CYCLIC POLYMERS OF ALDEHYDES

I. ALDEHYDE CO-TRIMERS

II. RATES OF DEPOLYMERIZATION

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II. RATES OF DEPOLYMERIZATION

by

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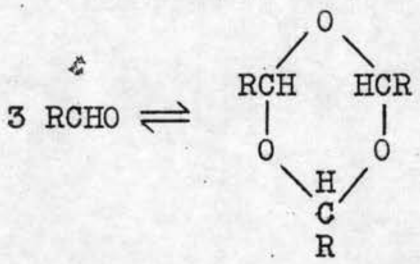
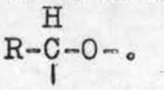
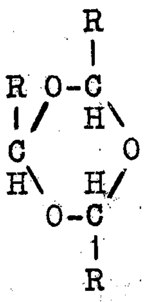
INTRODUCTION

Both simple and substituted aliphatic aldehydes polymerize on standing or under the influence of a catalyst, most often to symmetrical trimers. The catalyst may be a mineral acid such as sulfuric or gaseous hydrochloric acid, sulfur dioxide, or a salt such as zinc chloride. The reaction is reversible but the equilibrium at lower temperatures favors formation of the cyclic trimer.



The structure of these cyclic trimers is indicated by physical and chemical evidence. Molecular weight determinations indicate trimerization of the monomeric aldehydes. Chemically, the polymers do not show any of the characteristic aldehyde reactions. This evidence would indicate that the aldehyde molecules are joined by means of oxygen in the form of a ring by the union of three bivalent aldehyde residues,  $R\text{-}\overset{H}{\underset{|}{C}}\text{-}O\text{-}$. The cyclic nature of these compounds is confirmed by the experimental determination of the molar refractions, which are in close agreement with the theoretical value.

The presence of three alkyl groups on the ring in all but the trimer of formaldehyde renders possible the existence of two stereoisomers, <u>cis</u> and <u>trans</u> forms. The problem of



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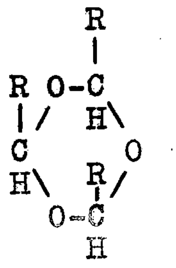
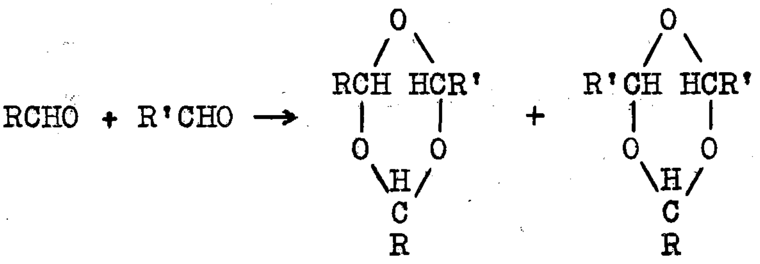


Cis

stereoisomerism has been studied in detail only in respect to paraldehyde. The results to date indicate that the problem is in need of further attention.

In addition to these cyclic trimers, solid polymers are usually obtained from aldehydes acidified at or below 0°. These polymers are designated by the prefix "meta," followed by the name of the aldehydes from which they are derived. At present they are generally believed to be the cyclic tetramers, although earlier work with metaldehyde indicated it to be a stereoisomer of paraldehyde.

Several unsymmetrical cyclic aldehyde trimers are known in which halogen-substituted aliphatic aldehydes are combined with lower aliphatic aldehydes. In a recent review on the polymerization of aldehydes, Bevington (8) has noted that the preparation of these unsymmetrical trimers from a binary aldehyde mixture appears to require that one of the aldehydes be halogen-substituted. These unsymmetrical trimers are also



prepared in the presence of acid. No unsymmetrical trimers containing three dissimilar aldehyde units have been prepared (8).

Polymerization to cyclic trimers in the presence of acids is also characteristic of the thio-analogs of aldehydes and ketones, and of many ammono-aldehydes. For this reason the formation and structure of such polymers are also reviewed in the historical portion of this thesis, even though almost no experimental work was done in that area.

The present work was initiated in order to test the possibility of preparing a series of new unsymmetrical trimers by copolymerizing various aldehyde mixtures. These mixtures consisted of saturated, unsaturated, and substituted aliphatic aldehydes.

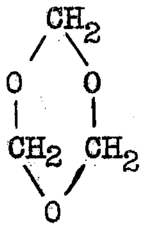
After various aldehyde mixtures had been successfully copolymerized and the reaction shown to be general, possibly excepting formaldehyde, a kinetic study of the acid-catalyzed depolymerization of some symmetrical trimers was made at various acid concentrations and in two dissimilar solvents. This study was aimed at determining the effect of increasing size of the substituted alkyl group, if any, upon the rate of depolymerization, and also the rate of the reaction with respect to both acid and trimer.

PART I

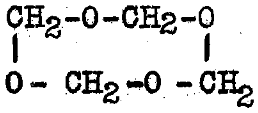
HISTORICAL

Polymers of Aldehydes.

Two cyclic polymers of formaldehyde are known, trioxane (I) and tetraoxymethylene (II). Trioxane was first



I

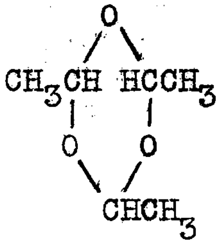


II

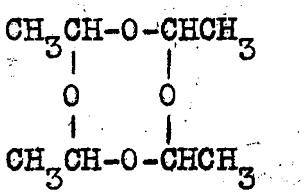
prepared by Pratesi (70) in 1885 by heating paraformaldehyde in a sealed tube with a trace of sulfuric acid at 115°. Walker (93, 95, 94: p. 94) has reviewed the various methods of preparing trioxane as well as the chemical and physical properties of this substance. Staudinger (94: p. 99) obtained tetraoxymethylene by heating polyoxymethylene diacetate in vacuo to 150°; it remains otherwise unstudied.

The molecular weights of these substances are consistent with the above structures. The Raman and infrared absorption spectra (71) of trioxane show that its cyclic molecule is a non-planar hexagonal ring similar to that of cyclohexane. It is used to some extent as a solid fuel and as a source of anhydrous formaldehyde.

The acid-catalyzed polymerization of acetaldehyde (1:19 385, 2:19 806), usually below 0°, forms two cyclic polymers, the liquid trimer paraldehyde (III) and the solid tetramer metaldehyde (IV). The polymerization cannot be made to produce exclusively one or the other; lowering of the temperature



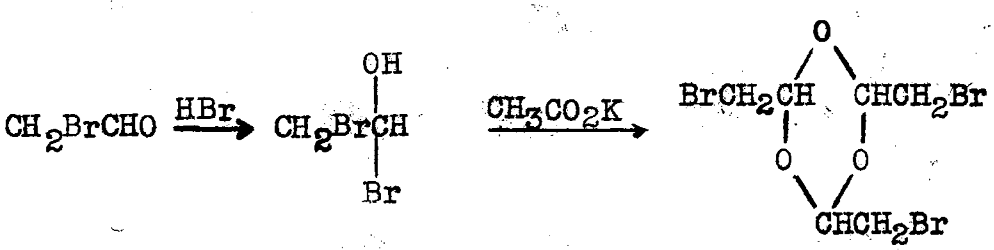
III



IV

merely slightly increases the formation of metaldehyde (89). The preparation and properties of these polymers have been extensively studied (66). Paraldehyde has a limited use in medicine as a soporific and metaldehyde as a convenient smokeless fuel and as a component of snail and slug poisons (27, 88).

Stepanow (83), in a study of the mechanism of this reaction, has offered evidence that the polymerization is initiated by addition of the catalyst to the carbonyl group, and terminated by a trimolecular or sequential elimination of the catalyst. The formation of such an intermediate has been demonstrated with bromoacetaldehyde, which yields a stable addition product with hydrogen bromide, and this in turn, when treated with potassium acetate, gives sym-tribromoparaldehyde (V). It is unlikely, however, that the reaction proceeds in this



V

manner and the formation of the addition product may well be the result of a side reaction. It is more likely that the reaction is ionic in nature and proceeds by the addition of a proton to the carbonyl group, followed, or accompanied, by its removal at another point.

$$CH_2Br\overset{H}{C}{=}O \rightleftharpoons CH_2Br\underset{+}{\overset{H}{C}}-\underset{-}{O} \xrightarrow{H^+} CH_2Br\underset{+}{\overset{H}{C}}-OH$$

Hatcher and Kay (44) have made a kinetic study of the polymerization of acetaldehyde to paraldehyde at 15°, phosphoric acid being used as a catalyst. Their findings indicated the reaction to be of the third order and the velocity of the reaction to be directly proportional to the quantity of added catalyst.

The molecular weight of paraldehyde as determined by the vapor-density method by Fehling (29) and by Weidenbusch (98), as well as by Kekule and Zincke (53), indicates the formula $C_6H_{12}O_3$. The results later obtained by Paterno and Nasini (68), using the cryoscopic method, were also in accord with this formula. Bruhl (12) has shown that the experimental determination of the molar refraction of paraldehyde is in close accordance with the theoretical value.

In an early work on the molecular structure of paraldehyde and metaldehyde, Orndorff and White (66) reported that these substances were isomeric trimers. However, Hantzsch and Oechslin (39) repeated the molecular-weight determinations of metaldehyde and found the formula to be $(C_2H_4O)_4$ in phenol and $(C_2H_4O)_6$ in thymol. They believed the higher value obtained in thymol to be due to a high degree of association of the substance in the solvent, and concluded that metaldehyde was a cyclic tetramer of acetaldehyde and not an isomer of paraldehyde.

More recently, the configurations of paraldehyde and metaldehyde have been established by electron diffraction and X-ray methods. Carpenter and Brockway (14) have shown that paraldehyde exists as a staggered six-membered ring of alternate carbon and oxygen atoms with a hydrogen atom and a methyl group attached to each of the ring carbon atoms, the methyl carbon atoms being approximately coplanar with the ring oxygen. They were unable to clearly distinguish between the model with all the methyl groups in the plane of the ring and the model having one methyl group above the plane. Pauling and Carpenter (69) have established that metaldehyde is the cyclic tetramer of acetaldehyde containing an eight-membered ring built up of alternate carbon and oxygen atoms and having a methyl group attached to each carbon atom. These methyl groups lie in the plane of the carbon atoms in the ring. The interatomic distances and bond angles were found to be the same as in paraldehyde.

Sutherland (87) noted that the infrared spectra of paraldehyde and metaldehyde were generally similar. A comparison of the Raman and infrared spectra indicates that paraldehyde is not planar, but an equilibrium mixture of cis and trans forms (33). The staggered bond configurations have been confirmed in both paraldehyde and metaldehyde (25). From the interpretation of electron diffraction data, Hassel (41) concluded that paraldehyde can be isolated in only one form because of instability of the ring in the other.

Travers (89) has prepared a polymer of acetaldehyde by polymerizing the aldehyde at -80° with a drop of alcoholic sulfuric acid. This substance distilled at 73-75° with some decomposition into aldehyde, and condensation to higher-boiling products. Cryoscopic molecular weights corresponded to $(C_2H_4O)_2$; and vapor-density determinations at 100° showed that the compound had initially the above formula, but that it dissociated rapidly. This is the only literature claim for an aldehyde dimer, and needs confirmation.

Craven (20) has isolated isomers of paraldehyde and metaldehyde from the reaction mixture obtained by the polymerization of acetaldehyde in large quantities. Distillation of this reaction mixture yielded a substance boiling 35° higher than paraldehyde. It was isomorphous with ordinary metaldehyde and had a molecular weight four times that of acetaldehyde. Infrared spectra of these two forms of metaldehyde were dissimilar.

The new trimer was partially purified by fractional crystallization of unpurified paraldehyde. It had a higher density and refractive index than ordinary paraldehyde. A mixture of ordinary and this newly-isolated paraldehyde showed new infrared bands not present in the spectrum of ordinary paraldehyde. These differences may be attributed to geometric isomerism.

Chattaway and Kellett (15) prepared two isomeric parachlorals and metachloral by treating chloral, CCl_3CHO, with an excess of sulfuric acid at room temperature. The isomerism of α- and β- parachloral is believed by the authors to be of the cis-trans type, corresponding to the two possibilities in the paraldehyde molecule, one having all three trichloromethyl groups on the same side of the plane of the ring, and the other having two on one side and one on the other. Isomerism attributed to cis-trans forms has also been observed in parabromopropionaldehyde, $(CH_3CHBrCHO)_3$ (1:19 389).

"Butylchloral," $CH_3CHClCCl_2CHO$, like chloral, forms two isomeric polymers of the para type when treated with an excess of sulfuric acid (15). No meta form has been observed. In fact, meta polymers have been observed only for chlorinated or brominated acetaldehydes.

Propionaldehyde polymerizes like acetaldehyde when acid is added to the cold aldehyde, forming both the cyclic trimer and the solid metapropionaldehyde (1:19 389). Since the formation of cyclic trimers from both simple and substituted aliphatic aldehydes is a general reaction, Tables I, II, III, and IV have been made to include not only those polymers which have been shown to be trimers, but also those formed under similar conditions and believed, but not proved, also to be 1,3,5-trioxanes.

Table I

UNSUBSTITUTED-ALDEHYDE TRIMERS

Aldehyde Polymerized	Trioxane-derived Trimers	Literature References
Butyraldehyde	2,4,6-Tri-*n*-propyl	2:*19* 807
Isobutyraldehyde	2,4,6-Triisopropyl	1:*19* 390, 2:*19* 807
Valeraldehyde*	2,4,6-Tri-*n*-butyl	
Isovaleraldehyde	2,4,6-Triisobutyl	2:*1* 353
Methylethylacetaldehyde	2,4,6-Tri-*sec*-butyl	1:*19* 391
Trimethylacetaldehyde	2,4,6-Tri-*tert*-butyl	2:*19* 807
Hexaldehyde	2,4,6-Tri-*n*-pentyl	1:*1* 688, 2:*1* 354
Heptaldehyde	2,4,6-Tri-*n*-hexyl	2:*19* 807
Octylaldehyde	2,4,6-Tri-*n*-heptyl	92
Nonylaldehyde	2,4,6-Tri-*n*-octyl	1:*1* 708
Decylaldehyde	2,4,6-Tri-*n*-nonyl	1:*1* 711
Undecylaldehyde	2,4,6-Tri-*n*-decyl	1:*1* 713
Dodecylaldehyde	2,4,6-Tri-*n*-undecyl	61
Tridecylaldehyde	2,4,6-Tri-*n*-dodecyl	1:*19* 392
Tetradecylaldehyde	2,4,6-Tri-*n*-tridecyl	"
Pentadecylaldehyde	2,4,6-Tri-*n*-tetradecyl	"
Hexadecylaldehyde	2,4,6-Tri-*n*-pentadecyl	"
Heptadecylaldehyde	2,4,6-Tri-*n*-hexadecyl	"
Octadecylaldehyde	2,4,6-Tri-*n*-heptadecyl	84

* Prepared by author

Table II

HALOGEN-SUBSTITUTED TRIMERS

Aldehyde Polymerized	Trioxane-derived Trimer	Literature References
CH_2ClCHO	2,4,6-Tris(chloromethyl)	1:19 386, 2:19 807,78
$CHCl_2CHO$	2,4,6-Tris(dichloromethyl)	1:1 614, 78
CCl_3CHO	2,4,6-Tris(trichloromethyl)	15
CH_2BrCHO	2,4,6-Tris(bromomethyl)	56, 46, 48, 82
$CHBr_2CHO$	2,4,6-Tris(dibromomethyl)	1:1 632
CBr_3CHO	2,4,6-Tris(tribromomethyl)	1:1 626, 2:1 331
$CH_3CHClCHO$	2,4,6-Tris(1-chloroethyl)	65
CH_2ClCH_2CHO	2,4,6-Tris(2-chloroethyl)	1:1 632
- - - - - -	2,4,6-Tris(1-bromoethyl)*	1:19 389
- - - - - -	2,4,6-Tris(2-iodoethyl)**	1:19 389
$(CH_3)_2CClCHO$	2,4,6-Tris(1-chloro-1-methylethyl)	1:19 391
$(CH_3)_2CBrCHO$	2,4,6-Tris(1-bromo-1-methylethyl)	1:19 391, 2:19 807
$CH_3CHClCH_2CHO$	2,4,6-Tris(2-chloropropyl)	1:1 663, 45
$CH_3CHClCCl_2CHO$	2,4,6-Tris(1,1,2-trichloropropyl	15
$CH_3CH_2CHBrCHO$	2,4,6-Tris(1-bromopropyl)	55

* Made by brominating 2,4,6-triethyltrioxane.

** Made by pyrolysis of 2,3-diiodopropanol *in vacuo*.

Table III

OTHER SYMMETRICAL TRIMERS

Aldehyde Polymerized	Trioxane-derived Trimer	Literature References
Hexahydrobenzaldehyde	2,4,6-Tricyclohexyl	1:19 384, 97
Aminoacetaldehyde	2,4,6-Tris(aminomethyl)	73
Phenylacetaldehyde	2,4,6-Tribenzyl	2:19 810, 62
Methoxyacetaldehyde	2,4,6-Tris(methoxymethyl)	24
Ethoxyacetaldehyde	2,4,6-Tris(ethoxymethyl)	24
Hydroxypyruvaldehyde*	2,4,6-Triglycolyl	28
Levulinaldehyde*	2,4,6-Tris(3-oxobutyl)	31
β-Benzylaminopropionaldehyde	2,4,6-Tris(2-benzylaminomethyl)	54
Acrolein*	2,4,6-Trivinyl	1:1 727
Crotonaldehyde*	2,4,6-Tri-1-propenyl	7

* There is more than the usual amount of doubt whether polymers of these are trioxanes.

Unsymmetrical trimers have been prepared in which halogen-substituted aldehydes have been condensed with aliphatic aldehydes, forming the corresponding mixed trimers. These unsymmetrical trimers are tabulated in Table IV. No other unsymmetrical trimers are reported in the literature.

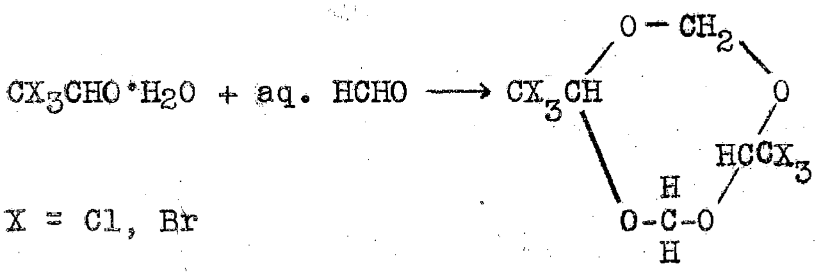
Table IV

UNSYMMETRICAL TRIOXANE-DERIVED TRIMERS

Trimer	Literature References
2,4- Bis(dichloromethyl)	2:<u>19</u> 807
2,4-Bis(trichloromethyl)	1:<u>19</u> 384
2,4-Bis(tribromomethyl)	1:<u>19</u> 385
2-Dichloromethyl-4,6-dimethyl	2:<u>19</u> 806
2,4-Bis(dichloromethyl)-6-methyl	2:<u>19</u> 807
2-Bromomethyl-4,6-dimethyl	83
2,4-Bis(bromomethyl)-6-methyl	82
2,4-Dimethyl-6-trichloromethyl	45
2,4-Di-*tert*-butyl-6-trichloromethyl	47
2,4-Diethyl-6-trichloromethyl	47
2,4-Diisopropyl-6-trichloromethyl	47
2-(2-Chloropropyl)-4,6-dimethyl	45
2-(1,2-Dichloropropyl)-4,6-dimethyl	45
2,4-Dimethyl-6-(1,1,2-trichloropropyl)	45
2-(1-Bromo-1-methylethyl)-4,6-diisopropyl	26

Hibbert (47) attempted to prepare mixed paraldehydes containing three different aldehyde units from a ternary mixture of propionaldehyde, chloral, and isobutyraldehyde as well as a mixture consisting of propionaldehyde, bromoacetaldehyde, and isobutyraldehyde. Only mixtures of paraldehydes containing two moles of one simple aldehyde to one mole of chloral were obtained.

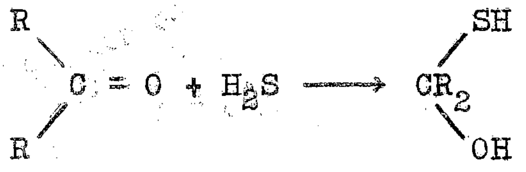
Two mixed tetramers (1:<u>19</u> 434) have been prepared by polymerizing aqueous formaldehyde with chloral hydrate and bromal hydrate, respectively, in an excess of concentrated sulfuric acid.



<u>Polymers of Thiocarbonyl Compounds.</u>

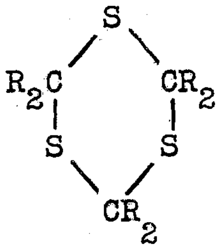
The most widely applied method currently employed for the preparation of cyclic trithials and trithiones consists of the treatment of an acid solution of the aldehyde or ketone with hydrogen sulfide. Aliphatic and aromatic aldehydes and dialkyl and aryl alkyl ketones all undergo this reaction. In fact, this tendency to polymerize is much increased in the thials and thiones; no monomeric thials have been isolated and only a very few thiones are known in the monomeric state. Campaigne (13) has reviewed this subject thoroughly and is the authority for all statements except where specific reference is otherwise made.

The following mechanism, obviously incomplete, has been proposed for the reaction between hydrogen sulfide and the carbonyl compounds:



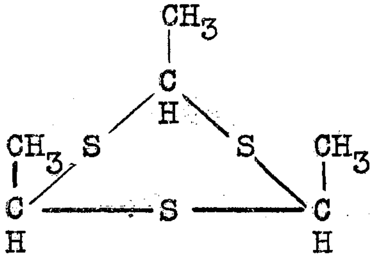
$$R_2C=O + H_2S \longrightarrow CR_2(SH)(OH)$$

Three molecules of the addition compound may then react to give the trimer (I).

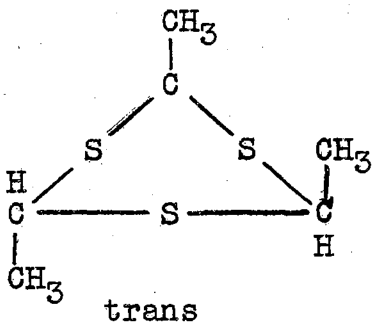


I

Acetaldehyde reacts with hydrogen sulfide to form two compounds; the lower-melting substance is called α-trithioacetaldehyde and the higher-melting one β-trithioacetaldehyde. Since molecular-weight determinations show them both to have the formula $(CH_3CHS)_3$, they are believed to be cis-trans isomers; but which is the α form and which is β is still uncertain.



cis



trans

Douglass and Martin (23) prepared both the α - and β-isomers of trithioparaldehyde by passing hydrogen sulfide into propionaldehyde dissolved in ethanol into which hydrogen chloride had been absorbed. The preparation of trithiobutyraldehyde was attempted by essentially the same method but no pure compound was isolated. Douglass and Hydro (22) have prepared the α- and β-forms of trithiophenylacetaldehyde. Stanfield and Reynolds (81) have recently isolated the α- and β-isomers of a series of monohalotrithiobenzaldehydes.

Cyclic thioaldehyde trimers can also be prepared by treating the aldehyde with a hydrochloric acid solution of sodium thiosulfate. It is reported that this reaction is limited to water-soluble aldehydes.

Substances with two halogen atoms attached to the same carbon atom may be converted to thioaldehydes or thioketones by the action of sodium hydrosulfide or sulfide.

$$3\ C_6H_5CHCl_2 + 3\ Na_2S \longrightarrow (C_6H_5CHS)_3 + 6\ NaCl$$

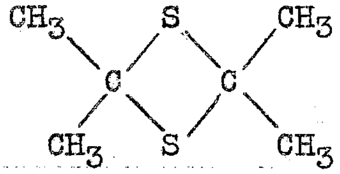
Trithioaldehydes are obtained by the hydrolysis of α,α'-dichlorodialkyl sulfides (30).

$$3\ (ClCH_2)_2S + 2\ H_2O \longrightarrow HOCH_2SCH_2OH + 2\ HCl$$

$$3\ HOCH_2SCH_2OH \longrightarrow (CH_2S)_3 + 3\ H_2O + 3\ CH_2O$$

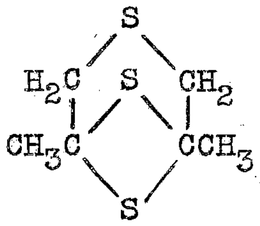
<u>Cyclic Thioketone Dimers</u>.

Phosphorus pentasulfide reacts with simple ketones to form the corresponding dimers. Thus acetone, ethyl methyl ketone, and di-*n*-propyl ketone give dimeric thiones.



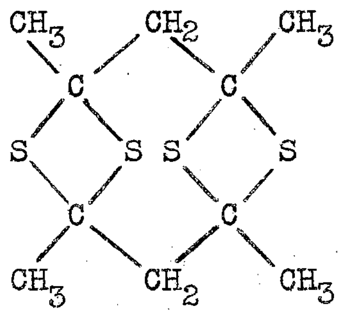
2,2,4,4-Tetramethyldithietane (from acetone)

Chloroacetone reacts with hydrogen chloride and carbon disulfide, forming 2,6-dimethyl-2,6-endothio-1,4-dithiane (II).



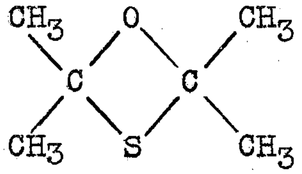
II

Diketones, such as acetylacetone, react with hydrogen sulfide to form similar, but complex cyclic dimers.



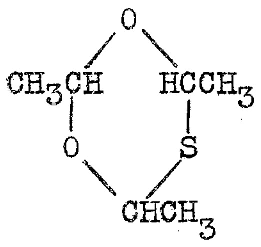
<u>Mixed Sulfur-Oxygen Cyclic Polymers</u>.

Acetone reacts with phosphorus pentasulfide, forming the mixed cyclic dimer, 2,2,4,4-tetramethyloxathietane (III).

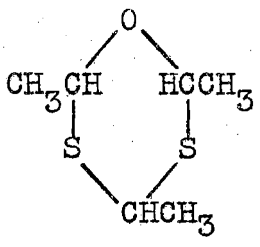


III

Acetaldehyde can be made to react with hydrogen chloride and hydrogen sulfide to form monothioparaldehyde (IV) and dithioparaldehyde (V).

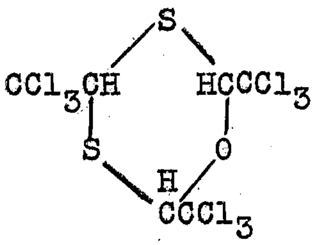


IV



V

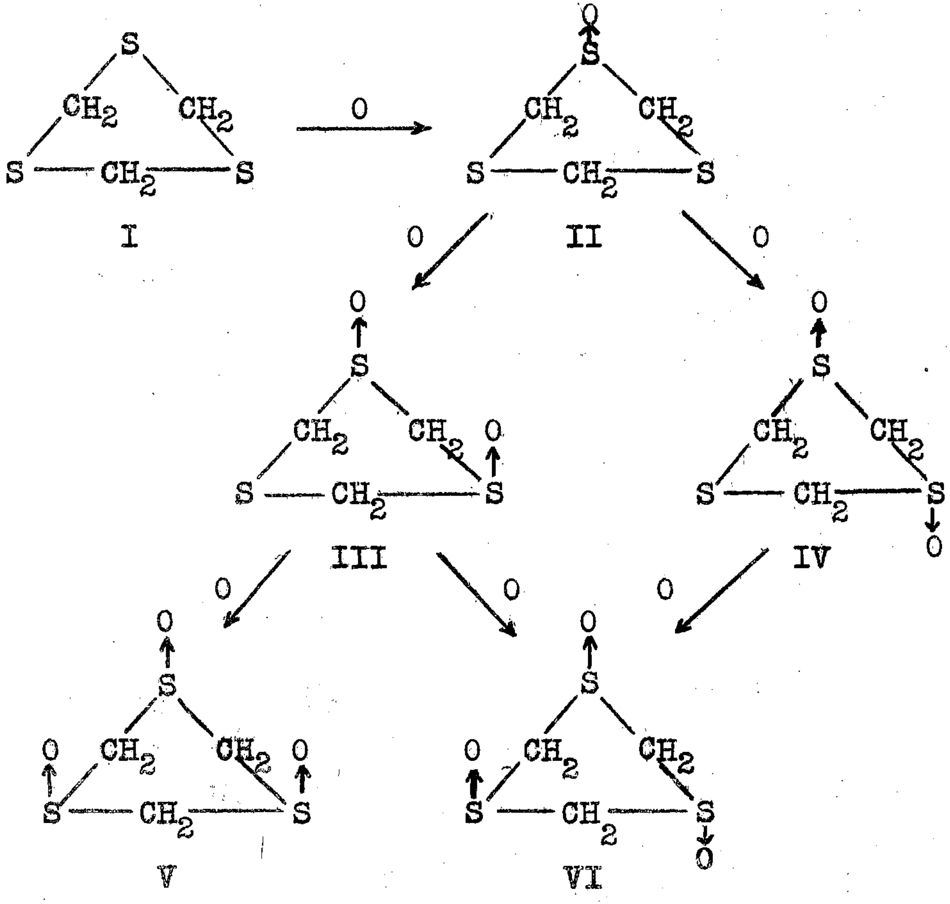
Chattaway and Kellett (16) prepared the α- and β-isomers of dithioparachloral (VI) by treating chloral sulfhydrate, $(CCl_3CHOH)_2S$, with concentrated sulfuric acid.



VI

Structure of the Trithianes

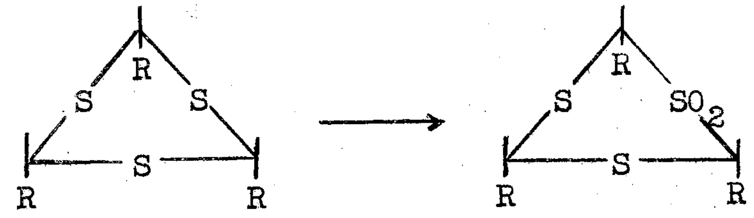
The planar ring structure of trithiane is indicated by the methods of classical stereochemistry. Since trithiane (I) exists in one form only, the controlled oxidation of this compound should yield but one monosulfoxide (II). Stereochemical theory indicates that further oxidation of this monosulfoxide should yield two disulfoxides, (III) and (IV), and these in turn should oxidize to form two trisulfoxides, (V) and (VI). All of these sulfoxides have been isolated.



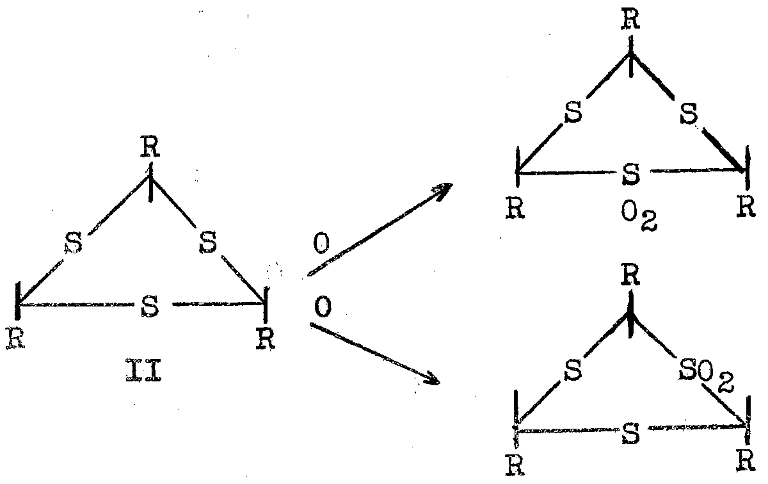
Thus is it seen that the oxidation of the monosulfoxide forms the <u>cis</u> (III) and <u>trans</u> (IV) disulfoxide isomers. Further oxidation of the <u>trans</u> isomer (IV) does form but one trisulfoxide (VI) as theory indicates, whereas the <u>cis</u> isomer (III) upon oxidation yields two trisulfoxides, the <u>cis</u> (V) and <u>trans</u> (VI) isomers. The latter trisulfoxide is identical with the trisulfoxide obtained by the oxidation of (IV).

Studies of the stereochemistry of the α- and β-forms of trithioacetaldehyde, employing similar chemical methods, have not entirely clarified the structure of these isomers. Oxidation of these isomers to the corresponding trisulfoxides has not yielded the theoretical number of isomers.

Oxidation of β-trithioacetaldehyde (I) yields one monosulfone and that of α-trithioacetaldehyde (II) forms two monosulfones. These results indicate that the β-isomer may possess the <u>cis</u> configuration and the α-isomer the <u>trans</u>.



I

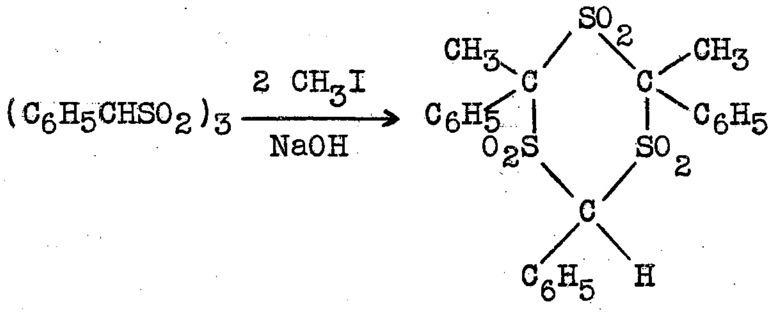


The Raman spectra of α- and β-trithioacetaldehyde (32) also indicate that the β-isomer has the cis structure. The infrared absorption spectra of α- and β-trithioacetaldehyde (33) indicate that the ring is staggered. Comparison with the absorption spectrum of paraldehyde indicates that the three compounds possess the same ring structure.

Hassel and Ore (41, 42), in an electron diffraction investigation of α- and β-trithioacetaldehyde, conclude that the structures are not planar but that the C_3S_3 ring has a symmetrical staggered form of the cyclohexane type. Three of the C-C or C-H bonds, one belonging to each ring carbon atom, are almost perpendicular to the plane of the C_3 and S_3 triangles. These three bonds are designated as ϵ bonds, the three others as a bonds. Steric hindrance prevents molecules with ϵ, ϵ, ϵ, or ϵ, ϵ, a configurations, whereas ϵ, a, a and a, a, a should be possible. They were, however, unable to differentiate between these two forms. Since α-trithioacetaldehyde forms two monosulfones and the β-isomer only one, they believe the α-isomer must have the ϵ, a, a configuration and the β-form the a, a, a structure.

The attempt to elucidate the structures of the α- and β-isomers of trithiobenzaldehydes by oxidation to the corresponding sulfones has not been successful. The theoretical numbers of isomers possible by this method have not been isolated.

The methylation of the trisulfone of β-trithiobenzaldehyde is incomplete, only two of the three possible methyl groups being substituted into the ring. It is believed that the non-replaceable methylene hydrogen atom is between two phenyl groups and is therefore less reactive.



The only definitive work on a selenoaldehyde polymer (11) shows that triselenane, $(CH_2Se)_3$, is analgous in mode of preparation, structure, and properties to trithiane.

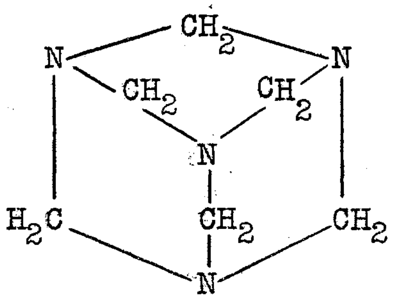
Polymers of Ammono-aldehydes.

Analgous to the aldehydes and thioketones, which are, respectively, characterized by oxygen and sulfur atoms doubly bound to a carbon atom, are the ammono-aldehydes. These ammono-analogs of aldehydes thus contain a carbon atom doubly bound to nitrogen. They are commonly known as aldimines or Schiff's bases and may be considered as substitution products of ammonia and formaldehyde, $CH_2=NH$. Simple aldimines, $RCH=NH$, are unknown in the monomeric state.

Cyclic Polymers Containing Only Nitrogen as Hetero Atoms.

1. Symmetrical polymers of simple imines

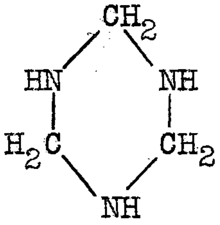
Ammonia reacts with either aqueous or gaseous formaldehyde to form hexamethylene-tetramine (I), the polycyclic ammono-analog of trioxane.



I

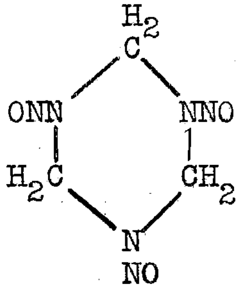
Walker (94: p. 276) has extensively reviewed the preparation, structure, mechanism of formation and the uses of this compound. Of the various structures proposed for this substance, the one above, in view of X-ray investigations which indicate the high symmetry of this structure, is generally accepted. Hexemethylenetetramine is used as a source of anhydrous formaldehyde and ammonia and has a limited use in medicine as a urinary antiseptic. It was one of the materials used at first in manufacturing cyclotrimethylene-trinitramine, the high explosive, but more efficient processes were developed.

The reaction between formaldehyde and ammonia apparently proceeds by the formation of the hypothetical methyleneimine, $CH_2=NH$, which polymerizes to form 1,3,5-hexahydrotriazine (II).



II

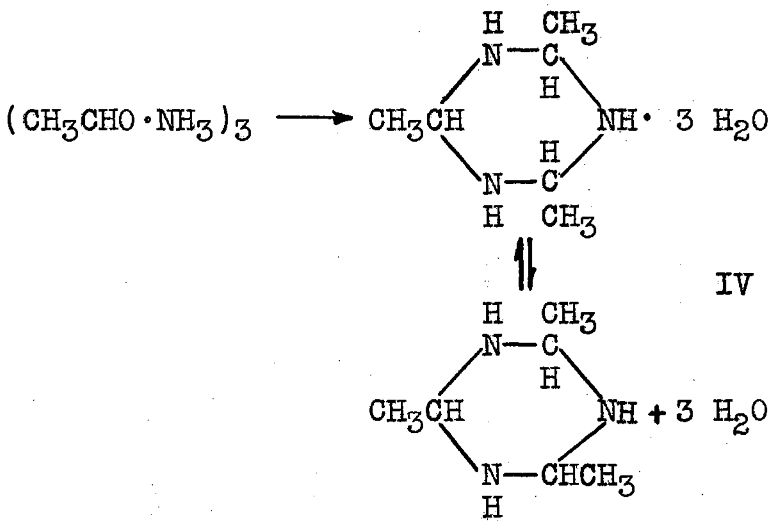
Although this substance has not been isolated from the reaction mixture, derivatives of this cyclic imine have been prepared and characterized. Nitrous acid reacts with freshly prepared formaldehyde-ammonia solution to form 1,3,5-trinitrosohexahydrotriazine (III). With benzoyl chloride, the formaldehyde-ammonia solution yields 1,3,5-tribenzoylhexahydrotriazine, $(CH_2=NCOC_6H_5)_3$, (94: p. 280, 74).



III

Acetaldehyde reacts with ammonia, yielding two forms of acetaldehyde-ammonia. Which one is formed depends upon the nature of the solvent used in the reaction (60). Each form has an equivalent weight corresponding to $CH_3CHO \cdot NH_3$. Either form, after dehydration, has an equivalent weight corresponding to $CH_3CH=NH$.

As a result of X-ray studies on acetaldehyde-ammonia, it has been suggested that it is the trihydrate of 2,4,6-trimethylhexahydrotriazine (IV), the anhydrous form being formed as shown. The trinitroso derivative of this substance has been prepared.

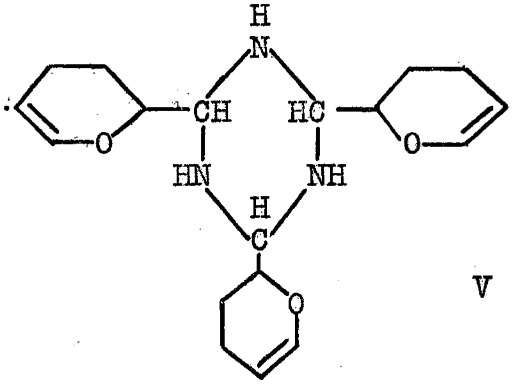


IV

A kinetic study of the acid-catalyzed depolymerization of acetaldehyde-ammonia (60) indicates the existence of at least two forms in solution. One of the products of this depolymerization is believed to be a dimer, but all attempts to isolate this substance were unsuccessful.

Bromoacetaldehyde in benzene (but not in ether) treated with ammonia is converted to the trimer 2,4,6-tris(bromomethyl)-hexahydrotriazine (90) and chloral reacts with ammonium acetate, yielding two isomeric forms of 2,4,6-tris(trichloromethyl)-hexahydrotriazine (1:26 9).

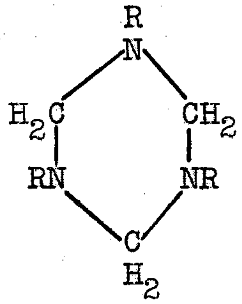
As a more complex example, 2-formyl-2,3-dihydropyran, the dimer of acrolein, is converted by ammonia into the substituted hexahydrotriazine (V) (77).



V

2. Symmetrical polymers of N-alkylimines

The ammono-analogs of substituted trioxanes (VI) are in many instances readily prepared by treating a primary alkyl- or arylamine with aqueous formaldehyde. These are listed in Table V below. Proof of the cyclic trimeric nature of the derivatives of aniline and p-toluidine was given by Miller and Wagner (63).



VI

Table V

SYMMETRICAL POLYMERS OF N-ALKYLIMINES:

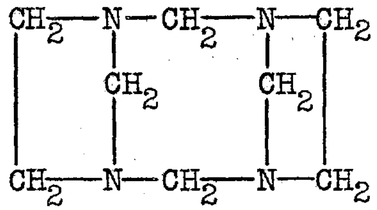
1,3,5-Trisubstituted Hexahydro-1,3,5-triazines

Substituent	Literature References	Substituent	Literature References
Methyl	1:26 1, 36	Benzyl**	1:26 5, 75, 72
Ethyl	1:26 2, 75, 36	o-Nitrobenzyl**	2:26 3, 72
Propyl	1:26 3, 36	p-Nitrobenzyl**	2:26 3, 72
iso-Propyl	52, 75	Phenyl	1:26 3, 75
Butyl	1:26 3, 75, 37	p-Chlorophenyl	1:26 4
iso-Butyl	52, 37	o-Tolyl	1:26 4
iso-Pentyl	52, 37	p-Tolyl	1:26 4, 75
Hexyl	75	p-Methoxyphenyl	1:26 5
2-Hydroxyethyl	75	p-Ethoxyphenyl	75
2-Phenylethyl	75	5,6,7,8-Tetrahydro 2-naphthyl	1:26 5
Cyanomethyl	94: p. 219	2-Thenyl	40
Cyclohexyl*	75	5-Methyl-2-thenyl	40
		2-Pyridyl	51

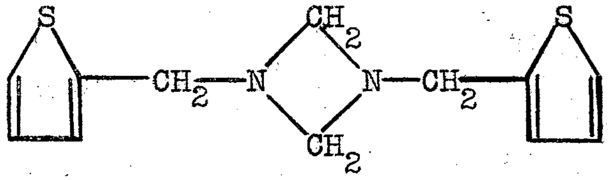
* Prepared by treating cyclohexylamine with methylene dichloride.

** Prepared by treating the corresponding benzylhexamethylenetetraminium halide with sulfur dioxide and then with sodium hydroxide.

One 8-membered ring is known in this family. Ethylenediamine reacts with formaldehyde to form a substance which is believed to have the following structure (94: p. 201):



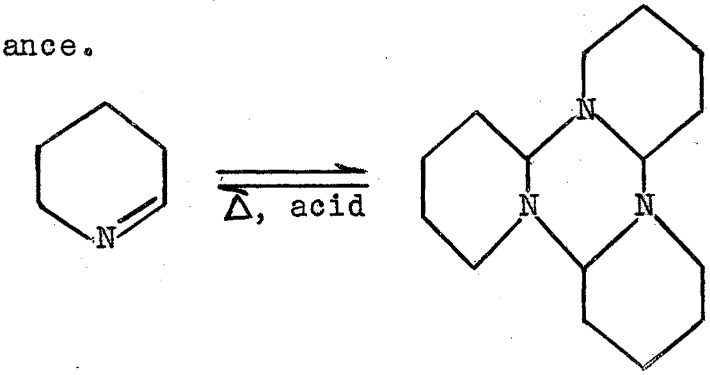
Likewise one 4-membered ring dimer has been reported. Thiophene, ammonium chloride, and formaldehyde react to form 1,3-diazacyclobutane (VII) (40).



VII

Polymers derived from higher aldehydes and primary amines are almost unknown (reflecting the smaller tendency of RCH=NR to polymerize). One such polymer has been prepared (76) by treating 1-chloropiperidine with alcoholic potassium hydroxide. The reaction is believed to proceed initially by the formation of the unstable intermediate monomer, tetrahydropyradine or piperideine (VIII), followed by subsequent polymerization to the isomeric trimers, α-tripiperideine and β-tripiperideine (IX). These are believed to be <u>cis</u>-<u>trans</u> isomers. Both depolymerize readily in acid to the monomeric tetrahydropyridine. The monomer can be considered to be a cyclic Schiff base in view of the functional -C=N- group in the substance.

VIII



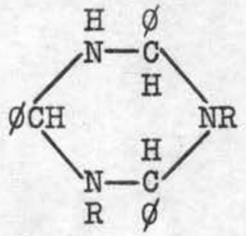
IX

3. Unsymmetrical polymers

Distillation of benzylhexamethylenetetraminium chloride (prepared from hexamethylenetetramine and benzyl chloride) under reduced pressure yields a substance which is believed to be 1,3,5-trimethyl-2,4-diphenyl-hexahydrotriazine. It depolymerizes readily on warming with mineral acids to give benzaldehyde, methylamine, and formaldehyde (38).

Benzylidene-aniline and benzylidene-p-toluidine, respectively, polymerize in a solution of potassium amide in liquid ammonia (86). It has been suggested that these polymers have the following structure:

R = phenyl or tolyl



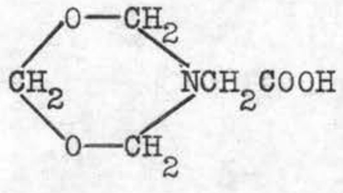
Since benzaldehyde and benzylideneimine are not known to form cyclic trimers, it appears unlikely that the above structure is correct. Furthermore, the molecular weight of the benzylidene-p-toluidine polymer is in wide variance with the theoretical value.

<u>Polymers Containing Nitrogen and Other Hetero Atoms.</u>

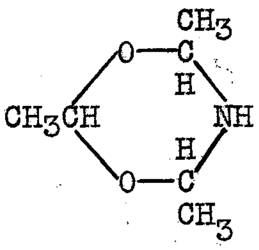
1. Dihydro-1,3,5-dioxazines (O,O,N)

The copper salt of glycine reacts with formaldehyde to form dihydro-1,3,5-dioxazinyl-(5)-acetic acid (X) (2:26 442).

X



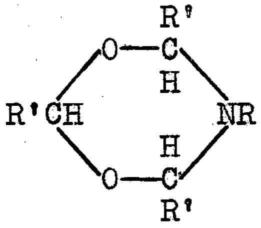
A moist ether solution of N-nitroso-2,4,6-trimethyl-dihydrodioxazine reacts with hydrogen chloride to form 2,4,6-trimethyl- dihydrodioxazine (XI) (1:27 460).



XI

Simple primary amines treated with a large excess of formaldehyde solution or acetaldehyde yield mixed cyclic trimers (6) in which one oxygen atom of the trioxane ring is replaced by an imino-group (XII).

known for R' = H when R = ethyl
R' = methyl R = ethyl
R' = H R = allyl
R' = methyl R = allyl
but failed for R' = phenyl



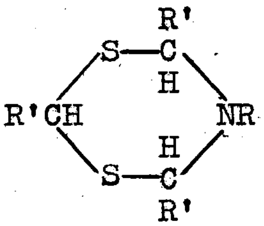
XII

2. Tetrahydro-1,3,5-oxadiazines (O,N,N)

None found

3. Dihydro-1,3,5-dithiazines (S,S,N)

These substances (XIII) are prepared by treating a simple aldehyde with ammonia and hydrogen sulfide or with ammonium sulfide. These are tabulated in Table VI.



XIII

Table VI

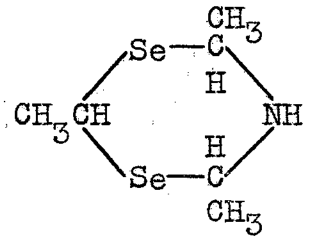
DIHYDRO-1,3,5-DITHIAZINES

R	R'	Literature References
Hydrogen	Hydrogen	59
Methyl*	Hydrogen	1:27 460
Hydrogen	Methyl	1:27 461
Methyl*	Methyl	1:27 462
Hydrogen	Isopropyl	1:27 462
Hydrogen	Isobutyl	1:27 462
Hydrogen	n-Hexyl	1:27 462
Cyclohexyl**	Hydrogen	10

* Prepared by using methylamine instead of ammonia.

** Prepared by treating N-methylenecyclohexylamine, $C_6H_{11}N{=}CH_2$, with hydrogen sulfide.

The analogous Se,Se,N trimer (XIV) has been prepared by the addition of hydrogen selenide to a solution of acetaldehyde-ammonia (1:27 462).



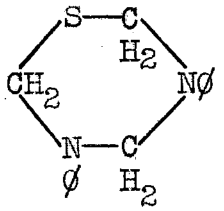
XIV

4. Tetrahydro-1,3,5-thiadiazines (S,N,N)

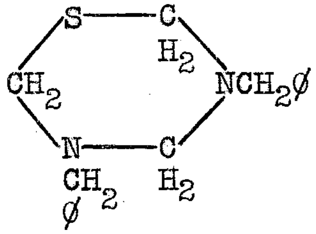
According to Levi (58), aniline reacts with formaldehyde and hydrogen sulfide as follows:

$$C_6H_5NH_2 + 3\ CH_2O + H_2S \longrightarrow C_{15}H_{16}N_2S$$

The following structural formula has been suggested for this substance, presumably by analogy.

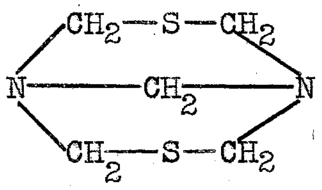


N-Methylenebenzylamine, $C_6H_5CH_2N=CH_2$, combines with hydrogen sulfide and formaldehyde to form 3,5-dibenzyltetrahydro-1,3,5-thiadiazine (XV) (10).



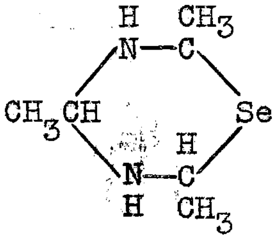
XV

Formaldehyde and ammonium sulfide react to form a substance (1:27 739) to which the following structure has been assigned:



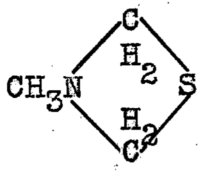
An isomeric form has been prepared from formaldehyde, ammonium chloride, and sodium sulfide (94: p. 131).

Hydrogen selenide and acetaldehyde-ammonia react to form a selenodiazine (60) which has the structure:



5. Sulfur-nitrogen cyclic dimers

Methylamine, hydrogen sulfide, and formaldehyde react to form 3-methyl-1,3-thiazetidine (XVI) (58).



XVI

Hydrogen sulfide also converts N-methylenecyclohexylamine, $C_6H_{11}N=CH_2$, into 3-cyclohexyl-1,3-thiazetidine (10).

EXPERIMENTAL

The aldehydes used in this work were of reagent and technical grades. The reagent-grade aldehydes were used as such and the technical grades, with the exception of acetaldehyde, were purified by distillation. Monomeric formaldehyde (94: p. 24) was prepared by vaporizing paraformaldehyde and condensing the gas thus obtained in the aldehyde with which it was to be copolymerized. Condensation of the gas was readily effected with a solid carbon dioxide-acetone bath. Aqueous formaldehyde solutions were prepared by dissolving paraformaldehyde in hot water. Almost any desired concentration of formaldehyde can be obtained at reflux temperatures in one or two hours. Formaldehyde solutions obtained in this way are identical with those obtained by dissolving gaseous formaldehyde in water (94: p. 73).

The general method employed in this work to polymerize an aldehyde mixture was as follows:

A stream of anhydrous hydrogen chloride gas was passed for several seconds into the aldehyde mixture, which had been cooled by an ice-salt bath. Since the reaction is exothermic, ebullition usually occurred whenever acetaldehyde was one of the constituent aldehydes. After several minutes' stirring of the contents, the flask was stoppered and the acidified mixture allowed to remain in the cold bath for several hours.

The reaction mixture was then poured into a separatory funnel containing aqueous potassium carbonate. After vigorous shaking of the mixture, the lower aqueous layer was drawn off and discarded. The non-aqueous layer was transferred to a flask containing anhydrous potassium carbonate and allowed to stand for several hours. The dried liquid was filtered and fractionated in either the 30-plate Oldershaw bubble-plate column or the Todd precise fractionation assembly, using the column packed with glass helices. Distillation was effected at either atmospheric or reduced pressure, depending upon the stability of the trimer.

Distillation of the acrolein-acetaldehyde reaction mixture in the Oldershaw column yielded only some unreacted acrolein and paraldehyde. There remained, however, about 15 ml of a yellowish liquid in the stillpot. This liquid was added to 100 ml of cold water and swirled vigorously for several minutes in order to remove the remaining paraldehyde. The non-aqueous layer was removed and dried over anhydrous potassium carbonate. Filtration gave 4 or 5 ml of liquid, which was micro-fractionated according to Gettler, Niederl, and Benedetti-Pichler (34). Boiling points of fractions were determined by Siwoloboff's method (80).

These compounds were characterized by carbon and hydrogen analyses, molar refractions (35), and molecular weights. Molecular weights were determined by the vapor-density method of Niederl and Niederl (64), and by freezing-point depression in benzene.

A chemical method that can be employed to further elucidate the composition of these compounds consists of the depolymerization of these trimers in an acid solution saturated with 2,4-dinitrophenylhydrazine, which causes precipitation of the 2,4-dinitrophenylhydrazone of the monomer (50). The reliability of this method was established with paraldehyde.

The bromine numbers of trimers containing unsaturated alkyl groups were determined by the method of Bradstreet and Lewis (9).

The physical constants and analyses of the unsymmetrical trimers which have been prepared are presented in the following tables.

Table VII

UNSYMMETRICAL TRIMERS OBTAINED FROM VARIOUS ALDEHYDE MIXTURES

Aldehyde Mixture	Mols of Each Used	Compound Obtained (substituted trioxane)	Yield, g.
Acetaldehyde	2.0	2,4-Dimethyl-6-ethyl	60
Propionaldehyde	4.0	2,4-Diethyl-6-methyl	16
Acetaldehyde	2.6	2,4-Dimethyl-6-propyl	8
Butyraldehyde	3.0	2,4-Dipropyl-6-methyl	42
Acetaldehyde	3.3	2,4-Dimethyl-6-isopropyl	46
Isobutyraldehyde	1.4	2,4-Diisopropyl-6-methyl	14
Acetaldehyde	1.8	2,4-Dimethyl-6-hexyl	21
Heptaldehyde	1.3	2,4-Dihexyl-6-methyl	12
Propionaldehyde	1.7	2,4-Diethyl-6-propyl	14
Butyraldehyde	2.5	2,4-Dipropyl-6-ethyl	19
Acetaldehyde	2.7	2,4-Dimethyl-6-β-ethoxyethyl	13
β-Ethoxypropionaldehyde	0.8	2,4-Bis(β-ethoxyethyl)-6-methyl	11
Acetaldehyde	1	2-Hexyl-4-methyl-6-propyl	8
Butyraldehyde	1		
Heptaldehyde	1		
Acetaldehyde	3.6	2,4-Dimethyl-6-vinyl	5
Acrolein	1.2		
Acetaldehyde	1.8	2,4-Dimethyl-6-propenyl	9
Crotonaldehyde	1.1		

Table VIII

PHYSICAL CONSTANTS OF THE UNSYMMETRICAL TRIMERS

Compound (substituted trimer)	B.P., °C	Pressure, mm.	n_D^t	Density, °t, g./ml.	t, °C
2,4-Dimethyl-6-ethyl	139.5	745	1.4098	0.9756	20
2,4-Diethyl-6-methyl	155.5	745	1.4131	0.9605	20
2,4-Dimethyl-6-propyl	96	80	1.4141	0.9530	20
2,4-Dipropyl-6-methyl	121	69	1.4208	0.9317	20
2,4-Dimethyl-6-isopropyl	97	140	1.4060	0.9388	31
2,4-Diisopropyl-6-methyl	113	131	1.4150	0.9234	29
2,4-Dimethyl-6-hexyl	102-103	11	1.4214	0.9167	30
2,4-Dihexyl-6-methyl	164	11	1.4337	0.8951	27
2,4-Diethyl-6-propyl	138-139	165	1.4156	0.9165	26.5
2,4-Dipropyl-6-ethyl	128	55	1.4192	0.9175	28
2,4-Dimethyl-6-β-ethoxyethyl	96	17	1.4202	0.9957	25.5
2,4-Bis(β-ethoxyethyl)-6-methyl	141-142	14	1.4294	0.9996	24
2-Hexyl-4-methyl-6-propyl	122	10	1.4289	0.9125	22
2,4-Dimethyl-6-vinyl	138-140	745	1.4199	0.999	26.5
2,4-Dimethyl-6-propenyl	94	40	1.4301	0.9826	29

Table IX

ANALYTICAL DATA ON NEW COMPOUNDS

Substituted Trioxane	C, %		H, %		Molar Refraction		Molecular Weight	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
2,4-Dimethyl-6-ethyl	57.30	57.51	10.03	9.65	37.1	37.3	144[b]	146
2,4-Diethyl-6-methyl	59.70	59.97	10.39	10.07	41.6	41.9	155[b]	160
2,4-Dimethyl-6-propyl	60.20	59.97	10.30	10.07	42.0	41.9	155[b]	160
2,4-Dipropyl-6-methyl	63.73	63.79	10.59	10.71	51.2	51.1	184[b]	188
2,4-Dimethyl-6-isopropyl	59.83	59.97	10.20	10.07	41.9	41.9	159[a]	160
2,4-Diisopropyl-6-methyl	63.87	63.79	10.68	10.71	51.1	51.1	186[b]	188
2,4-Dimethyl-6-hexyl	65.20	65.31	11.31	10.96	56.0	55.7	196[b]	202
2,4-Dihexyl-6-methyl					79.2	78.8	267[b]	272
2,4-Diethyl-6-propyl	64.05	63.79	10.92	10.71	51.5	51.1	193[a]	188
2,4-Dipropyl-6-ethyl	65.47	65.31	11.15	10.96	55.7	55.7	193[b]	202
2,4-Dimethyl-6-β-ethoxyethyl					48.4	48.1	188[b]	190
2,4-Bis(β-ethoxyethyl)-6-methyl					64.1	63.6	235[b]	248
2-Hexyl-4-methyl-6-propyl	67.9	67.8	11.20	11.38	65.1	65.0	217[b]	230
2,4-Dimethyl-6-vinyl	58.3	58.3	8.98	8.39	36.5	36.8	146[a]	144
2,4-Dimethyl-6-propenyl	60.75	60.74	9.38	8.92	41.6	41.4	154[a]	158

a. Vapor-density measurement. b. Depression of f. p. of benzene.

Table X

TOTAL ALDEHYDE CONTENT OF TRIMERS

Substituted Trioxane	Wt. 2,4-Dinitrophenylhydrazone, g. Found	Wt. 2,4-Dinitrophenylhydrazone, g. Calculated	Aldehyde, % Found
2,4,6-Trimethyl*	1.1341	1.1667	97.2
2,4-Dimethyl-6-ethyl	0.5401	0.5650	95.6
2,4-Diethyl-6-methyl	0.6590	0.6874	95.9

* Used as control

Table XI

BROMINE NUMBERS OF UNSATURATED TRIMERS

Substituted Trioxane	Bromine Number Found	Bromine Number Calculated
2,4-Dimethyl-6-vinyl	73	111
2,4-Dimethyl-6-propenyl	99	101

The attempt to copolymerize a mixture of acetone and acetaldehyde by the usual method was unsuccessful, as were attempts to copolymerize acetaldehyde and formaldehyde, either anhydrous or aqueous. A mixture of acetaldehyde and benzaldehyde also resisted copolymerization.

Anhydrous formaldehyde reacted with propionaldehyde, but fractionation of the reaction mixture was unsatisfactory owing to the close proximity of boiling points of the various substances in the reaction mixture. The molecular weight of the lowest-boiling fraction (136°/746 mm.) corresponded to the trimer with molecules consisting of two formaldehyde and one propionaldehyde units. However, the molar refraction of this fraction was considerably higher than the theoretical values obtained from the calculations based on either the structure consisting of two formaldehyde and one propionaldehyde units or that consisting of one formaldehyde and two propionaldehyde units.

The attempt to prepare either oxadithiane or dioxathiane by passing a limited amount of hydrogen sulfide into an acidified aqueous solution of formaldehyde was unsuccessful. The only substance isolated was trithiane, the cyclic trimer of thioformaldehyde.

DISCUSSION

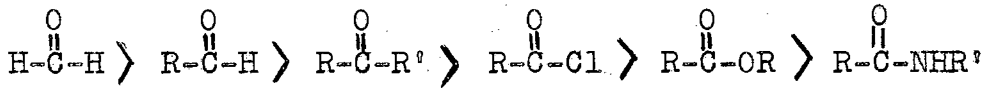
The results obtained from the acid-catalyzed polymerization of various binary aliphatic aldehyde mixtures to the corresponding unsymmetrical trimers indicate that the reaction may be considered general, and if desired, could probably be extended to other aldehyde mixtures. Any aldehyde that will polymerize by itself will probably cotrimerize with other similar aldehydes. Bevington's (8) supposition that only halogenated aldehydes will cotrimerize is obviously baseless.

However, any attempt to survey and compare the reactivity of the aldehydes used in this work by comparison of trimer yields would be of no practical significance since the unsymmetrical trimers separated during fractionation of the reaction mixtures were only the middle portions. The reported yields, therefore, do not at all represent the actual amounts present in the reaction mixtures.

It should be noted that the most reactive of the aldehydes, formaldehyde, did not lead to pure cotrimers. However, the failure of separation of formaldehyde-acetaldehyde cotrimers by distillation is accountable when it is noted that trioxane boils at 115° and paraldehyde at 124°, so that the two cotrimers must boil between these temperatures--four compounds within nine degrees! Anhydrous formaldehyde gave every evidence of copolymerizing with propionaldehyde, but separation of the unsymmetrical trimers was again incomplete and consequently characterization of the lowest-boiling fraction was inconclusive. This work might profitably be repeated using a more precise fractionation column to effect a clean separation of the unsymmetrical trimers. Formaldehyde may very well be copolymerized with other higher aldehydes in order to form unsymmetrical trimers possessing a greater differential in their boiling points, thus permitting precise fractionation of these compounds.

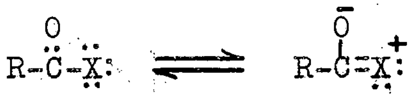
Unsymmetrical trimers containing formaldehyde may possibly be prepared by treating a mixture of either trioxane and aldehyde or trioxane and trimer with hydrogen chloride at about -10^{0} and allowing the reaction mixture to attain equilibrium. Since equilibrium between monomer and trimer is of a dynamic nature, it is quite possible that interchange of aldehydes between trimers may occur, thus forming both unsymmetrical trimers. This method, if successful, is not only convenient, but obviates the necessity of preparing anhydrous formaldehyde gas. Of course, it has nothing to do with the difficulty of separating the products.

Since the reactivity of a carbonyl group is markedly influenced not only by the presence of adjacent substituents, but also upon the nature of these substituents, the factors influencing relative reactivities of carbonyl groups may well be examined. It is generally known that adjacent substituents which increase the positive character of the carbonyl carbon atom invariably increase the reactivity of the carbonyl group towards addition reactions. Thus it is well known empirically that reactivity of a carbonyl group generally decreases in the order:



$$H-\overset{O}{\overset{\|}{C}}-H > R-\overset{O}{\overset{\|}{C}}-H > R-\overset{O}{\overset{\|}{C}}-R' > R-\overset{O}{\overset{\|}{C}}-Cl > R-\overset{O}{\overset{\|}{C}}-OR > R-\overset{O}{\overset{\|}{C}}-NHR'$$

The extreme reactivity of formaldehyde is probably due to the negligible electron-donating character of the hydrogen atom. The alkyl groups of higher aldehydes are electron-donating to some extent, and these aldehydes are therefore less reactive than formaldehyde. The effect of two alkyl groups materially increases the pressure of electrons toward the carbonyl group, thus reducing the positive character of the carbonyl carbon atom, which in turn decreases the reactivity of the carbonyl group. Substituents which are attached to the carbonyl carbon atom and posses a pair of free electrons make possible the following type of resonance, thus considerably decreasing the positive character of the carbonyl carbon atom.



$$R-\overset{O}{\ddot{C}}-\ddot{X}: \rightleftharpoons R-\overset{\bar{O}}{\overset{|}{C}}=\overset{+}{X}:$$

Electronegative substituents adjacent to the carbonyl group increase the positive character of the carbonyl carbon atom, thus enhancing the reactivity of the carbonyl group. This inductive effect is noted in the formation of stable hydrates by chloral and glyoxal. Although halogen-substituted acetaldehydes readily polymerize, it is speculative whether they can be considered more reactive than acetaldehyde. It would be informative to attempt the copolymerization of a halogen-substituted acetone with an aldehyde since the inductive effect of the halogen atoms may possibly increase the reactivity of the carbonyl group sufficiently to undergo the usual type of copolymerization. Cyclopentanone and cyclohexanone have repeatedly been found more reactive as carbonyl compounds than acetone is; possibly they too would copolymerize with formaldehyde.

The complete unreactivity of benzaldehyde in copolymerization as in polymerization must be due to the electronic effect of the conjugated benzene ring. Since cyclohexanecarboxaldehyde polymerizes to the corresponding trimer, it appears that steric hindrance is not an important factor in this instance. This electronic or conjugation effect is emphasized by the difficulty encountered in copolymerizing acrolein and crotonaldehyde with acetaldehyde. The small amounts of unsymmetrical trimers obtained from these reactions indicate the inhibiting effect of conjugated double bonds upon the reactivity of the carbonyl group regarding its tendency to undergo this type of polymerization. It may further be noted that glyoxal, which has conjugated double bonds of another sort, is not known to polymerize to a trioxane; its polymers are of a different kind.

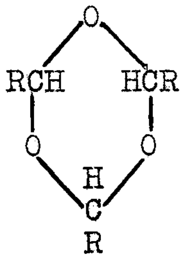
It should not be supposed, however, that steric effects play no part in such additive reactions as polymerization and copolymerization. Campaigne (13) has suggested that one reason thiocarbonyl compounds polymerize so much more completely than carbonyl compounds is the larger size of the sulfur atom compared to oxygen.

The attempt to prepare oxadithiane and dioxathiane by passing hydrogen sulfide into aqueous formaldehyde was unsuccessful, although this corresponds to the way that the methyl homologs were made from hydrogen sulfide and acetaldehyde. Apparently the extreme reactivity of thioformaldehyde or else the insolubility of trithiane drive the reaction to exclude oxygenated units from the ring. It may be possible that treating an acidified solution of trioxane with hydrogen sulfide would be more successful.

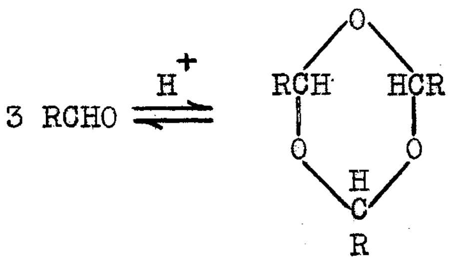
PART II

HISTORICAL

Cyclic aldehyde trimers (I) depolymerize only very slowly at ordinary temperatures and under neutral or alkaline conditions. However, these trimers are all readily depolymerized in the presence of acidic reagents such as strong mineral and organic acids, zinc chloride, sulfur dioxide, and carbonyl chloride until equilibrium is attained between monomer and trimer (49, 91). At temperatures above 200°, in the vapor phase, depolymerization is complete in the presence of these catalysts.



I



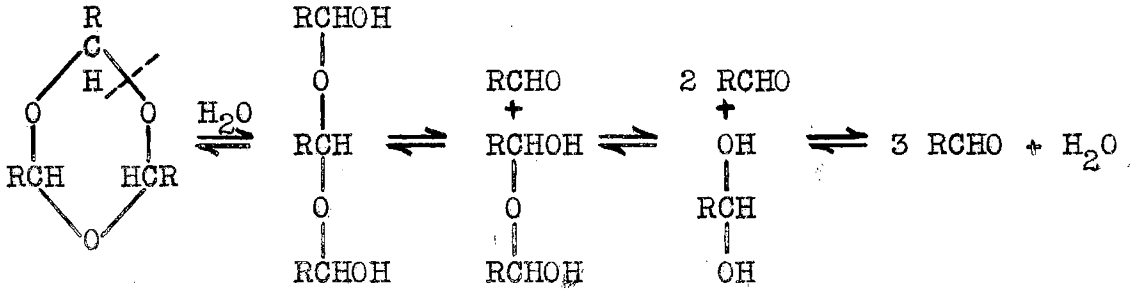
Although the effect of various catalysts and solvents upon the equilibrium of the system monomer-trimer has been frequently investigated, such study has been limited almost wholly to trioxane and paraldehyde. Likewise, the rate at which this equilibrium is established in aqueous and non-aqueous solvents has been studied only for trioxane and paraldehyde.

The only kinetic study of approaching equilibrium from the monomer was conducted by Hatcher (43, 44). He examined the polymerization of pure acetaldehyde to paraldehyde at 15° using phosphoric acid as catalyst. The reaction at low concentrations of catalyst is of the third order. At higher concentrations of catalyst the specific reaction rate tends to increase with time. The velocity of the reaction is directly proportional to the quantity of added catalyst. Hatcher also studied the reaction in benzene solution with similar results.

Depolymerization of Trioxane and Paraldehyde in Aqueous Solutions.

At a given temperature and a given acid concentration in aqueous solution, trioxane hydrolyzes at a much slower rate than paraldehyde (79, 96). The depolymerization of both trimers is a first-order reaction. However, the reaction of highly concentrated trioxane solutions deviate from first-order kinetics in that the rate increases rapidly with increasing concentration of trioxane.

Skrabal (79) has postulated the following mechanism for the hydrolysis of these trimers:



The first step of the reaction is accelerated by hydrogen ions and is rate-determining. The subsequent reactions proceed intramolecularly. It has been observed that these rate measurements were not satisfactorily reproducible (79). Bell (5) attributes these anomalous results to the irreversible polymerization of acetaldehyde to aldol and other substances.

Turbaba (91) has studied the effect of a series of acids upon the rate of depolymerization of paraldehyde in aqueous solutions and observed that the catalytic effect of an acid is directly proportional to its conductivity, i. e., the strong acids are much more effective than the weaker, less ionized acids. The addition of salts such as potassium chloride to these acid solutions effects an increase in the rate of depolymerization.

Depolymerization of Trioxane in Nonaqueous Solution.

Walker (96) has determined the rates of depolymerization of trioxane in glacial acetic acid, benzene, toluene, and trichloroethylene, using various acids and salts as catalysts. It was observed that nonaqueous solutions require relatively low concentrations of strong acids compared to the concentrations of acid required in aqueous solutions to effect a comparable rate of depolymerization. For example, in glacial acetic acid with sulfuric acid as catalyst, the reaction proceeds a thousand times as fast as in water at the same acid concentration.

The catalytic effect of various reagents was compared in toluene and trichloroethylene and it was found that all catalysts were more effective in the former solvent.

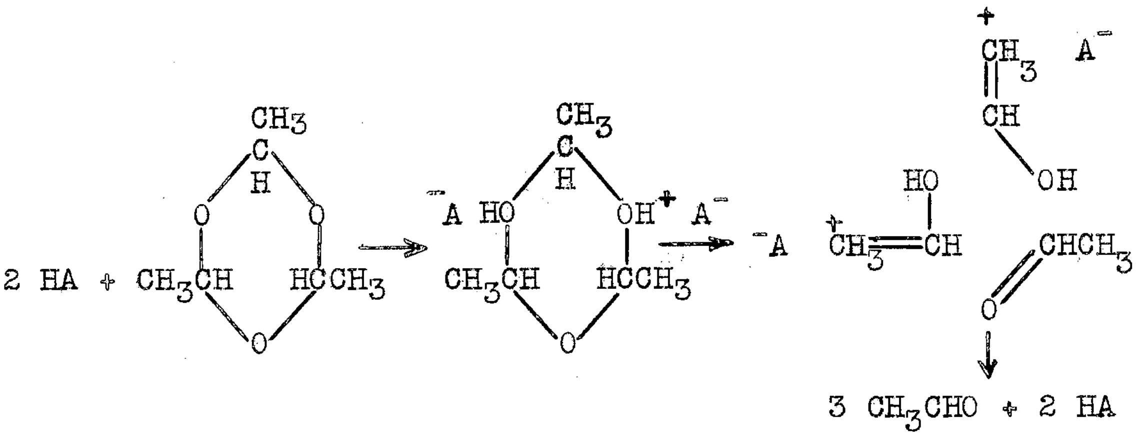
Depolymerization of Paraldehyde in Nonaqueous Solvents

Bell (5) has studied the rate of depolymerization of paraldehyde in various acidified nonaqueous solutions between 0° and 150°. The reaction was followed by a dilatometric and an analytical method. The analytical method consisted of the determination of acetaldehyde by the bisulfite method.

The reaction is first order with respect to paraldehyde and varies in order between 1.5 and 2.5 with respect to the acid. Under identical conditions, the catalytic effects of a series of acids correspond to their respective acid strengths.

The solvent exerts a modifying influence upon the catalytic effect of the acid. The rate of depolymerization in various solvents under the same conditions decreases according to the following sequence: nitrobenzene, benzene, anisole, and amyl acetate. It is believed that the decrease in velocity in anisole and amyl acetate is due to combination of the acid with the basic oxygen atoms of these substances.

Bell (5) has proposed the following reaction mechanism for the depolymerization of paraldehyde:



Bell has thus suggested that one or more protons may become attached to the basic oxygen atoms and in this way weaken the carbon-oxygen bonds and effect rupture of such bonds.

Depolymerization of Trimers in the Gaseous State

The rates of depolymerization of trioxane and paraldehyde in the gaseous state under various conditions of temperature and pressure have been thoroughly investigated (4, 3, 17, 18). At temperatures above 100° the reaction proceeds without catalysts. However, the acid-catalyzed depolymerizations of both trimers in the vapor state have been studied in the presence of hydrogen chloride and hydrogen bromide. The reaction has been found to be homogeneous and of the first order in either the presence or absence of catalyst.

The depolymerization of parabutyraldehyde and paraisobutyraldehyde have also been studied in the vapor phase. These trimers also decompose according to first-order kinetics (19).

EXPERIMENTAL

The symmetrical cyclic trimers used in this work were prepared in the same general manner as were the unsymmetrical trimers. This procedure is discussed in detail in the experimental section of Part I. The solvents used in this research, anisole and nitrobenzene, were obtained from The Matheson Company, Inc. These were dried over sodium and then distilled. Trichloroacetic acid was purchased from Baker and Adamson. Being reagent grade, it was used as such.

Analytical Method.

The amount of monomeric aldehyde formed during the reaction was determined by a modified bisulfite method (21, 57, 67, 85). The analytical solution consisted of 20 ml. of freshly-prepared 0.5 M sodium bisulfite, 6 ml. of 3 M potassium bicarbonate, and 5 ml. of ethyl alcohol. The procedure followed throughout this work is as follows:

To the analytical solution contained in a 125-ml. ground-glass-stoppered Erlenmeyer flask, 2 ml. of the reaction mixture was transferred by means of a pipette. The solution was swirled for about 5 minutes and then 3 ml. of dilute acetic acid was added. Most of the excess bisulfite was oxidized by means of 0.4 M iodine solution. When the end-point was approached, several ml. of starch indicator were added and the remaining excess bisulfite was precisely oxidized by means of standard iodine solution (about 0.05 N) added in very small portions. Small amounts of solid sodium bicarbonate were carefully added to the solution and the bisulfite liberated from the aldehyde-bisulfite compound by the alkaline solution was titrated to the iodine color again with dilute standard iodine solution. The process of adding bicarbonate and titrating back to the iodine color was continued until a permanent iodine end-point was attained in the presence of an excess of sodium bicarbonate.

The reliability of this method was determined by analysis of prepared aldehyde solutions. The results are tabulated below:

Aldehyde	Solvent	$\frac{\text{Aldehyde Found} \times 100}{\text{Aldehyde Present}}$
Propionaldehyde	Nitrobenzene	95, 100
Isobutyraldehyde	Anisole	95, 96
Heptaldehyde	Anisole	95, 96
Heptaldehyde	Nitrobenzene	95, 99

The rate measurements of the depolymerization of these trimers was followed as follows:

The solvents were maintained in the thermostat at $30^\circ \pm 0.2^\circ$ for about two hours before use. After the flask containing the solvent was weighed, the trimer was added and thoroughly mixed with the solvent before weighing again. The trichloroacetic acid was added and the time noted. After re-weighing, the tightly stoppered flask was placed in the thermostat. At selected intervals, 2 ml. of the reaction mixture was transferred to the prepared analytical solution and analyzed for free aldehyde. These samplings and analyses were repeated until equilibrium had been attained. The density of each reaction mixture was determined by weighing the quantity of liquid transferred by the pipette.

The data for two experiments are given in Tables I and II. The unimolecular velocity constants were computed from the kinetic equation for a reaction of the first order:

$$k = \frac{2.3}{t} \times \log \frac{a}{a-x}$$

where a is the initial concentration of trimer (expressed as monomer) in moles per 1000 g. of solution and x is the amount of free aldehyde formed at time t in moles per 1000 g. of solution. The specific reaction rates were also evaluated by obtaining the slope of the plot of t against log (a-x). The slope of the line is equal to -2.3/k. The linear plots obtained throughout this work confirm that the depolymerization of these trimers in dilute solution is first order with respect to the trimers. The plots obtained from the data of Tables I and II are included. The order of the reaction with respect to the acid is obtained from the slope of the plot of log c against log k. These plots are also included.

Table I

RATE OF DEPOLYMERIZATION OF PARAISOBUTYRALDEHYDE IN ANISOLE WITH 0.701 MOLAL TRICHLOROACETIC ACID

t, min.	100x	100(a-x)	10^3k	t, min.	100x	100(a-x)	10^3k
0	0.00	6.55	----	70	3.51	3.04	11.0
10	0.65	5.90	10.2	85	4.04	2.51	11.3
20	1.29	5.26	10.9	105	4.50	2.05	11.0
30	1.88	4.67	11.3	132	4.97	1.58	10.8
40	2.40	4.15	11.4	190	5.65	0.90	10.4
50	2.80	3.75	11.3	510	6.34	----	----
60	3.29	3.26	11.6	816	6.34	----	----

Mean $k = 11.0 \times 10^3$ From graph, $k = 10.9 \times 10^3$

Table II.

RATE OF DEPOLYMERIZATION OF PARAPROPIONALDEHYDE IN NITROBENZENE WITH 0.1125 MOLAL TRICHLOROACETIC ACID

t, min.	100x	100(a-x)	10^3k	t, min.	100x	100(a-x)	10^3k
0	0.00	5.75	----	38	3.40	2.35	23.5
5.5	0.50	5.25	17.7	49	3.88	1.87	22.9
10	1.10	4.65	21.4	60	4.24	1.51	22.3
15	1.62	4.13	22.1	78	4.70	1.05	21.7
20.5	2.15	3.60	22.8	110	5.15	0.60	20.5
29	2.90	2.85	24.1	267	5.35	----	----

Mean $k = 21.9 \times 10^3$ From graph, $k = 23.0 \times 10^3$

In the following tables c_a = acid concentration, moles per 1000 g. of solution; c_t = trimer concentration, weight per cent; k = unimolecular specific reaction rate.

Table III

EQUILIBRIA AND RATES IN DEPOLYMERIZATION OF TRIMERS IN NITROBENZENE

Parapropionaldehyde

c_a	c_t	% RCHO at equil.	10^3k
0.1125	0.335	93	23.0
0.1315	0.220	94	32.1
0.1670	0.279	93	35.2
0.1785	0.352	94	72.1
0.2475	0.291	91	144

Parabutyraldehyde

c_a	c_t	% RCHO at equil.	10^3k
0.0633	0.441	94	16.0
0.0877	0.366	95	41.6
0.1090	0.409	99	83.1

Paraisobutyraldehyde

c_a	c_t	% RCHO at equil.	10^3k
0.1355	0.400	96	18.2
0.1616	0.509	97	28.6
0.1835	0.483	100	42.7
0.2195	0.256	99	72.1

Paravaleraldehyde

c_a	c_t	% RCHO at equil.	10^3k
0.0646	0.430	93	4.42
0.0888	0.441	96	11.8
0.1258	0.492	96	28.5

Paraisovaleraldehyde

c_a	c_t	% RCHO at equil.	10^3k
0.0539	0.403	87	2.94
0.0693	0.508	84	5.56
0.1207	0.438	86	18.7
0.1170	0.620	83	19.3
0.1500	0.508	82	31.1

Table IV

EQUILIBRIA AND RATES IN DEPOLYMERIZATION OF TRIMERS IN ANISOLE

Parapropionaldehyde

c_a	c_t	% RCHO at equil.	10^3k
0.441	0.341	94	3.38
0.494	0.336	94	4.62
0.568	0.405	94	6.50
0.689	0.390	94	11.0

Parabutyraldehyde

c_a	c_t	% RCHO at equil.	10^3k
0.510	0.403	95	4.46
0.610	0.442	97	7.08
0.762	0.490	92	11.8

Paraisobutyraldehyde

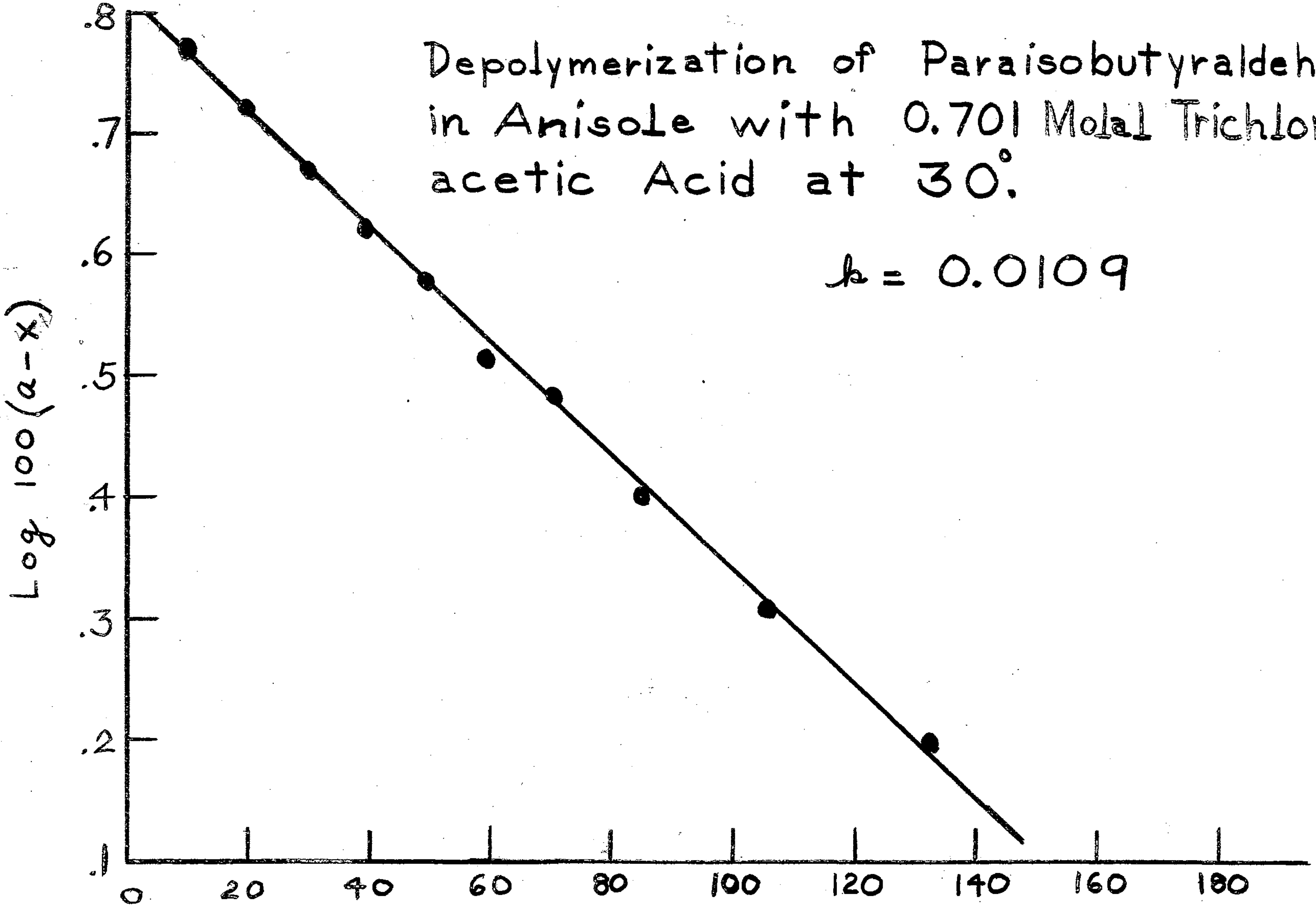
c_a	c_t	% RCHO at equil.	10^3k
0.402	0.390	97	2.85
0.478	0.410	97	4.44
0.589	0.417	97	7.21
0.701	0.468	97	10.9

Paravaleraldehyde

c_a	c_t	% RCHO at equil.	10^3k
0.390	0.530	91	2.81
0.631	0.526	92	8.69
0.758	0.453	92	13.7

Paraisovaleraldehyde

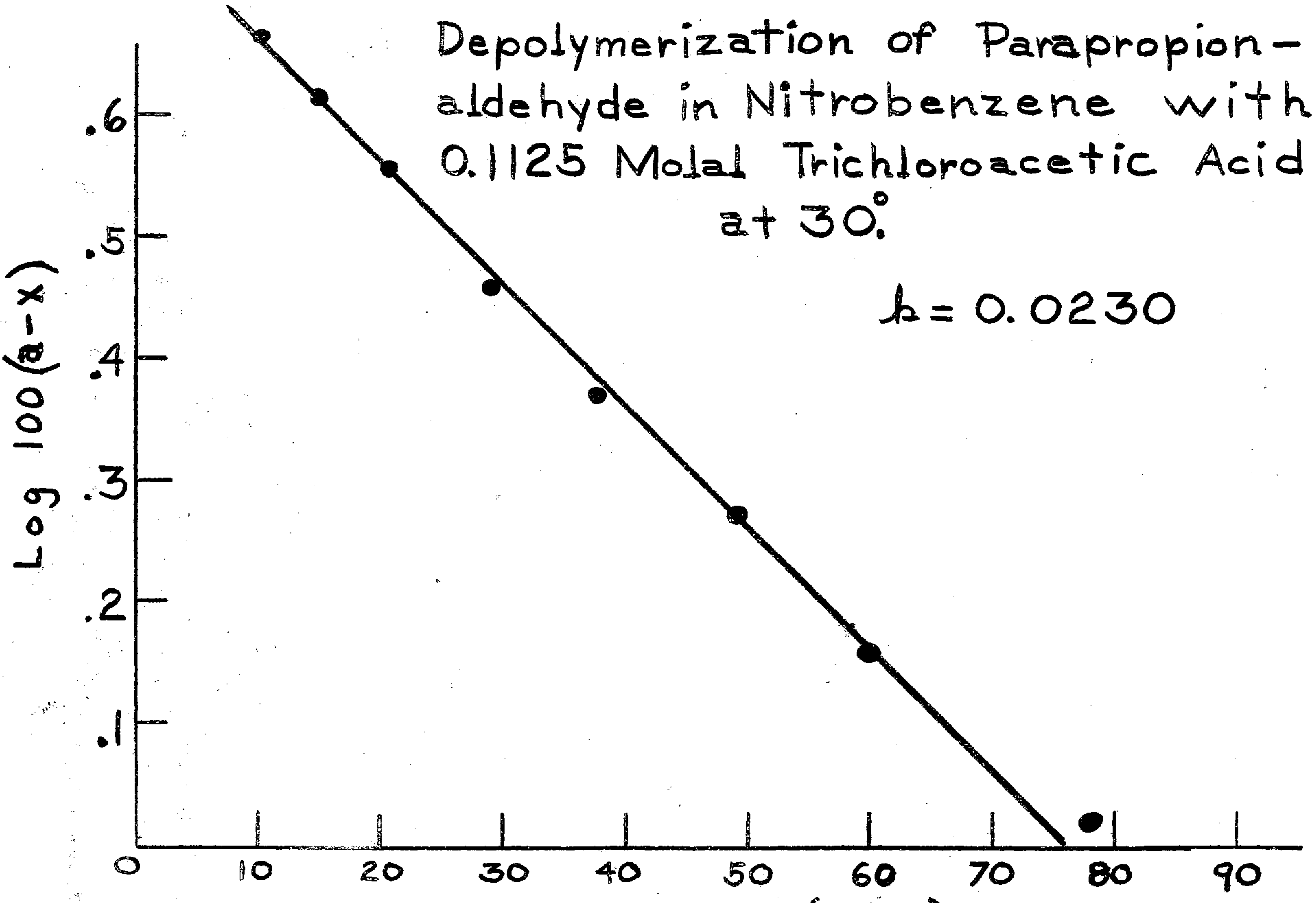
c_a	c_t	% RCHO at equil.	10^3k
0.403	0.709	92	2.66
0.530	0.669	92	5.5
0.716	0.694	91	13.7



Depolymerization of Paraisobutyraldehyde in Anisole with 0.701 Molal Trichloro-acetic Acid at 30°.

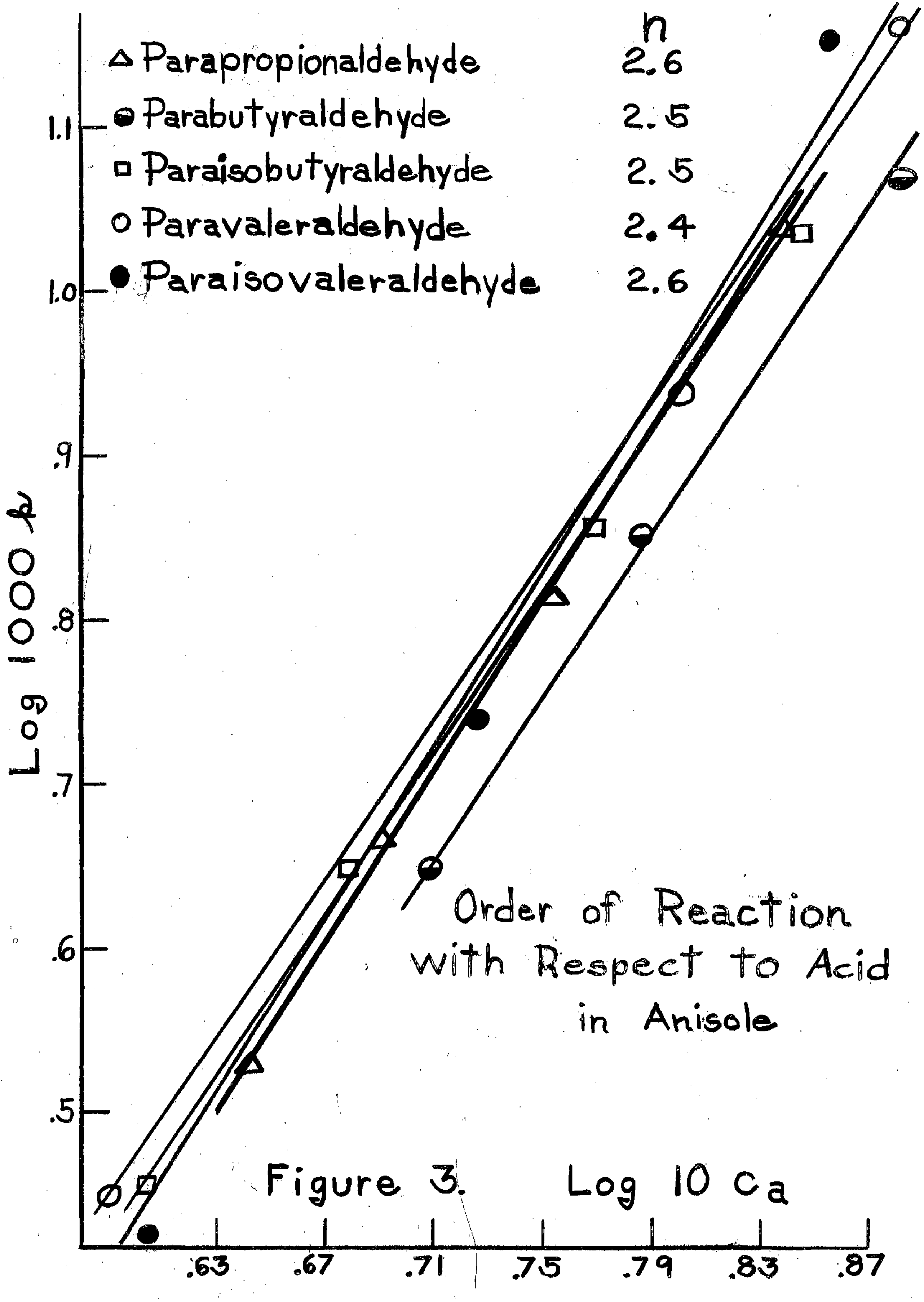
$k = 0.0109$

Figure 1.



Depolymerization of Parapropionaldehyde in Nitrobenzene with 0.1125 Molal Trichloroacetic Acid at 30°.

Figure 2.



Order of Reaction with Respect to Acid in Anisole

Figure 3.

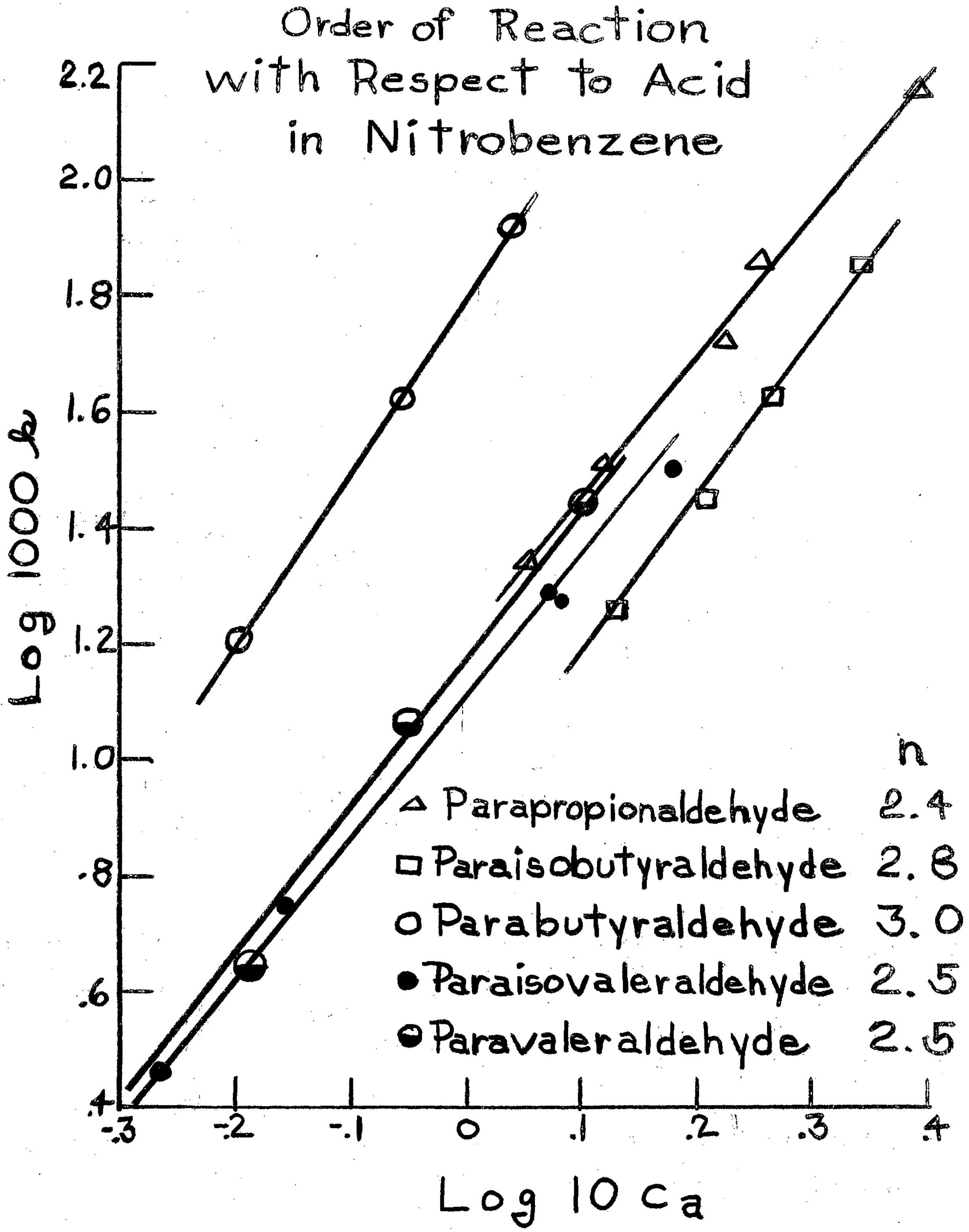

Order of Reaction with Respect to Acid in Nitrobenzene
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
Log 1000 k
-.3
-.2
-.1
0
.1
.2
.3
.4
Log 10 ca
n
△ Parapropionaldehyde 2.4
□ Paraisobutyraldehyde 2.8
○ Parabutyraldehyde 3.0
● Paraisovaleraldehyde 2.5
⊖ Paravaleraldehyde 2.5

Figure 4.

DISCUSSION

The results obtained from the acid-catalyzed depolymerization of the cyclic aldehyde trimers substantiate and extend the work of Bell (5). Bell studied the effect of varying nature of the acid, acid concentration, temperature, and solvent; the present work studied the effect of varying the trimer substrate, the acid concentration, and the solvent. All the trimers in dilute solution depolymerize according to first order kinetics, irrespective of solvent. It is also seen that for a given quantity of acid, in a particular solvent, the rate of depolymerization of each trimer is approximately the same. Thus it appears that the size of the substituted alkyl group not only has practically no effect upon the rate and order of the reaction, but has little effect upon the equilibrium between monomer and trimer.

It is believed that the initial step occurring in the rupture of these C-O linkages of the trioxane ring consists of proton attack upon the basic oxygen atoms. Since the order of the reaction with respect to acid is about 2.5, it appears that, in the main, the rupture of these bonds is effected by the attack of either two or three protons upon these linkages. The contribution to the depolymerization made by a single proton attack can be considered negligible. The mechanism by which subsequent degradation of the complex occurs is uncertain, but it is believed to occur rapidly.

It is also observed, in agreement with Bell, that depolymerization occurs much faster in nitrobenzene than in anisole. The role of the solvent upon the reaction is obscure. Since nitrobenzene has a greater dielectric constant than anisole, it is possible that the acid ionizes to a greater extent in the former solvent, thus making more protons available for the reaction and consequently allowing the reaction to proceed at a greater rate. Another possible explanation for the disparity of reaction rates in these solvents may be had in a consideration of their basicities. Anisole is an ether and is known to associate appreciably with acids; such a process would reduce the amount of acid available in the reaction. Nitrobenzene has little tendency to combine with acids; and, therefore, more protons would be available for the depolymerization.

The effect and role of the solvent upon the rate of depolymerization of these trimers could better be studied by measuring the rate of depolymerization in a series of solvents of selected dielectric strengths at constant acid concentration. The conductivity of these solutions could be determined in order to obtain the degree of ionization of the acid in the solvent. Thus evaluation of dielectric constant, rate of depolymerization, and conductivity of these solutions might very well clarify the role of the solvent.

SUMMARY

A series of new unsymmetrical trimers was prepared by copolymerizing various aliphatic aldehyde mixtures in the presence of hydrogen chloride. Mixtures of saturated aldehydes, simple or substituted, readily copolymerized, whereas binary mixtures containing an unsaturated aldehyde reacted with difficulty, forming in each instance only a little of the trimer containing two saturated aldehyde and one unsaturated aldehyde units. The suggestion that these cotrimers must contain at least one halogenated aldehyde unit is manifestly untrue.

A ternary aldehyde mixture of acetaldehyde, butyraldehyde, and heptaldehyde was successfully copolymerized. The trimer containing three dissimilar aldehyde units was separated from the complex reaction mixture with difficulty.

Attempts to copolymerize acetaldehyde and formaldehyde may have succeeded but fractional distillation of the reaction mixture was unsatisfactory, presumably because the boiling points of the simple and mixed trimers are too close together. It appears quite certain that formaldehyde and propionaldehyde were successfully copolymerized, but again separation by distillation was incomplete. The molecular weight and molar refraction of the first fraction indicated that it may be a mixture of the two unsymmetrical trimers.

Copolymerization of acetaldehyde with benzaldehyde and with acetone was unsuccessful, as was the attempt to prepare

an oxygen-sulfur heterocyclic trimer from hydrogen sulfide and formaldehyde.

A kinetic study of the acid-catalyzed depolymerization of a homologous series of symmetrical trimers was made at various concentrations of trichloroacetic acid and in two dissimilar solvents, anisole and nitrobenzene. The results of this work indicate that the size of the substituted alkyl group has virtually no effect upon the rate of depolymerization of a trioxane, and little effect on the extent of depolymerization at equilibrium. In agreement with Bell, the depolymerization of these trimers was found to be first order with respect to the trimers and approximately 2.5 in order with respect to the acid, irrespective of solvent. The reaction proceeded much faster in nitrobenzene than in anisole.

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