ml. of 5% ammonium nitrate solution removes practically all of the divalent metallic ions. Finally 1 mg. of the divalent metallic ions can be detected in the filtrate after precipitation of 500 mg. of any one of the trivalent or combination of them. Before testing the filtrate for the divalent ions the benzoic acid present is removed by evaporating until crystallization just begins, cooling and filtering with suction.

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Polymerization of Dihydroxyacetone

BY HAROLD H. STRAIN AND W. H. DORE

x-Ray diffraction measurements demonstrate the polymerization of crystalline monomolecular dihydroxyacetone to dimolecular dihydroxyacetone. These measurements also indicate that the polymerization begins shortly after the preparation of the monomolecular form and that it is complete in twenty-five to thirty days. At the end of this period, higher polymers and condensation products were not detectable by x-ray, cryoscopic or solubility methods.

Experimental

Dimolecular dihydroxyacetone, prepared by crystallization (from ethanol) of dihydroxyacetone which had stood for several months[1] and shown to be dimolecular by cryoscopic measurements of freshly prepared aqueous solutions, exhibited (when powdered) a clear and characteristic x-ray diffraction pattern (Column B, Table I). Monomolecular dihydroxyacetone, prepared by distillation of the dimolecular form[2] and shown to be monomolecular by cryoscopic measurements of freshly prepared aqueous solutions, likewise exhibited a clear and characteristic x-ray diffraction pattern (Column A, Table I). After crystals of the monomolecular dihydroxyacetone had stood for several days it was observed that the diffraction pattern resembled that obtained from the dimolecular form even though molecular weight determinations demonstrated that the crystals were composed of the monomolecular form. This indicated that the monomolecular form was slowly polymerizing to the dimolecular form and, in order to determine the rate of the polymerization, x-ray diffraction patterns of monomolecular dihydroxyacetone were obtained at intervals over a period of thirty days. The results indicated that, at room temperature and within the experimental error, polymerization to the dimolecular form was complete in twenty-five to thirty days and was independent of radiation with x-rays. The average molecular weight of the polymerized product determined by cryoscopic methods corresponds to that of dimolecular dihydroxyacetone.[3]

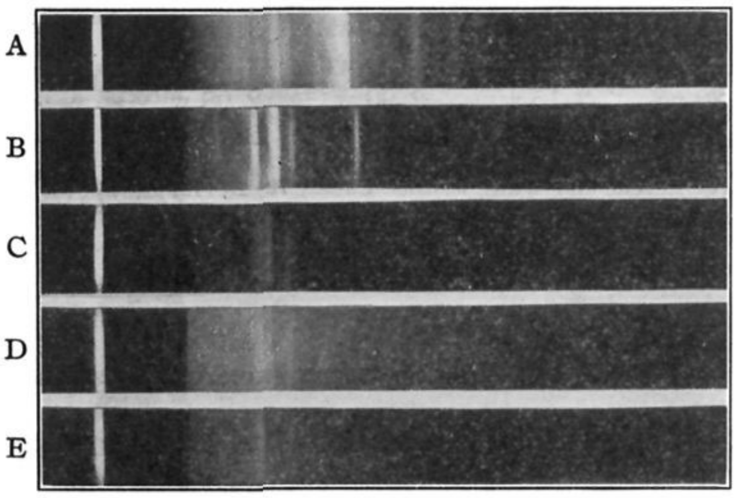

Fig. 1.—x-Ray patterns of some forms of dihydroxyacetone: A, monomolecular dihydroxyacetone, m. p. 72°; B, dimolecular dihydroxyacetone, m. p. 78–81°; C, polymolecular dihydroxyacetone, m. p. 130–133°; D, polymolecular dihydroxyacetone, m. p. 230–260° with dec.; E, polymolecular dihydroxyacetone, m. p. 230–250° with dec.

Attempts were made to determine whether or not higher polymers and condensation were

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(1) Bertrand, *Compt. rend.*, **126**, 842, 984 (1898); *Ann. chim. phys.*, [8] **3**, 215, 246 (1904).

(2) Fischer and Mildbrand, *Ber.*, **57**, 707 (1924); Reeves and Renbom, *Biochem. J.*, **25**, 412 (1931).

(3) Single crystals of dimolecular dihydroxyacetone of sufficient size for optical, goniometric and Laue diffraction measurements were obtained by crystallizing the sugar from ethanol. Optical examination revealed that the crystals were monoclinic but that they were twinned in some complex fashion and clear Laue diffraction patterns could not be obtained. The results indicated a unit cell composed of two molecules of dimolecular dihydroxyacetone. Single crystals of monomolecular dihydroxyacetone could not be obtained by crystallization because of the rapid polymerization to the dimolecular form described in this paper.

formed when dihydroxyacetone polymerized to the dimolecular form.[4] To this end, three condensation products were isolated from dihydroxyacetone which had stood for many months. Each of these products exhibited characteristic x-ray diffraction patterns (Columns C, D and E, Table I). As far as could be determined by the diffraction patterns, these condensation products were not present in the dihydroxyacetone which had stood for thirty days. The latter was readily soluble in isopropanol, a further proof of the absence of the slightly soluble condensation products.

TABLE I

INTERPLANAR SPACINGS OF DIHYDROXYACETONE

Patterns were obtained by exposure of powdered crystalline material to the Kα radiation of molybdenum. The interplanar spacings are reported in Ångström units. Intensity designations are: s, strong; m, medium; w, weak; v, very.

M. p., 72° (A)	M. p., 78–81° (B)	M. p., 130–133° (C)	M. p., 230–260° dec. (D)	M. p., 230–250° dec. (E)
5.5 m-s	6.8 w-m	6.4 w	6.3 w	5.10 vs
5.1 w	5.2 vs	5.1 vs	5.2 vs	4.25 m
4.6 m-s	4.6 vs	4.8 vs	4.8 vs	
4.3 m-s	4.2 m-s	4.3 vs	4.25 vs	
3.70 m	4.0 w	3.58 w	3.90 ?	
3.58 vw	3.65 w	3.25 w	3.55 w	
3.48 vw	3.32 vw	3.00 w	3.30 w	
3.30 vs	3.15 s	2.90 w	2.98 w	
3.18 w	2.98 w	2.75 w-m	2.76 w	
2.94 vw	2.90 w	2.57 w	2.57 w	
2.75 w	2.75 w	2.47 w	2.48 ?	
2.58 m-s	2.60 vw	2.30 w	2.12 w	
2.42 m-s	2.48 w-m	2.12 w	1.90 w-m	
2.28 m	2.40 w-m	2.01 w	1.80 w	
2.17 m	2.30 m	1.91 m		
2.12 m	2.20 m	1.80 w		
2.05 vw	2.10 m	1.70 w		
1.96 vw	2.05 w			
1.87 vw	2.01 w			
1.78 w-m	1.96 w			
1.73 w	1.85 w			
	1.82 vw			
	1.75 m			
	1.68 vw			
	1.62 w			
	1.58 w			
	1.53 ?			
	1.40 ?			
	1.30 w			
	1.25 w			

Typical x-ray diffraction patterns for monomolecular, dimolecular and polymolecular dihydroxyacetone are shown in Fig. 1. The stronger lines which are given in the lists of Table I may be identified by their sequence in the respective patterns.

Summary

Crystalline monomolecular dihydroxyacetone rapidly polymerizes to dimolecular dihydroxyacetone.

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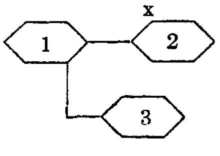
(4) Levene and Walti, *J. Biol. Chem.*, **78**, 23 (1928); Spoehr and Strain, *ibid.*, **89**, 507 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

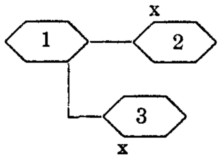
Ortho Phenyl Biphenyls and "Synchronized Rotation"

BY A. M. SADLER AND G. POWELL

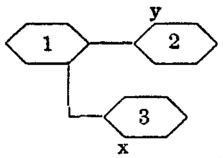
"Synchronized rotation" has been suggested as a possible cause for the non-resolution of certain ortho substituted biphenyls.[1,2] We have attempted to gain evidence concerning this postulated motion by a study of the substituted *o*-phenylbiphenyls. In this series any argument concerning the obstructive effect or shape of the substituent group is buttressed by the results already known in the simple biphenyl series from an examination in the same way. In addition, the calculated amount of obstruction is very large. We have chosen the following types for study.



"A"



"B"



"C"

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(1) Abstracted from a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Columbia University, New York, N. Y., 1934.

(2) Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933); Maclean and Adams, THIS JOURNAL, **55**, 4683 (1933).