Evidence has now been obtained which indicates that the isomeric phosphate which was obtained is that isomer which occurs as a moiety in the vitamin B_{12} molecule.

The ease of phosphoryl migration in the purine and pyrimidine nucleotides brought about by acids has been observed.[2] The conditions of acid hydrolysis, which were applied to vitamin B_{12} for its degradation to α-ribazole phosphate, might have given a mixture of the 2′- and 3′-phosphates, but only one isomer was isolated by the purification procedures used.

A study of the reaction of vitamin B_{12} with 6 N hydrochloric acid at 25°, with time as a variable, was made. The formation and isomerization of α-ribazole phosphate was determined by paper chromatography.

The results of these experiments show that, after a reaction time of 5–16 hours, only one isomer of α-ribazole phosphate was detectable in the reaction mixture; this phosphate and the isolated crystalline phosphate are identical. Furthermore, it was shown that, when the residue from one of the above reactions which contained only one isomer of α-ribazole phosphate was refluxed with 80% acetic acid, an equilibrium mixture of approximately equal parts of the two isomers was obtained. This mixture when chromatographed on paper strips gave two fluorescent spots with R_f values of 0.73 and 0.78 which corresponded to the R_f values for the isomers obtained from the isomerization[1] of the crystalline phosphate.

If the isolated phosphate does not exist as a moiety in the vitamin B_{12} molecule and is the result of a structural rearrangement of the phosphoryl group, then the rearrangement must have been essentially quantitative and not detectable by the methods used. If the isolated phosphate is the result of a partial hydrolysis of a 2′-3′-cyclic phosphate, then the hydrolysis must likewise have been essentially quantitative and unidirectional and undetected. The adenylic acids *a* and *b* have been identified[3] as the adenosine-2′- and 3′-phosphates and have R_f values of 0.74 and 0.67, respectively, in the system described below. The R_f values (0.78, 0.73) of the two α-ribazole phosphates have a magnitude and differential which are comparable with the R_f values of adenosine-2′- and 3′-phosphates. Adenosine-3′-phosphate has the lower R_f value; it is noted that the crystalline α-ribazole phosphate which appears to exist as a moiety in vitamin B_{12} has the lower R_f value and by analogy would be α-ribazole-3′-phosphate (II); this deduction is only tentative.

Experimental

Two and one-half mg. of cyanocobalamin was dissolved in *ca.* 2 ml. of 6 N hydrochloric acid, and after *ca.* 16 hours at 25°, the solution was evaporated *in vacuo* to dryness. Paper strip chromatography of this residue and the crystalline phosphate, using the system[4] 5% aqueous disodium hydrogen phosphate–isoamyl alcohol, gave one fluorescent spot for each, with identical R_f values of 0.73. One-half of the above acid hydrolysis residue and *ca.* 0.5 mg. of the crystalline phosphate were each dissolved in *ca.* 5 ml. of 80% acetic acid, and the two solutions were heated at reflux for 15 minutes. The solutions were evaporated to dryness *in vacuo* and chromatographed as described.[1] In each case, two fluorescent spots of similar visual intensities were obtained with identical R_f values of 0.73 and 0.78.

The fluorescent spots were detected under a mineralite lamp after the dried paper chromatograms were sprayed with a 2% acetic acid solution. The spots were of greater intensity when the paper was still wet with the acetic acid solution.

There were slight variations in the R_f values with different ascending chromatograms which appeared to be due mainly to the relative distance between the position of the applied spots on the paper strip and the surface of the mixed solvent system.

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[2] D. M. Brown and A. R. Todd, *J. Chem. Soc.*, 52 (1952).

[3] J. X. Khym, D. G. Doherty, E. Volkin and W. E. Cohn, THIS JOURNAL, **75**, 1262 (1953).

[4] C. E. Carter, *ibid.*, **72**, 1466 (1950).

The Addition of Dithiols to Dibenzalketones[1]

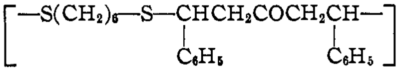
BY C. S. MARVEL AND HERMAN WEXLER

RECEIVED JULY 15, 1953

Recently it was reported[2] that a polymer could be obtained by the base-catalyzed addition of hexamethylenedithiol to dibenzalacetone in an emulsion system. We have now studied this polymer-forming reaction further to determine its limitations and possible usefulness.

The addition of hexamethylenedithiol to dibenzalacetone takes place readily in benzene solution at 30° with piperidine as the catalyst. Emulsion systems do not seem as successful as solution systems perhaps due to some addition of water to stop the growth of the polymer. Free radical initiators which are effective for the addition of dithiols to non-conjugated diolefinic hydrocarbons do not function with these conjugated systems. The highest molecular weight polymers as judged by inherent viscosity were obtained in 18 hours at 50° or 36 hours at 30°. After longer periods there was degradation in molecular weight. Exact balance of reacting monomers is very essential to the success of the reaction.

The addition polymer apparently has the expected structure I since the elementary analysis



$$\left[-S(CH_2)_6-S-\underset{C_6H_5}{\underset{|}{CH}}CH_2COCH_2\underset{C_6H_5}{\underset{|}{CH}}-\right]$$

I

agrees with this composition and the infrared spectrum shows strong carbonyl bands at 1715–1722 cm.$^{-1}$ and 1722–1729 cm.$^{-1}$ and strong bands for the grouping $-CH_2CO-$ at 1410 cm.$^{-1}$.[3] It is believed that the end groups are neither mercaptan nor olefin double bond. No infrared bands for the conjugated carbon–carbon double bond could be found. No evidence for mercaptan end groups could be obtained either in the spectrum or by oxidation experiments. It seems probable that some side reaction involves addition

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[1] The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] C. S. Marvel and A. H. Markhart, Jr., *J. Polymer Sci.*, **6**, 711 (1951).

[3] We are indebted to the Anderson Physical Laboratories, Champaign, Ill., for these infrared data.

of a catalyst fragment, an active hydrogen, or other material present as an impurity to give a saturated hydrocarbon end group.

The reaction of hexamethylenedithiol and dibenzalcyclohexanone also produces a polymer of low molecular weight. However, it was not possible to extend the reaction to include dimercaptan addition to 3,3′-dinitrodibenzalacetone, diethyl 1,7-octadiene-1,8-dicarboxylate, 1,6-diphenyl-1,5-hexadiene-3,4-dione or dimethyl acetylenedicarboxylate.

Experimental

Preparation of Polymers from Dibenzalacetone and Hexamethylenedithiol.—A typical solution polymerization consisted of charging a four-ounce polymerization bottle with 1.981 g. (0.01349 mole) of hexamethylenedithiol and 3.088 g. (0.01348 mole) of dibenzalacetone in 15 ml. of dry benzene and adding 0.2 ml. of piperidine. The solution was protected by a nitrogen atmosphere and the bottle was tumbled in a 30° constant temperature bath for 24 hours. The polymer was precipitated with 25 ml. of methanol, dried and reprecipitated. The inherent viscosity[4] as determined in benzene was 0.31 at 25°.

Anal. Calcd.[5] for $C_{23}H_{28}S_2O$: C, 71.82; H, 7.34; S, 16.68. Found: C, 72.06; H, 7.58; S, 16.56.

Polymers from Dibenzalcyclohexanone and Hexamethylenedithiol.—A polymer was produced from these monomers by the same general method as shown above. The inherent viscosity in benzene at 25° was 0.14.

Anal. Calcd. for $C_{26}H_{32}S_2O$: C, 73.53; H, 7.60; S, 15.10. Found: C, 73.95; H, 7.66; S, 14.38.

Attempted Oxidation of Polymer End Groups.—To a solution of 1.015 g. of polymer from dibenzalacetone and hexamethylenedithiol (inherent viscosity 0.22) dissolved in 50 ml. of chloroform was added 0.1 g. of iodine. The solution was shaken at room temperature for 24 hours after which it was poured into a mixture of 100 ml. of methanol and 50 ml. of water containing 1 g. of sodium bisulfite. The polymer was isolated by decantation and was washed with two 100-ml. portions of methanol. The inherent viscosity was 0.06.

Effect of Monomer Balance.—The molar ratio of hexamethylenedithiol and dibenzalcyclohexanone in a typical polymerization was varied and the effect upon the viscosity of the polymer was noted. These experiments are recorded in Table I.

TABLE I

EFFECT OF MONOMER BALANCE ON INHERENT VISCOSITY OF POLYMER

Hexamethylenedithiol, g.	Dibenzalcyclohexanone, g.	Molar ratio dithiol/ketone	Inherent viscosity
0.996	1.894	96/100	0.16
.990	1.863	97/100	.16
.991	1.846	98/100	.19
.987	1.820	99/100	.21
.975	1.780	100/100	.23
.991	1.791	100/99	.24
.987	1.766	100/98	.20
1.002	1.774	100/97	.18
0.989	1.733	100/96	.15
1.000	1.734	100/95	.16

Time Required for Polymer Formation.—At 30° a solution of 0.0067 mole of hexamethylenedithiol and dibenzalacetone in 10 ml. of benzene was polymerized and the reaction followed by noting the viscosity and yield of the polymer. The polymers were dried *in vacuo* until there was no further loss of weight. The results are reported in Table II.

TABLE II

TIME REQUIRED FOR POLYMER FORMATION

Time, hr.	Inherent viscosity	Yield, %	Time, hr.	Inherent viscosity	Yield, %
0.005	0.12	12	1	0.27	82
.083	.21	48	2	.26	75
.167	.33	68	6	.25	80
.250	.34	76	9	.24	72
.500	.29	71	24	.27	71
.750	.29	71	48	.20	71
			72	.21	54

Mercaptan Disappearance.—By amperometric titration[6] the rate of disappearance of thiol end groups was followed in an emulsion polymerization.

These titrations showed that in the addition of hexamethylenedithiol to dibenzalacetone, the mercaptan groups disappeared very rapidly; nearly 70% in a minute, nearly 80% in seven minutes, 95% in an hour and 99% in twelve hours. Thereafter there appeared to be no further decrease in mercaptan groups and even possibly a slight increase.

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(4) We are indebted to Messrs. Donald Janssen and Norbert Goeckner for all inherent viscosities reported.

(5) We are indebted to the Micro-Tech Laboratories, Skokie, Ill., and to Mr. Joseph Nemeth of the University of Illinois for the microanalytical results.

(6) I. W. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18** 161 (1946).

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Equilibrium Sorption of Several Organic Diluents in Polyvinyl Acetate[1]

BY R. J. KOKES, A. R. DIPIETRO AND F. A. LONG

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In the course of an investigation of the kinetics of vapor take-up by thin polymer films,[2] the equilibrium sorption has been determined for several organic diluents in polyvinyl acetate (viscosity average molecular weight approximately 170,000). Experiments have been made at 30, 40 and 50° with acetone, benzene and 1-propanol and at 40° with propyl chloride, allyl chloride, propylamine and isopropylamine. In all cases the solutions were concentrated in polymer; values of v_1, the volume fraction of solvent, ranged from 0.02 to 0.20. In these experiments the diluent concentration in the swollen polymer in equilibrium with a given vapor pressure of diluent was determined gravimetrically using a quartz spiral balance. The procedure, apparatus, and materials used have been discussed in detail elsewhere.[2-4] Results of the present experiments are summarized in Table I, which gives v_1[5] as a function of p/p_0, the ratio of diluent vapor pressure for the swollen polymer to that for the pure diluent. The systems studied, although polar, are relatively simple inasmuch as the polymer is non-crystalline and above its second-order transition temperature. It is of interest, therefore, to consider these data in the light of the Flory–Huggins[6,7] theory of polymer solutions.

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(1) Work supported by a grant from Office of Ordnance Research, U. S. Army.

(2) R. J. Kokes and F. A. Long, submitted for publication.

(3) S. Prager and F. A. Long, THIS JOURNAL, **73**, 4072 (1951).

(4) R. J. Kokes, F. A. Long and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1952).

(5) The volume fractions were calculated from the experimentally determined weight fractions assuming that solvent and polymer volumes were additive on mixing.

(6) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(7) M. L. Huggins, *ibid.*, **9**, 440 (1941).