changed from $a = 5.40$ in the unmercerized to $a = 4.53$ in the mercerized and from $b = 6.10$, to $b = 7.61$ Å. The angle between axes a and b has been changed from 90 to 83°.

3. As a result of mercerization the chains of glucose units have been shifted laterally in the wall of the fiber and have remained unbroken.

4. Within the chain the original glucose unit has remained unchanged except for a shift of the hydroxyl of the sixth carbon atom. The x-ray diffraction patterns indicate that there has been a partial rotation of some of the glucose units about the long axis of the chain.

5. A comparative study of the structures of mercerized and unmercerized cellulose has produced additional support to the view that the constituent units of cellulose are united in chains by primary valence linkages.

LOS ANGELES, CALIFORNIA
BERKELEY, CALIFORNIA

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XIV. POLYMERIZATION OF ALDEHYDES

BY HAROLD HIBBERT, W. F. GILLESPIE[1] AND R. E. MONTONNA[2]

RECEIVED MARCH 8, 1928 PUBLISHED JULY 6, 1928

The nature of polymerization, aggregation and disaggregation is one of peculiar importance in relation to the valence, surface tension, crystal and absorption forces which come into play in the formation of large crystalline and colloidal aggregates in plant and animal life, since "permanence of form" and "capacity to exist" are both dependent on the ability of specific substances to exhibit the pheonomenon of "aggregation." The nature of the forces through which this increased permanence and stability are attained is, as yet, quite unknown, as is evident from the work of Bergmann,[3] R. O. Herzog,[4]

---

[1] Presented to the Faculty of the Graduate School, McGill University, June, 1927, in candidacy for the degree of Master of Science.

[2] Taken in part from the thesis of R. E. Montonna as presented to the Graduate School of Yale University in June, 1924, in candidacy for the degree of Doctor of Philosophy.

[3] Bergmann, "Allgemeine Strukturchemie der complexen Kohlenhydrate und Proteine," *Ber.*, **59**, 2973 (1926); "Beiträge zur Chemie hochmolekularer Stoffe," *Ann.* **445**, 1 (1925); "Über den hochmolekularen Zustand von Kohlenhydraten und Proteinen und seine Synthese," *Z. angew. Chem.*, **38**, 114 (1925); *Naturwissenschaften*, **1925**, p. 1045; "Über ein assoziierendes Hexosan," *Ann.*, **448**, 76 (1926).

[4] Herzog, "Published Researches from the Kaiser Wilhelm Institut für Faserstoffchemie," **1920–1927.**

H. Mark,[5] Hess,[6] Pringsheim,[7] Staudinger,[8] Karrer,[9] Waldschmidt-Leitz[10] and others.[11]

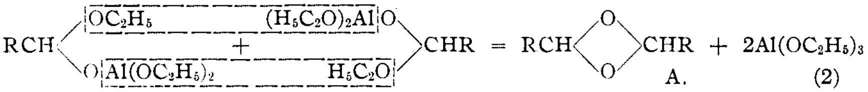
As illustrating the complexity of the problem involved, the recent work of Bergmann,[12] on cellobiose anhydride and of Hess[6d] on cellulose may be cited. In the form of their acetates these substances are present in solution as monomolecular derivatives which, however, on saponification yield the original, highly polymerized, hydroxy compounds.

There seems to be little doubt, as suggested by Bergmann,[13] that in the case of the polysaccharides the factors responsible for the polymerization are concerned with the *entire* molecule (*a*) the hydroxyl groups, (*b*) latent aldehyde groups and (*c*) oxygen bridge rings.

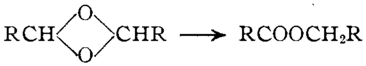
In order to throw some light on the subject, work has been carried out for some considerable time by the author and his co-workers on the properties of the carbonyl group.

In connection with an investigation carried out several years ago on the mechanism of the formation of esters from aldehydes by the catalytic action of an aluminum alkylate (Tischtschenko)[14] it seemed possible that the function of the catalyst might be explained by the formation of an intermediate, unstable four-membered oxygen ring (A) which, through

$$2RCHO + 2Al(OC_2H_5)_3 = 2RCH(OC_2H_5)[OAl(OC_2H_5)_2] \qquad (1)$$



(2)



(3)

---

[5] Mark, "Über die roentgenographische Ermittelung der Struktur organischer besonders hochmolekularer Verbindungen," *Ber.*, **59**, 2982 (1926).

[6] (a) Hess, "Über Cellulose," *Ann.*, **435**, 1 (1923); (b) *Papierfabrikant*, **35**, 541 (1927); (c) *Kolloid-Chemische Beihefte*, **1926**, p. 93; (d) "Ueber Lösung und Abbau von Cellulose, ein Beitrag zur Chemie hochmolekularer Körper," *Z. angew. Chem.*, **39**, 1189 (1926); see also (e) *Naturwissenschaften*, **19**, 435.

[7] Pringsheim, "Abbau und Aufbau der hochmolekularen organischen Stoffen," *Ber.*, **59**, 3008 (1926).

[8] Staudinger, "Die Chemie der hochmolekularen organischen Stoffen," *Ber.*, **59**, 3019 (1926).

[9] Karrer, "Der Aufbau der polymeren Kohlenhydrate," see *Ergebnisse der Physiologie*, **20**, 443 (1922).

[10] Waldschmidt-Leitz, "Zur Struktur der Proteine," *Ber.*, **59**, 3000 (1926).

[11] For synopsis see "Handbuch der normalen und pathologischen Physiologie," **1927**, pp. 922–924.

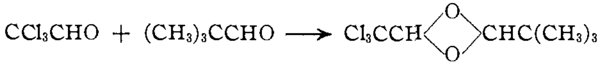
[12] Bergmann, *Ber.*, **57**, 1276 (1924).

[13] Bergmann, *Ann.*, **445**, 5 (1925).

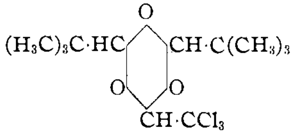
[14] Tischtschenko, *J. Russ. Phys. Chem. Ges.*, **38**, 355, 482 (1906); *Chem. Centr.*, **1906**, (II), 1309, 1552.

the wandering of a hydrogen atom would be capable of yielding the corresponding ester.[15]

An attempt to prepare such a ring by the interaction of chloral with trimethylacetaldehyde



yielded instead a mixed paraldehyde, formed from the union of two moles of trimethylacetaldehyde with one of chloral



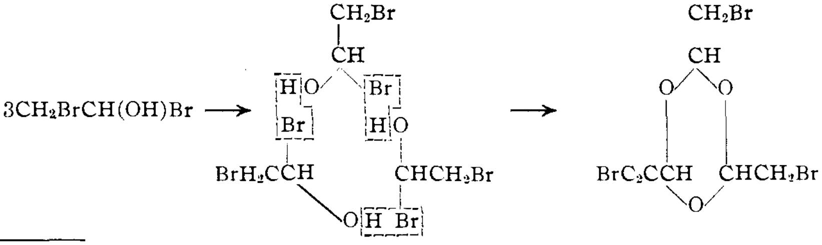
The substance[16] is a crystalline product, remarkably stable toward aqueous and alcoholic alkali. Owing to a temporary interruption in the work it was not possible to carry it further and in the meantime two other interesting communications on the same subject have appeared.

Helferich[17] has shown that mixed paraldehydes can be obtained readily from acetaldehyde and both the halogenated butyraldehydes and chloral in which two moles of acetaldehyde are united with one mole each of the chlorinated aldehydes.

These products are oils which possess a strong paraldehyde odor, are difficultly soluble in water and decompose slowly into their component parts on standing, more rapidly under the influence of acids.

Stepanow and co-workers[18] in an interesting re-investigation of the work of Hibbert and Hill[19] on the synthesis of bromo-acetaldehyde from paracetaldehyde were able to prepare mono-, di- and tribromoparacetaldehydes.

They also were able to isolate α,β-dibromo-ethyl alcohol [$CH_2BrCH(OH)Br$] and to show that the product readily loses hydrobromic acid to give tribromoparacetaldehyde, thus indicating the mechanism by which the acid probably functions as a catalyst in paraldehyde formation.



---

[15] A review of this and similar reactions is to be given in a series of forthcoming papers on "The Mechanism of Organic Reactions."

[16] This product was first prepared by R. E. Montonna in February, 1924.

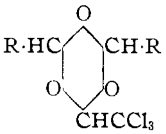
[17] Helferich, *Ber.*, **59**, 1276 (1924).

[18] Stepanow, *Ber.*, **58**, 1718 (1925); **59**, 2533 (1926).

[19] Hibbert and Hill, THIS JOURNAL, **45**, 734 (1923).

The action of other catalysts such as sulfuric acid, zinc chloride, etc., may thus be satisfactorily explained.

In the present investigation the work of Stepanow and co-workers on the bromoparaldehydes was confirmed and in addition new paraldehyde derivatives were prepared from both propionaldehyde and *iso*butyraldehyde with chloral in which two moles of each of the former are combined with one of chloral. Each of the members of a series of substituted acetaldehydes, namely, $H{-}CH_2CHO$, $CH_3{-}CH_2CHO$, $(CH_3)_2{=}CHCHO$, $(CH_3)_3{\equiv}CCHO$, is thus found to condense readily with chloral to give a mixed paraldehyde of the general type:



These paraldehydes are stable crystalline products which are insoluble in water and show no tendency to alter on standing. They decompose on continued boiling with sulfuric acid but are very stable toward alkali.

All attempts to prepare mixed paraldehydes involving three different aldehydes were unsuccessful. Thus with molecular proportions of *iso*butyraldehyde (A), propionaldehyde (B) and chloral (C), instead of the expected A B C paraldehyde derivative, there was obtained a mixture of two paraldehydes, the one being formed from two moles of propionaldehyde, the other from two moles of di-*iso*butyraldehyde with one mole of chloral.

Similar attempts using bromo-acetaldehyde in place of chloral were also unsuccessful.[20] It is of interest that a paraldehyde of hydroxypyruvic aldehyde has been isolated[21] and that the recent work of Klason[22] assigns to lignin the role of a paraldehyde derivative of coniferyl aldehyde.

Practical Part

Paraldehyde Formation from Trimethylacetaldehyde and Chloral, $CCl_3CHO + 2(CH_3)_3C{\cdot}CHO$.—14.75 g. of chloral (1 mole) was mixed with 8.6 g. of trimethylacetaldehyde[23] (1 mole) (b. p. 74–78°) at room temperature. There was an increase in tem-

---

[20] The explanation apparently lies in the different reaction velocities with which the components unite. From this standpoint it might be of interest to see whether acetol, dioxyacetone and glyceric aldehyde are capable of forming a mixed paraldehyde of the A B C type, since there is the possibility that abnormal biochemical changes possibly may be due in certain cases to the formation of the relatively stable paraldehyde derivatives, thus interrupting the normal course of oxidation, etc.

[21] Evans and Waring, THIS JOURNAL, **48**, 2679 (1926).

[22] Klason, *Ber.*, **58**, 1761 (1925); **61**, 171 (1928).

[23] This was prepared by Richard's method, *Ann. chim. phys.*, [8] **21**, 360 (1910), by first decomposing the trimethylpyruvic acid with aniline. It was found better to hydrolyze this reaction product by refluxing with 20% sulfuric acid for two hours instead of attempting to distil it as he recommends. After washing the bisulfite compound with ether and drying, it should then be decomposed with sulfuric acid and steam distilled, since sodium carbonate tends to cause polymerization.

perature of about 6°. After standing for two days the product had become almost solid. The crystals were separated from the small amount of mother liquor and recrystallized from hot, absolute alcohol, m. p. 114–115°; yield, 16 g.

Anal. Subs., 0.2700, 0.2548: H_2O, 0.1570, 0.1510; CO_2, 0.4436, 0.4222. Subs., 0.1149, 0.2183: AgCl, 0.1537, 0.2908. Calcd. for $C_{12}H_{21}O_3Cl_3$: H, 6.62; C, 45.06; Cl, 33.29. Found: H, 6.51, 6.63; C, 44.75, 45.17; Cl, 33.09, 32.96.

Mol. wt. Subs., 0.2564, 0.2817, 0.2982: benzene, 17.543. ΔT, 0.241, 0.259, 0.280. Calcd.: 319. Found: 311, 333, 311.

The substance is insoluble in hot and cold water and in dilute alcohol, readily soluble in hot absolute alcohol and cold benzene. It is very stable toward aqueous and alcoholic alkali.

The product may be obtained more readily by using a trace of concentrated sulfuric acid as a catalyst and warming until solution occurs. After standing for two hours at room temperature the semi-solid, crystalline mass is filtered and the product recrystallized.

Propionaldehyde and Chloral ($CCl_3CHO + 2CH_3CH_2CHO$).—Fourteen and one-half grams of propionaldehyde (2 moles) was mixed with 18.4 g. (1 mole) of chloral, the flask placed in a freezing mixture (−10°) and a few bubbles of dry hydrogen chloride gas passed into the mixture. The contents were allowed to stand at 0° for about twelve hours, the crystals formed removed by suction filtration, washed with a small quantity of 50% alcohol and then dissolved in absolute alcohol. The solution was diluted by adding one-fifth its volume of water and the oil separating out redissolved by warming. It was filtered hot and allowed to crystallize slowly. The crystals, after filtering, washing with alcohol (50%) and drying, melted sharply at 62.5°; yield, 35–40%

The same product was also obtained without the use of a catalyst (HCl).

Anal. Subs., 0.1804, 0.1760: H_2O, 0.0798, 0.0791; CO_2, 0.2387, 0.2391. Subs., 0.1287: AgCl, 0.2097. Calcd. for $C_8H_{13}O_3Cl_3$: H, 4.93; C, 36.43; Cl, 40.39. Found: H, 4.92, 4.98; C, 36.40, 37.00; Cl, 40.27.

Mol. wt. Subs., 0.4365, 0.8884: benzene, 17.60. ΔT, 0.490, 1.001. Calcd.: 263.5. Found: 259, 256.

*Iso*butyraldehyde and Chloral ($CCl_3CHO + 2(CH_3)_2CHCHO$).—This compound was prepared similarly, both with and without a catalyst; needle crystals from 80% alcohol; m. p. 68.5–69°; yield, 39%.

Anal. Subs., 0.1674, 0.1718: H_2O, 0.0896, 0.0891; CO_2, 0.2565, 0.2601. Subs., 0.1123, 0.1061: AgCl, 0.1680, 0.1569. Calcd. for $C_{10}H_{17}O_3Cl_3$: H, 5.83; C, 41.30; Cl, 36.58. Found: H, 5.93, 5.78; C, 41.80, 41.30; Cl, 36.84, 36.60.

Mol. wt. Subs., 0.3057, 0.8806: benzene, 17.60. ΔT, 0.310, 0.890. Calcd.: 291.5. Found: 287, 289.6.

All three paraldehydes are very insoluble in hot and cold water but are readily soluble in organic solvents. They show no sign of decomposition on standing for several months; are stable toward alkalies, but decompose on boiling with dilute sulfuric acid.

All attempts to prepare paraldehydes involving three different aldehydes (propionaldehyde, *iso*butyraldehyde and chloral; acetaldehyde, *iso*-butyraldehyde and chloral, etc.) were unsuccessful, only mixtures of paraldehydes containing two moles of the aldehyde to one mole of chloral being obtained. Negative results were also obtained using bromoacetaldehyde in place of chloral.

It was not found possible to condense acetaldol with chloral to give a mixed paraldehyde.

Summary

1. Chloral either alone or, better, in the presence of a trace of hydrogen chloride, combines with acetaldehyde,[17] propionaldehyde, *iso*butyraldehyde and trimethylacetaldehyde to give paraldehydes corresponding to the general type ($2RCHO + CCl_3CHO$).
2. It apparently does not combine with acetaldol under similar conditions.
3. Attempts to prepare a mixed paraldehyde containing three different aldehydes were unsuccessful.
4. The possible role played by such derivatives in plant and animal life would seem to call for some consideration.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE RICE INSTITUTE]

ALPHA-FURFURYL CHLORIDE (FURYL-2-METHYL CHLORIDE) AND ITS DERIVATIVES.

I. THE PREPARATION AND PROPERTIES OF ALPHA-FURFURYL CHLORIDE AND A FEW ALPHA-FURFURYL ETHERS[1]

BY W. R. KIRNER

RECEIVED MARCH 12, 1928 PUBLISHED JULY 6, 1928

The synthesis of many relatively simple derivatives of furan has hitherto been impossible or, at best, extremely difficult and complicated, due to the fact that reactive starting materials such as the ω-halogen derivatives of furan homologs have been practically unknown. A halogen in the side chain of a furan ring corresponds in reactivity to that possessed by a halogen in the side chain of a benzene ring.

Fenton and co-workers[1a] were the first to prepare a reactive halogen derivative of methylfuran when they succeeded in isolating 2-chloromethyl- and 2-bromomethyl-5-furfuraldehyde from a large variety of carbohydrates using a non-aqueous solvent (for example, ether, chloroform or carbon tetrachloride) saturated, respectively, with hydrogen chloride and hydrogen bromide. They pointed out the high order of reactivity of the halogen and prepared a number of derivatives in which the halogen was substituted by groups such as H, OH, $OCOCH_3$, $OCOC_6H_5$, C_6H_5 and $CH_2C_4H_2OCOH$, while subsequent workers[2] extended the list of sub-

---

[1] Presented before the Organic Chemistry Division of the American Chemical Society at the St. Louis meeting, April, 1928.

[1a] Fenton and Gostling, *J. Chem. Soc.*, **73**, 556 (1898); *ibid.*, **75**, 423 (1899); *ibid.*, **79**, 361, 807 (1901); Fenton and Robinson, *ibid.*, **95**, 1334 (1909).

[2] Erdmann, *Ber.*, **43**, 2392 (1910); Cooper and Nuttall, *J. Chem. Soc.*, **99**, 1197 (1911); E. Fischer and v. Neyman, *Ber.*, **47**, 974 (1914); see also Middendorp, *Rec. trav. chim.*, **38**, 23–38 (1919).