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THE ROLE OF OXYGEN IN THE MECHANISM OF VINYL POLYMERIZATION

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Reactivation cases by treatment of hydrogen cyanide or cyanide.

Compounds are specific re-enzyme inactivators; they have no significant effect on pancreatic amylase or pancreatic

the influence of two upon the activity of the first two sections of

II BY SPECIFIC SULPHHYDRYL REACTIVATION WITH CYSTEINE

Units*	After inactivation Activity*	After reactivation Activity*	% of control
920	100	1000	100
0	0	1010	101
1253	100	1330	100
0	0	1110	83
0	0	1070	80
1100	100	1200	100
430	20	470	26

To 0.1 M acetate, pH 4.3, 5 minutes at 0°. Amylase 1 M phosphate, pH 6.8, held at 25° for one hundred hours was treated in the same way as added. Aliquots with distilled water. Aliquots with a solution of hydrochloric acid of maltose formed a milligram of enzyme acting at pH 4.5 in the presence of 10% of amylase were added was linearly proportional to the amount used.

3d amylase solution added pH 4.5 was allowed to stand thirty minutes at 0°. were then diluted either 10 or 100 times with distilled water. Hydrogen sulfide was used for 0.5% of phenylmercuric acetate for the reactivation of amylase. The first two sections of the amylase were completely or largely reactivated with hydrogen sulfide. These results are further evidence of the activity of β -amylase. The conclusion was that the amylase which had been inactivated by treatment with either of these mercuric reagents no longer gave a nitroprusside reaction and by the close agreement between the concentration of *p*-chloromercuribenzoic acid necessary to inactivate the amylase completely and the concentration of sulfhydryl shown to be present in the untreated amylase solution.

Iodoacetamide is another reagent which reacts with sulfhydryl groups. If the hydrogen-ion activities of the solutions are kept below pH 8, the reaction is considered specific for thiol groups.¹³ Certain enzymes such as urease⁹ are irreversibly inactivated by iodoacetamide while the activity of others such as pancreatic amylase¹² is not appreciably influenced by this reagent.

The data given in the last section of Table II, are typical of the results obtained when β -amylase was treated with iodoacetamide under conditions reported to be specific for sulfhydryl groups.¹³ The amylase was markedly inactivated under these conditions and the inactivation was not reversed by subsequent treatment of the solutions with cysteine. β -Amylase resembles urease in this respect.¹³ The results with iodoacetamide increase the evidence that free sulfhydryl groups are essential to the activity of β -amylase from barley and from malted barley.

Summary

The results of experiments with a number of oxidizing agents and of other reagents which have been reported to be specific for sulfhydryl groups confirm and extend previous evidence which leads to the conclusion that free sulfhydryl groups of the protein are necessary to the activity of β -amylase from barley and from malted barley.

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Mechanism of Vinyl Polymerization. I. Role of Oxygen¹

BY CARL E. BARNES²

It has been known since the very beginning of polymerization studies that light, heat and air are effective agents for inducing the polymerization of certain vinyl compounds.³ For example vinyl chloride⁴ and vinyl acetate⁵ may be polymerized by irradiation with ultraviolet light. Both these substances also polymerize readily upon heating to moderate temperatures, and it has been reported frequently that oxygen, ozone and peroxides have a pronounced catalytic effect upon the rate of this thermal polymerization. In fact, it has been demonstrated repeatedly that in the complete absence of oxygen, many vinyl compounds either fail to polymerize altogether or the rate is very slow.⁶ On the other hand it has been established that oxygen acts as a marked inhibitor in the photopolymerization of vinyl acetate.⁷ This paper is concerned with the elucidation of this apparent anomaly and its relation to the mechanism of polymerization reactions of the vinyl type.

The mechanism of the catalytic action of oxygen is undoubtedly related to peroxide formation. The presence of peroxides in many vinyl com-

pounds has been observed by various investigators.⁸ Moureu and Dufraisse⁹ clearly established that it is combined oxygen rather than oxygen itself which catalyzes the polymerization of acrolein. Conant¹⁰ concluded that the catalytic effect of oxygen in the pressure polymerization of isoprene is due to the formation of a peroxide.

These conclusions of Moureu and Dufraisse and of Conant, *et al.*, are undoubtedly of a very general nature. During the course of this investigation no compound containing the vinyl or vinylidene group has been found which does not readily form a peroxide upon exposure to air under ordinary conditions; furthermore these peroxides have all been found to act as polymerization catalysts.

Less well established is the nature of the inhibiting action of oxygen in photopolymerization. It seemed to the author that this apparent anomaly might be explained very simply by assuming peroxide formation to occur in preference to polymerization in accordance with the following scheme



where M represents the unactivated monomer molecule; M*, the active center and MO₂, a peroxide. It must be further assumed that the catalytic activity of the peroxide is due to its tendency to generate M* (or similar active centers) and that these active centers exhibit the same

- (1) The experimental work described here was carried out in 1939 while the author was with the Norton Company, Worcester, Mass., and has now appeared in British Patent 540,231 (1942).
- (2) Present address: General Aniline and Film Corp., Central Research Laboratory, Boston, Penna.
- (3) Reitenbach, *Ann.*, 47, 113 (1843); Baumann, *ibid.*, 168, 312 (1872).
- (4) Baumann, *ibid.*, 168, 317 (1872).
- (5) Staudinger, *Frey and Storch, Ber.*, 60B, 1782 (1927).
- (6) Moureu and Dufraisse, *Bull. soc. chim.*, (4) 38, 1664 (1924); Staudinger and Schwalluck, *Ann.*, 468, 8 (1921); E. L. de Fontenay, *Remours & Co., Ind. Eng. Chem.*, 24, 1161 (1932).
- (7) Staudinger and Schwalluck, *loc. cit.*; Taylor and Vernon, *Ind. Journal*, 22, 2626 (1931).

- (8) Staudinger and Lautenschlager, *Ann.*, 478, 1 (1931); Staudinger and Celchini, *Chim. ind. (Mil.)*, 66, 735 (1935).
- (9) Moureu and Dufraisse, *Chimistry & Industry*, 41, 61 (1924).
- (10) Conant and Tongberg, *Text. Journal*, 62, 1066 (1931); Conant and Peterson, *ibid.*, 64, 628 (1933).

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preferential reactivity with oxygen as those formed by the action of ultraviolet light.¹¹

The theory requires (a) that peroxides be formed in vinyl compounds by the action of ultraviolet light and (b) that, in the presence of excess oxygen, polymerization be either greatly retarded, or entirely prevented. Both these requirements have been substantiated experimentally in the following manner. Two Pyrex tubes were filled half way with carefully purified, peroxide-free, vinyl acetate. One of these tubes was evacuated, boiled for a moment to free it of air, cooled, and then sealed under vacuum. The other tube was flushed with oxygen and then connected to a large flask filled with oxygen to ensure a plentiful supply. Both tubes were immersed horizontally in a water-bath maintained at 0° and then irradiated with ultraviolet light. After twenty-seven hours the material in the evacuated tube had become viscous. Precipitation with methanol showed the presence of 13% polymer. The liquid in the tube under oxygen contained no polymer but a test with a potassium iodide solution indicated the presence of 0.005 mole % peroxide. Similar results have been obtained with methyl acrylate and methyl methacrylate. Therefore, when sufficient oxygen is present, peroxides are formed exclusively under conditions otherwise favorable to photopolymerization.

If the foregoing explanation of the action of oxygen is valid for photopolymerization, then it should apply to thermal polymerization as well. In this case it is a well known fact¹² that the catalytic activity of the peroxide is due to its tendency to generate active centers. These active centers then should exhibit the same preferential reactivity with oxygen as those formed in the photopolymerization. Furthermore, the peroxide should be formed from the monomer and oxygen by the action of heat. Both these requirements have been fulfilled experimentally.

In one experiment, for example, a sample of methyl methacrylate was heated at 65° in the dark in contact with an oxygen reservoir bearing a manometer. During a period of twenty-six hours the monomer absorbed oxygen at a steadily increasing rate. At the end of this time it had absorbed twice its volume of oxygen (at 65°) and had not visibly increased in viscosity. A portion of the sample, at this point, was placed in a tube under nitrogen and another portion was placed in a similar tube under oxygen. The portion under nitrogen polymerized to a solid within a few hours while no visible change took place in the sample under oxygen. The ordinary benzoyl peroxide catalyzed thermal polymerization is likewise inhibited by oxygen as shown in Table IV.

(11) It is also possible that oxygen may attack a growing chain at the moment of chain stage, i. e., $MM^{\bullet}$ or $MM^{\bullet}$.

(12) Schuler and Huenemann, *Z. physik. Chem.*, **B89**, 210 (1938); Cuthbertson, Gee and Riddell, *Proc. Roy. Soc. (London)*, **A170**, 300 (1939); Melville, *Ann. Repts. Chem. Soc.*, **36**, 61 (1939); Price and Bell, *Trans. Faraday Soc.*, **37**, 2798 (1941).

Thus the inhibiting action of oxygen (or more accurately, preferential peroxide formation in the presence of oxygen) appears to be of a very general nature, applying to virtually all polymerizable vinyl compounds and to thermal as well as photopolymerization.

(It may be pointed out that it is this preferential reactivity of the activated monomer with oxygen which accounts for the erratic induction period observed when pure monomer is polymerized in the presence of air. The length of this induction period depends upon the amount of oxygen present which in turn depends upon such customarily uncontrolled factors as the design of the container, the extent to which it is filled, whether or not it is sealed,¹³ etc.)

If a polymerization is carried out in a vessel open to the air the two competing reactions of peroxide formation from active centers¹⁴ and peroxide generation of active centers eventually reach a delicate balance. As the concentration of peroxide builds up the oxygen available may no longer be adequate to react with all the active centers generated; therefore the surface layers of the monomer exhaust the oxygen supply allowing the lower portion to polymerize under essentially oxygen-free conditions, catalyzed by a relatively large amount of peroxide. This explanation is consistent with the commonly observed soft or sometimes fluid layer at the surface of an otherwise hard mass of polymer formed by the polymerization of such monomers as vinyl acetate or methyl methacrylate in contact with air.

Experimental

Peroxide Test.—For this work a reliable sensitive test for peroxide in monomer was required. Several common reagents were tried and none proved entirely satisfactory. Ferrous thiocyanate was found to be much too sensitive and rapidly oxidized by air. The liberation of iodine from acidified potassium iodide was found to vary markedly with different batches of the salt, being very sensitive to variations in the iodate content. By using a neutral solution of potassium iodide, most of these difficulties were avoided, and the test finally adopted was as follows:

To 4 cc. of a freshly prepared saturated solution of reagent grade neutral potassium iodide (containing less than 0.0001% iodate) in a 15 × 150 mm. test-tube was added 10 cc. of the liquid containing the peroxide. The contents of the tube were then shaken vigorously for one minute. A quantitative estimation of the peroxide present was obtained by comparison of the yellow color of the liberated iodine with that liberated from known solutions of recrystallized benzoyl peroxide in the particular (peroxide-free) monomer. Although a definite end-point is reached, the eventual deepening of the color (caused by the slow liberation of more iodine in the light) made it de-

(13) If a polymerization (either photo- or thermal) is carried out in a sealed tube under air this very easily demonstrated that oxygen is used up. Upon opening the tube under water when polymerization is complete, one-fifth the original air space will be filled with water.

(14) It is not contended in the case of thermal polymerization that peroxide is formed only from active centers. It is contended, however, that in this case also the active centers, whether they be formed directly from the monomer or generated by the peroxide, do react preferentially with oxygen, providing it is present in adequate amount.

scribable to a small amount of potassium dichromate. Iodine color very accurately was made up and made above mentioned from a mixture of 0.001 g. of peroxide in peroxide-free monomer. Concentrations were determined by matching the color with a standard solution of benzoyl peroxide in the same monomer.

Purification of Monomer.—The monomer was obtained from under reduced pressure as an inhibitor as well as columns were used to prevent the formation of a sign which is not to be polymerizable compounds such as acrylic anhydride. The ester and three feet long and (it had been previously) distilled through an original packed with glass beads. Various pressures were used (73 mm.), and 21° (62 in. following tests was found by the above test).

The vinyl acetate used Carbon Chemicals Corp. It was kept dry and peroxide-free condition.

Formation of Peroxides.—Methyl acrylate, acetate could be stored in in contact with air with peroxide content. Under uninhibited monomer temperature in diffuse day peroxide is present in less contribute to the formation conditions as shown by since this work was done, aid the formation of perox-

FORMATION OF PEROXIDE EXPOSED

Time, days	Exposed to a 100-watt bulb at one foot
1	0.0003
2	.0010
3	.0035
5	.030

By irradiating at 0° in action of light alone. A solution of peroxide by light it will be observed that upon heat, heat was more effective formation of peroxide in reverse was true with vinyl.

An attempt was made from the two samples of vinyl of the monomer under reduced a yellow oil was obtained under light and a sample of oil was obtained by exposure to light in the dark. The oil was found to be a solid.

(15) U. S. Patent 2,211,175.

(16) Farman, *Macmillan*, *Science*, **28**, 318 (1942).

attempts to employ as secondary standards, solutions of benzoyl peroxide which could be diluted to match the same color very accurately. A series of these standards was made up and matched to the colors produced in the same manner from solutions of known concentration ranging from 0.0001 to 0.01% of recrystallized benzoyl peroxide in peroxide-free methyl methacrylate. Higher concentrations were determined directly, owing to the difficulty of matching the color of these solutions with dilutions. It is easily possible to detect less than 0.0001% benzoyl peroxide by this test.

Purification of Monomers.—The methyl methacrylate used was obtained from du Pont and carefully distilled under reduced pressure to remove the hydroquinone (added as an inhibitor) as well as any other impurities. The columns actually used were of the type developed for preventing the formation of polymer in the column, a design which is essential for the distillation of such easily polymerizable compounds as methacrylic acid and methacryl anhydride. These columns were one inch in diameter and three feet long and are packed with copper cloth.¹² It had been previously established that the distilled material exhibited the same polymerization activity as that distilled through an eight-foot column of one-half inch bore, packed with glass helices. Boiling points obtained at various pressures are 49° (120 mm.), 43° (90 mm.), 39° (75 mm.), and 24° (32 mm.). The material used for the following tests was found to be completely free of peroxides by the above test.

The vinyl acetate used was obtained from Carbide & Carbon Chemicals Corp. and was distilled in the same manner. It was kept dry to avoid hydrolysis and used in peroxide-free condition.

Formation of Peroxides.—It was found that such monomers as methyl acrylate, methyl methacrylate and vinyl acetate could be stored in the dark at 0° for several days in contact with air without developing an appreciable peroxide content. Under ordinary room conditions (i. e., uninhibited monomer stored in a colorless bottle at room temperature in diffuse daylight) a measurable amount of peroxide is present in less than a day. Both light and heat contribute to the formation of the peroxide under these conditions as shown by Table I. Farmer¹³ has shown, since this work was done, that heat, light and catalysts aid the formation of peroxides from olefins and oxygen.

TABLE I
FORMATION OF PEROXIDE IN METHYL METHACRYLATE
EXPOSED TO AIR AT 27°

Time, days	Peroxide, mole %	
	Exposed to a 100-watt bulb at one foot	Dark
1	0.0003	Less than 0.00005
2	.0010	.00005
3	.0035	.0001
5	.030	.00015

By irradiating at 0° a peroxide may be formed by the action of light alone. A comparison of the rates of formation of peroxide by light and by heat is given in Table II. It will be observed that under the conditions of this experiment, heat was more effective than light in causing the formation of peroxide in methyl methacrylate while the reverse was true with vinyl acetate.

An attempt was made to isolate the peroxide formed from the two samples of vinyl acetate. Upon evaporation of the monomer under reduced pressure about 0.005 mole % of a yellow oil was obtained from the tube under ultraviolet light and a smaller (unweighed) quantity of a yellow oil was obtained by evaporating the sample which had been heated in the dark. Both these oily residues liberate iodine rapidly from potassium iodide. A small

TABLE II
RELATIVE EFFECT OF LIGHT AND HEAT ON PEROXIDE
FORMATION*

Monomer	Peroxide content, mole %	
	UVI., 0°C.	Dark, 60°C.
Methyl methacrylate	0.002	0.03
Vinyl acetate	0.004	0.001

* Treated for seventeen hours in Pyrex tubes connected with a 2-liter oxygen reservoir. Heated tubes were kept dark by wrapping completely with tinfoil; illuminated tubes were immersed horizontally in water maintained at 0° by refrigeration and irradiated at a distance of 15 inches with a G. E. type A-H4 mercury arc lamp with outer glass removed.

amount of the yellow oil on a spatula was placed in a flame; it exploded in much the same manner as does benzoyl peroxide on similar treatment.

Other vinyl compounds in which peroxides were observed to form are as follows: methyl and ethyl acrylates; ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, allyl, methallyl and cyclohexyl methacrylate; methyl α -chloroacrylate; methyl α -bromoacrylate; acrylonitrile; vinyl isobutyl ether; vinyl *n*-propyl ether; methyl vinyl ketone; and butadiene.

Inhibition of Polymerization by Oxygen.—The inhibiting action of oxygen in photopolymerization is shown in Table III. The amount of polymer was determined

TABLE III
INHIBITING ACTION OF OXYGEN IN PHOTOPOLYMERIZATION*

Monomer	Atmosphere	Peroxide concn, mole %	Polymer, %
Methyl methacrylate	O ₂	0.0025	None
Methyl methacrylate	Vacuum		5.48
Vinyl acetate	O ₂	0.005	None
Vinyl acetate	Vacuum		13.0

* Samples were placed in Pyrex tubes which were immersed horizontally in a water-bath maintained at 0° and irradiated for twenty-seven hours at a distance of 8 inches with a type A-H4 G. E. mercury arc lamp with outer glass removed. The evacuated tubes were sealed and those under oxygen were connected with a 2-liter reservoir.

by precipitation with methanol and drying. The inhibiting action of oxygen in thermal polymerization is shown in Table IV.

TABLE IV
INHIBITING ACTION OF OXYGEN IN THE THERMAL (CATALYZED) POLYMERIZATION OF METHYL METHACRYLATE*

Sample no.	Atmosphere	Benzoyl peroxide, %	Viscosity
1	N ₂	0.01	Solid polymer
2	O ₂	0.01	Viscous liquid
3	O ₂	None	No polymer but 0.001 mole % peroxide

* All three samples were taken from the same batch of peroxide-free monomer, and Samples 1 and 2 were prepared as one solution and divided. All were heated at 65° for four and one-half hours in the dark.

Acknowledgment.—The author wishes to thank Loring Coes, Jr., of Norton Company for help with the experimental work.

Summary

An explanation has been given for the frequently observed inhibiting action of oxygen on the photopolymerization of vinyl compounds and some addi-

¹² U. S. Patent 2,241,175 (1941).
¹³ Farmer, Bloomfield, Goodrillingham and Satter, *Trans. Soc. 28*, 248 (1942).

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