloroform; S = in substance. Peaks printed in bold type are the strongest in this region; those in parentheses are weak. Shoulders and very weak peaks have been omitted.

TABLE 3.

Frequencies (cm^{-1}) of the strongest peaks in the infrared spectra of oligoformals * in the 2200—1800 cm^{-1} region.

No.	Value of α						No.	Value of α					
	1	2	3	4	5	6		1	2	3	4	5	6
If	2070	2050	2055	2050	2050	—	Ig	2040	2060	2055	2040	—	—
	2000	1910	1885	1875	1865	—		1940	1945	1940	1940	—	—
Id	1990	2045,	2030	2030	2035	2035	Im	1920	1950	1950	—	—	—
		2000											
	1860	1850	1865	1865	1865	1860							

* At 10—25% concentration, in carbon tetrachloride for Id, If, and Ig, and in chloroform for Im. Other weaker absorptions also occur in the region.

Similar variations in frequency of one band with the value of α are found in the 1800—2200 cm^{-1} region (see Table 3) of the spectra of the n-propyl oligoformals, but the effect is not universal in this region. No similar effect is observable in the 4000 cm^{-1} region; any third overtones present are probably obscured by C-H overtone and combination

bands.¹³ The bands in the 1800—2200 cm^{-1} region may be combination bands (cf. ref. 14), which would not necessarily show comparable systematic variation.

The nuclear magnetic resonance spectra of diallyl and di-n-propyl oligoformals (Table 4 and Fig. 2) prove unequivocally the correctness of structures (Id and f) for these substances, and, by extrapolation, the general correctness of formula (I). The absorption due to the formal-methylene protons in the mono- and di-formals (Id and f; $x = 1$ and 2) occurs as a single peak, the two groups in the diformal being in equivalent environments. In tri- and tetra-formals (Id and f; $x = 3$ and 4), however, the central formal protons have different overall environments ($\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{O}\cdot$ as opposed to $\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\cdot$) and

TABLE 4.
Nuclear magnetic resonance spectra of oligoformals.

τ for protons *				τ for protons *					
No.	x	$\text{O}\cdot\text{CH}_2\cdot\text{O}$	$\text{O}\cdot\text{CH}_2\cdot\text{C}$	Other groupings (a)	No.	x	$\text{O}\cdot\text{CH}_2\cdot\text{O}$	$\text{O}\cdot\text{CH}_2\cdot\text{C}$	Other groupings (a)
Id	1	5.37	5.95, 6.07 (b)	4.37, 4.63, 4.79	If	1	5.42	6.57 (c)	9.08
Id	2	5.27	5.92, 6.05 (b)	4.38, 4.65, 4.79	If	2	5.30	6.55 (c)	9.10
Id	3	5.21, 5.30	5.91, 6.01 (b)	4.40, 4.65, 4.79	If	3	5.21, 5.31	6.52 (c)	9.10
Id	4	5.16, 5.26	5.87, 6.00 (b)	4.38, 4.63, 4.78	If	4	5.18, 5.30	6.56 (c)	9.10
Id	5	5.17, 5.26	5.90, 6.01 (b)	4.37, 4.63, 4.77	If	5	5.17, 5.30	6.55 (c)	9.09
Id	6	5.19, 5.27	5.90, 6.03 (b)	4.36, 4.61, 4.75					

* (a) Major peak(s) of a complex multiplet; (b) peaks of the duplet show further splitting; (c) centre peak of a triplet.

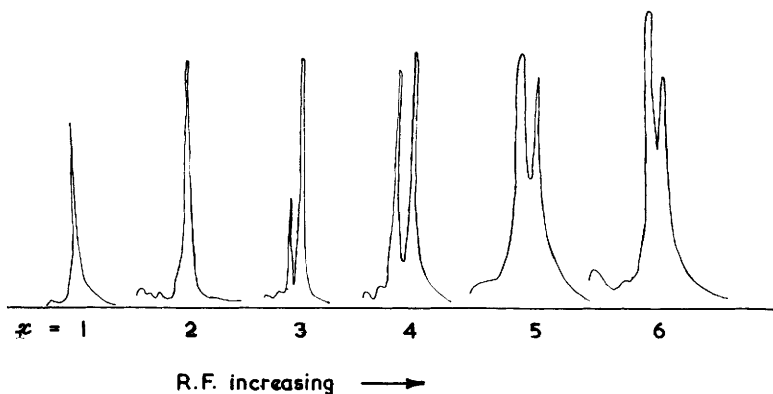


FIG. 2. Nuclear magnetic resonance absorptions at $\tau = 5.2$ — 5.4 for diallyl oligoformals (Id); x as indicated.

accordingly absorb at a different frequency from the "outer" formal protons. In the spectra of the pentaformals (Id and f; $x = 5$) and the hexaformal (Id; $x = 6$), the band due to the "inner" atoms broadens (Fig. 2), probably because the further distinction between the environments of the central and fourth such groups causes a further slight shift. This appears to be the longest range over which an effect on the chemical shift of a proton absorption has been observed.¹⁵ The absorptions due to the allyl and n-propyl end-groups are as expected.^{15,16}

The stability of the monomeric oligoformals to acid-catalysed hydrolysis and to thermal degradation has been examined in order to establish their suitability for the production

¹³ Proc. Internat. Symposium on Microchemistry (Birmingham), Pergamon Press, London, 1959, p. 384.

¹⁴ Cf. Tarte, Laurent, and Rogister-Paris, *Bull. Soc. chim. France*, 1960, 365.

¹⁵ Pople, Schneider, and Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, pp. 279—280; cf. Bothner-By and Naar-Colin, *J. Amer. Chem. Soc.*, 1953, **80**, 1728.

¹⁶ Nukada and Maeda, *Bull. Chem. Soc. Japan*, 1959, **32**, 655.

of high polymers. Complete hydrolysis of a mole of a compound (I) gives x moles of formaldehyde, and the molecule can be protonated at $(x + 1)$ positions. Therefore, if oligoformals hydrolyse by an S_N1 mechanism, as do monoformals,¹⁷ the dependency of the rate of formaldehyde liberation upon x would be greater than x^2 . A few units in which x is high would cause chain-breaking to be very fast and might render high polymers based on unseparated mixtures of oligoformals too acid-labile to be useful. However, the dependency of the rate of hydrolysis on x could be reduced by formal interchange, part only of the formaldehyde content of an oligoformal group being liberated without chain fission, leaving a less easily hydrolysed lower oligoformal grouping. We examined the hydrolysis of the di-*n*-propyl oligoformals (If; $x = 1$ to 4–5) at lower water concentration and acid strength than were used in previous work on acetal hydrolysis,¹³ the new conditions being more analogous to those affecting the oligoformal group when part of a polymer molecule. The hydrolysis curves in Figs. 3 and 4 show the expected effect. The rate

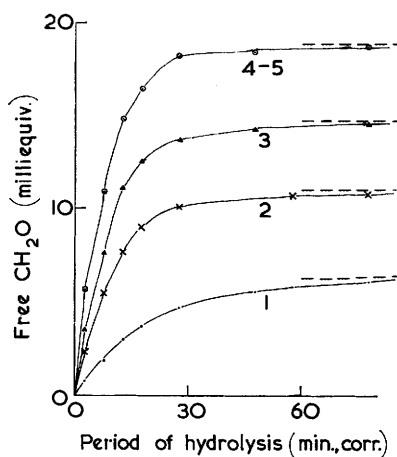


FIG. 3.

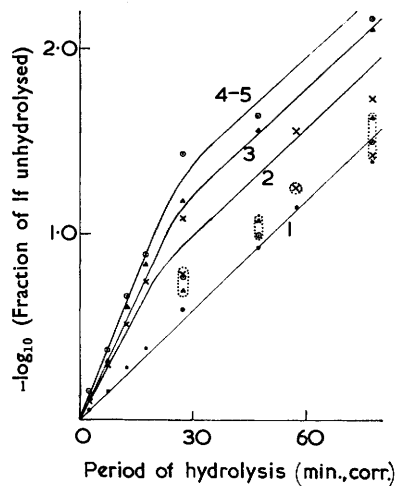


FIG. 4.

FIGS. 3 and 4. Acid-catalysed hydrolysis of di-*n*-propyl oligoformals (If); x as indicated.

constant for the initial first-order hydrolysis increases with, but less rapidly, than x (the rate of formaldehyde liberation increasing less rapidly than x^2), and the slopes of the curves tend during the later stages towards that for hydrolysis of the monoformal. The increased concentration of free propan-1-ol and the longer time during which exchange has been occurring both contribute to the rather sudden change of slope of the first-order plots after about half an hour.

The oligoformals also react more rapidly with thiols, without requiring catalysis, than do the corresponding monoformals (see Experimental section). This reaction is almost completely inhibited by traces of alkali, and therefore presumably involves protonation of the oligoformal by the thiol. It prevents the isolation of oligoformals containing thiol groups. A similar reaction has been observed with simple, higher acetals.¹⁸

Various oligoformals not containing free hydroxyl groups have been kept above 200° for several days *in vacuo* without major degradative loss, except that, in the di-(2-chloroethyl) series, traces of hydrogen chloride are eliminated and catalyse decomposition.

¹⁷ O'Gorman and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5489; Kreevoy and Taft, *ibid.*, 1955, **77**, 3146, 5590.

¹⁸ Shostakovskii, Bogdanova, and Plotnikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1960, 1524; Bogdanova, Shostakovskii, and Plotnikova, *Doklady Akad. Nauk S.S.S.R.*, 1960, **134**, 587.

However, di-(2-hydroxyethyl) oligoformals are significantly labile at about 150–160°, even *in vacuo*. When dialkyl oligoformals are heated with a large surface area exposed to air, degradation is fairly rapid at temperatures as low as 160°. The mechanisms involved have been elucidated for formaldehyde polymers of high molecular weight.¹⁹ The considerably lower viscosities of our materials of low molecular weight result in faster diffusion of both oxygen and primary degradation products¹⁹ within the decomposing sample.

Formed samples of cross-linked high polymers incorporating oligoformal groupings are no more labile to heat or acid than are those incorporating the corresponding monoformal units.

EXPERIMENTAL

Preparation of Oligoformals: General Method.—The reaction mixtures were refluxed with stirring into an appropriate water-entraining head until the evolution of water became slow, or until formaldehyde was evolved at a comparable rate and began to be deposited in the condenser or the entrainer head as its low polymers. The catalyst and by-products were then destroyed in one step by cautious addition of aqueous sodium hydroxide ($\leq 50\%$) to the refluxing mixture, with refluxing for a further 15–60 min.; alternatively, when the oligoformals were base-labile, the catalyst was extracted into water or precipitated, and hemioformals and free formaldehyde were removed by pyrolytic distillation at $\leq 120^\circ$ (liquid) or by washing with cold aqueous alkali or sodium hydrogen sulphite. Complete removal of the catalyst is essential to avoid degradation to monoformal on distillation.

Secondary require higher catalyst concentrations than do primary alcohols.

Details of the oligoformals prepared are given in Table 1.

Effectiveness of Water Removal in Oligoformal Production.—Two mixtures of allyl alcohol (116 g.), paraformaldehyde (90 g.), toluene-*p*-sulphonic acid (1 g.), and benzene (40 ml.) were heated, one (*a*) under simple reflux, and the other (*b*) at the b. p. under a Dean–Stark water entrainer previously filled with benzene, until the latter mixture had evolved 21 ml. of aqueous phase. 40% Sodium hydroxide solution (100 ml.) was then run slowly into each mixture, refluxing was continued overnight, and the organic phases were separated and washed with water. Benzene was separated by fractional distillation, leaving as residues diallyl oligoformals (*a*) 89.9, (*b*) 122.7 g., with formaldehyde content (*a*) 36.0, (*b*) 39.0%.

Diallyl Oligoformals (*Id*; $x = 1-6$).—Allyl alcohol (5.81 kg., 100.5 moles), paraformaldehyde (4.53 g., 151 moles as CH_2O), anhydrous calcium chloride (250 g.), and benzene (1.2 l.) were refluxed with stirring into a water entrainer, evolving 960 ml. of water during 24 hr. The supernatant liquid was then decanted, washed with water (500 ml.), 10% aqueous sodium hydroxide (6×500 ml.), and again water (500 ml.), and fractionally distilled, initially through conventional columns. After nearly 2 kg. of forerun, there were obtained diallyl formal (1036 g.) and diallyl diformal (911 g.); from the latter fraction a small quantity of tetraoxymethylene, m. p. 110–112°, was isolated at -40° . Distillation was continued on a thermal rectifier constructed substantially according to ref. 20, but having only eight elements and embodying a conventional solenoid-actuated partial-return take-off head, controlled automatically by the head vapour-temperature. Boil-up rate was also automatically controlled. Pure fractions were then obtained of diallyl triformal (463 g.), tetraformal (239 g.), pentaformal (144 g.), and hexaformal (84 g.), with small intermediate fractions. Gas evolution set in at this stage, the liquid temperature having been above 200° for > 1 hr.

Fractions above the diformal from similar preparations in which ferric or stannic chloride was used as catalyst had high n_D and low m. p. and gave high carbon and low formaldehyde analyses. These fractions had absorption at 1020–1040 cm^{-1} , and acid solvolysis has given rise to an unidentified di- or poly-alcohol. The use of iodine or toluene-*p*-sulphonic acid as catalyst does not give rise to these contaminants.

Di-(2-chloroethyl) Oligoformals (*Ig*; $x = 1-4$).—These formals were prepared similarly, but with 20% aqueous sodium hydroxide and saturated brine for the washings, water or weaker solutions giving intractable emulsions. Iodine was also a satisfactory catalyst under similar conditions, giving somewhat higher conversions.

¹⁹ Kern and Cherdron, *Makromol. Chem.*, 1960, **40**, 101.

²⁰ Schaffner, Bowman, and Coull, *J. Amer. Inst. Chem. Eng.*, 1943, **39**, 77.

Di-(2-cyanoethyl) Oligoformals (Ih; $x = 1-3$).—2-Cyanoethanol (114.0 g., 2 moles), paraformaldehyde (72.0 g., 2.4 moles as CH_2O), and anhydrous calcium chloride (14.4 g.) were stirred at 100° for 5 hr., then cooled. A little sodium chloride and benzene were added, and solids were centrifuged off and washed twice with benzene at the centrifuge. The combined supernatant liquids were dried (MgSO_4) and distilled, giving *di-(2-cyanoethyl) mono-, di-, and tri-formal*.

Ferric chloride led to higher yields, but pure individual oligoformals were not then isolable.

Di-(2-acetoxyethyl) Oligoformals (Ik; $x = 1-4$).—Commercial 2-acetoxyethanol (5 l.) (containing 16% of glycol and 25% of glycol diacetate) in benzene (5.5 l.) was shaken with a solution prepared by saturation of 10% aqueous sodium hydroxide (200 ml.) with boric acid. The aqueous layer was separated, water (25 ml.) was added to the organic phase, the deposited aqueous layer was again separated, and the organic phase was dried (MgSO_4) and concentrated under reduced pressure to 7.3 l. Periodate titration and the saponification value of an evaporated sample showed the product to contain 2.75 kg. of 2-acetoxyethanol, 1.70 kg. of glycol diacetate, and 290 g. of ethylene glycol.

To the treated 2-acetoxyethanol (2.75 kg.) in benzene were added paraformaldehyde (1.05 kg.) and ferric chloride (22 g., in a portion of the ester-alcohol mixture). Reaction as usual produced 300 ml. of water during 5 hr. Calcium carbonate (14 g.) was added to the hot mixture, which was then allowed to cool overnight, filtered, washed with aqueous sodium sulphate (3×200 ml.) and water (2×100 ml.), and distilled until the head-temperature reached $97^\circ/13$ mm.; the residue was distilled rapidly (boiling range $142-300^\circ/1$ mm.). Dry air was drawn through the latter distillate overnight to remove free formaldehyde, and fractional redistillation then gave a forerun of di-(2-acetoxyethyl) formal [containing about 10% of di-(2-hydroxyethyl) formal] (304 g.), b. p. $108-113^\circ/0.35$ mm., and subsequently fractions of *di-(2-acetoxyethyl) mono-, di-, tri-, and tetra-formal*.

A similar experiment with glycol diacetate instead of the monoacetate gave <10% of acetoxyethyl oligoformals.

Di-(2-hydroxyethyl) Oligoformals (Im; $x = 1-3$).—A di-(2-acetoxyethyl) oligoformal and a slight (0.5—5%) excess of 15—20% aqueous sodium hydroxide was refluxed for 1—2 hr., then evaporated, and the residue was extracted with tetrahydrofuran (three times for the monoformal, twice for the higher oligoformals). Distillation of the filtered extract gave the *di-(2-hydroxyethyl) mono-, di-, and tri-formal*, of which the di- and tri-formal were recrystallised from ethyl acetate, at 5° in the former case. Di(2-hydroxyethyl) tetraformal was not obtained pure, but had b. p. $165^\circ/0.5$ mm., m. p. $>50^\circ$.

Di-(2-phthalimidoethyl) (In) and di-(2-aminoethyl) Oligoformals (Ip; $x = 1-3$).—Ethanolamine (1220 g., 20 moles) was added during 45 min. to phthalic anhydride (2960 g., 20 moles), and the mixture was heated to 220° with stirring during 2 hr. Water (360 ml.) distilled. After cooling, benzene (10 l.), paraformaldehyde (960 g., 30 moles as CH_2O), and toluene-*p*-sulphonic acid (20 g.) were added, and the mixture was treated as usual, evolving 220 ml. of aqueous phase (theor., 180 ml.) during 2 hr. Sodium hydroxide (3.2 kg., 80 moles) in water (7 l.) was then added during 1.5 hr., the benzene simultaneously distilling. The remaining mixture was refluxed for 48 hr., cooled, and filtered through glass cloth, and the disodium phthalate was washed with 30% aqueous sodium hydroxide (1 l.) and dioxan (1 l.). The filtrate was extracted continuously for several days with dioxan in an extractor equipped with a centrifugal stirrer, and the extract was evaporated and distilled, giving mixed di-(2-aminoethyl) oligoformals, b. p. $80-200^\circ/0.5$ mm. (735 g.). A portion (191 g.) of this product was fractionally distilled and the fractions were redistilled, giving *di-(2-aminoethyl) mono-, di-, and tri-formal*.

For the production of the monoformals (In and Ip; $x = 1$) alone, *N*-(2-hydroxyethyl)-phthalimide (191 g., 1.0 mole), paraformaldehyde (15.5 g.), benzene (500 ml.), and toluene-*p*-sulphonic acid (2.5 g.) were treated as usual, 9.0 ml. of water being evolved during 2 hr. *Di-(2-phthalimidoethyl) formal*, deposited on cooling and recrystallised twice from benzene, had m. p. $130-132^\circ$ (117.5 g., 63%) (Found: C, 64.1; H, 4.6; N, 7.3. $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_6$ requires C, 63.9; H, 4.6; N, 7.1%). Hydrolysis, as for the mixed oligoformals, of the entire hot benzene solution of crude di-(2-phthalimidoethyl) formal from a similar preparation gave di-(2-aminoethyl) formal, b. p. $77-98^\circ/2$ mm. (38.8 g., 57.8%).

Dibut-2-enyl Mono- and Di-formal from Aqueous Formaldehyde.—But-2-enol (22.7 g.), 37% aqueous formaldehyde (39 ml.), and concentrated hydrochloric acid (1 ml.) were refluxed

under a short column into a water entrainer. After evolution of 35 ml. of water, the residue was washed with water (25 ml.) and twice with 20% aqueous sodium hydrogen sulphite, filtered, washed twice more with sodium hydrogen sulphite solution, and dried (MgSO_4). The product (18.2 g.) was fractionally distilled and redistilled, giving impure di-(but-2-enyl) mono- and di-formal.

Di-n-butyl mono- and di-formal were obtained similarly.

Di-n-propyl Oligoformals (If; $x = 1-3$).—Propan-1-ol was treated with paraformaldehyde (2 mol.) and anhydrous ferric chloride according to the general conditions. The di- and tri-formal fractions from a preliminary fractionation were redistilled to give analytical samples with the properties given in Table 1. Redistillation of the monoformal fraction, however, gave fractions of b. p. 137.5—138°/758 mm., n_D^{25} 1.3914, which were not pure monoformal (Found: C, 62.5, 62.8; H, 11.8, 12.1. Calc. for $\text{C}_7\text{H}_{16}\text{O}_2$: C, 63.5; H, 12.2%). These fractions had an infrared band at 996 cm^{-1} , indicating a content of ca. 20% of diformal, in agreement with the analytical data, and they appear to be an azeotropic mixture of mono- and di-formal.

Pure monoformal was obtained from a similar reaction, in which <0.5 mol. of paraformaldehyde was used; formation of appreciable amounts of diformal was thus avoided.

Di-n-propyl Tetra- and Penta-formal (If; $x = 4-5$).—Diallyl tetra- or penta-formal (Id; $x = 4$ or 5) (5 g.) in methanol (25 ml.) was reduced with hydrogen at room temperature and atmospheric pressure in the presence of palladium black. The solution was filtered and evaporated under reduced pressure. The *di-n-propyl tetra- or penta-formal* was dried *in vacuo* at 60°, and was analytically pure without distillation.

Effectiveness of Various Catalysts.—Mixtures of propan-1-ol (60 g., 1 mole), paraformaldehyde (30 g., 1 mole), benzene (30 ml.), and the catalyst (1 g. of solid catalysts, finely powdered; 1 ml. of liquids; or 0.1 g. of strong acids) were refluxed into a water entrainer of 10-ml. capacity until appreciable deposition of polyformaldehyde occurred in the head or the lower regions of the condenser. 40% Sodium hydroxide solution was then run in slowly to the refluxing mixture, and refluxing was continued overnight. The organic layer was separated and washed with water (3×100 ml.) (which removed all spectroscopically detectable free propanol) and distilled fractionally until the head-temperature reached 100—115°. Infrared spectra were determined of both the distilled fraction (consisting of benzene and monoformal) and the undistilled (benzene-free) residue, in ca. 1.5% solutions in mineral oil at ~0.1 mm. thickness. The absorbancies above base line at the analytical frequencies (see Table 5) were divided by

TABLE 5.

Analytical frequency, ν (cm^{-1})	1042	996	971	955	675
Compound absorbing at this frequency ...	If, $x = 1$	If, $x = 2$	If, $x = 3$	If, $x > 3$	Benzene
Correction for solvent absorption	0.29	0.27	0.44	0.37	0.03

that at 725 cm^{-1} (due solely to the mineral oil) to allow for variations of thickness, and the ratios were corrected for solvent absorption and to a standard concentration of 0.1 g. per ml. The proportions of the components in the two fractions were computed by inserting these values (A_ν) in the equation $c_X = \sum \frac{A_\nu}{k_{\nu,X}} \cdot A$, in which c_X is the proportion by weight of compound X in the mixture, and the matrix ($k_{\nu,X}$) has the values ($\times 10^{-3}$):

x	$\nu =$	1042	675
(If; $x = 1$)		10.7	-0.33
Benzene		0.0	4.7

for the distilled fraction, and

x	$\nu =$	1042	996	971	955
(If; $x = 1$)		10.8	-0.9	-0.5	-1.1
(If; $x = 2$)		0.1	7.5	-1.5	-1.7
(If; $x = 3$)		0.3	-0.3	7.7	-4.4
(If; $x > 3$)		-0.9	-0.8	-2.9	12.3

for the undistilled residue. The derived c_X values were corrected to a total of 100%, and used in calculating propanol and formaldehyde conversions, which are given in Fig. 1.

The determination of all oligoformals above the triformal from the absorbance at 955 cm.^{-1} results in errors less than the experimental error, since the test conditions adopted produce only a very small proportion of these higher oligoformals. Traces of benzene in the undistilled fraction could be allowed for as a fraction $0.0047 A_{675}$.

During the survey, an empirical correlation was found between the proportions of mono-, di-, and higher formals produced, and the ratio

$$\frac{(\text{Absorbance}_{1042\text{ corr}} - \text{Absorbance}_{996})/(\text{Absorbance}_{1042\text{ corr}})}$$

for the undistilled fraction. The absorbance at 1042 cm.^{-1} was corrected for monoformal in the distilled fraction by multiplication by a factor

$$\left\{ 1 + \frac{\text{Wt. of distilled frn.}}{\text{Wt. of undistilled frn.}} [3.33(A'_{1042} - 0.29A'_{725}) - 0.06] \right\}$$

where A' are absorbancies for the distilled fraction. The correlation is shown in Fig. 5, and subsequent determinations were made by its application.

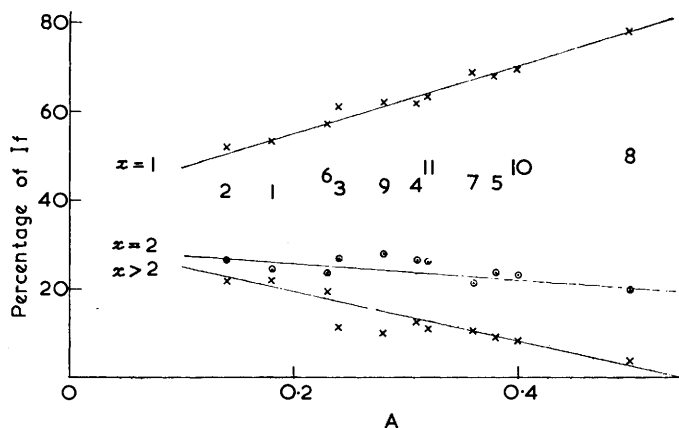


FIG. 5. 1, HCl; 2, $p\text{-Me-C}_6\text{H}_4\text{-SO}_3\text{H}$; 3, BeCl_2 ; 4, CaCl_2 ; 5, FeCl_3 ; 6, iodine; 7, LiCl; 8, HgCl_2 ; 9, MnCl_2 ; 10, NaHSO_4 ; 11, SnCl_4 .

$$A = [\text{Absorption (1042, corr.)} - \text{Absorption (996)}] / \text{Absorption (1042, corr.)}$$

The following compounds were substantially inactive, less than 0.5 ml. of water being evolving during ≤ 4 hr.: $\text{H}\cdot\text{CO}_2\text{H}$, AcOH , LiF , LiBr , LiI , LiClO_4 , NaCl , NaI , MgF_2 , $\text{Mg}(\text{CNS})_2$, MgSO_4 , MgHPO_4 , CaBr_2 , CaI_2 , SrCl_2 , BaCl_2 , BaBr_2 , ZnI_2 , CdI_2 , Hg_2Cl_2 , $\text{Al}_2(\text{CrO}_4)_3$, PbCl_2 , PbBr_2 , BiOCl , $\text{Fe}(\text{OAc})_2\text{OH}$, Fe^{II} oxalate, FeSO_4 , and FePO_4 . CdCl_2 , ZnCl_2 , and Cu_2Cl_2 were only weakly active.

Salt-catalysed Interconversions of Oligoformals.—(i) *Conversion into lower oligoformals.* Diallyl triformal (Id; $x = 3$) (71.8 g.) containing anhydrous calcium chloride (10 g.) was refluxed for 3 hr. at $130\text{--}135^\circ$ (bath)/15 mm. Fractional distillation then showed the bulk of the liquid to be unchanged triformal, distilling at $103^\circ/13$ mm., with less than 1 ml. of forerun.

A similar reaction was conducted, with the addition of allyl alcohol (10 g.). The mixture was refluxed for 24 hr. at 120° (bath)/1 atm. Fractional distillation gave first imperfectly separated allyl alcohol and diallyl monoformal, then pure diallyl monoformal (5.4 g.; b. p. $39\text{--}40^\circ/16$ mm., n_D^{22} 1.4223), diallyl diformal (20.0 g.; b. p. $75\text{--}81^\circ/16$ mm., n_D^{23} 1.4272—1.4286), diallyl triformal (7.2 g., b. p. $91\text{--}111^\circ/16$ mm., n_D^{24} 1.4325), and higher diallyl oligoformals (7.3 g.; b. p. $>111^\circ/16$ mm., n_D^{25} 1.4356).

(ii) *Conversion into higher oligoformals.* Diallyl monoformal (Id; $x = 1$) (64 g.), paraformaldehyde (30 g.), allyl alcohol (1 ml.), anhydrous ferric chloride (5 g.), and benzene (75 ml.)

were refluxed for 4 hr. The product was centrifuged, and the supernatant liquid was washed twice with water and distilled. After benzene and diallyl monoformal (b. p. 40°/14 mm.), there were obtained diallyl diformal (7.4 g.; b. p. 74—81°/13 mm., n_D^{22} 1.4304—1.4314), diallyl triformal (4.3 g.; b. p. 100—106°/13 mm., n_D^{23} 1.4363), and higher diallyl oligoformals (2.5 g.; b. p. >86°/1.0 mm., n_D^{24} 1.4438). These fractions were contaminated by small amounts of Prins adducts.

A similar reaction without the addition of allyl alcohol gave similar fractions. However, no interconversion was found when anhydrous calcium chloride (5 g.) was substituted for ferric chloride, even if a greater amount (10 ml.) or no allyl alcohol was added as above, or at 140°: in each case, only diallyl monoformal was recovered on distillation (b. p. <140°, n_D 1.4198—1.4215). Iodine also did not catalyse such interconversion, at least in the absence of added alcohol.

Nuclear Magnetic Resonance Spectra.—Spectra were determined in substance at 40 Mc./sec., with cyclohexane as internal standard for compounds (Id; $x = 1$ —5), and tetramethylsilane for compounds (Id; $x = 5$ and 6) and (If; $x = 1$ —5). τ for cyclohexane was taken as 8.60, giving a root-mean-square deviation between the two standards for all peaks for (Id; $x = 5$) of 0.015 p.p.m.

Lability of Oligoformals to Acid.—(i) *Formic acid.* Solutions of di-n-propyl oligoformals in two volumes of formic acid were examined by infrared spectroscopy. The solution of the triformal originally showed only one peak in the 960—1060 cm.^{-1} region, at about 970 cm.^{-1} , but after 3 hr. at room temperature it showed equal intensities at 1020, 990, and 970 cm.^{-1} , indicating substantial interconversion. After the same period the spectrum of the solution of the monoformal was essentially unchanged.

(ii) *Aqueous acid.* Samples of di-n-propyl oligoformals (1 ml. of the mono-, di-, and tri-formal, and of a 1:1 mixture of tetra- and penta-formal, boiling range 110°/0.25 mm. to 135°/0.6 mm.), were sealed in ampoules with 0.1N-sulphuric acid (5 ml.) and aldehyde- and acetal-free dioxan (15 ml.). After the requisite period at 100°, the mixtures were analysed for free formaldehyde by the hydroxylamine hydrochloride method.²¹ The results, corrected for heating-up period, are plotted in Fig. 3. Fig. 4 is a unimolecular plot of $-\log_{10}$ (% oligoformal unhydrolysed) against time. If interconversion proceeds to such an extent that only monoformal is being hydrolysed during the last stages of the runs, $-\log_{10}(qM_x/w_x)$ should then vary linearly with time, where q is the amount of free formaldehyde in equivalents, M_x is the molecular weight of the oligoformal hydrolysed, and w_x is the sample weight in grams. The points corresponding to this quantity are also plotted (encircled) in Fig. 4 for the determinations at periods of 30 min. and longer, and show as linear a variation as can be expected in view of the small differences involved in the determinations at this stage.

Reaction of Oligoformals with a Thiol.—Samples of di-n-propyl mono-, di-, and tri-formal (If; $x = 1$ —3) (1 ml.) were sealed in Pyrex ampoules with dodecan-1-thiol (1 ml.). To one set of ampoules 0.2 ml. of a solution of potassium (1 g.) in propan-1-ol (50 ml.) was added. The ampoules were heated as indicated, cooled, broken into N-iodine (5 ml.) containing chloroform (5 ml.) and methanol (5 ml.), and titrated with 0.1N-thiosulphate. Under these conditions, formaldehyde does not react with iodine, and dodecylthiomethanol reacts only very slowly. Little reaction occurred at 135° in 1.25 hr.; after 6 hours' reaction at 140°, the titres, respectively with and without propoxide were: $x = 1$, 14.0, 18.9; $x = 2$, 13.8, 48.3; $x = 3$, 14.1, 48.0. The mean titre before reaction was 14.0.

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²¹ Walker, "Formaldehyde," 2nd edn., Reinhold Publ. Inc., New York, 1953, p. 389.