

From optical data, however, a distance is calculated of  $1.15 \text{ \AA}$ .<sup>6</sup> and even of  $1.09 \text{ \AA}$ .<sup>7</sup>

<sup>6</sup> Zachariasen cited from V. M. Goldschmidt, *Geochem. V.*, 2, 66 (1926).

<sup>7</sup> W. L. Bragg, *Proc. Roy. Soc. (London)*, A106, 356 (1924).

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## POLYMERIZATION REACTIONS UNDER HIGH PRESSURE. II. THE MECHANISM OF THE REACTION

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Unsaturated hydrocarbons and certain aliphatic aldehydes are polymerized at room temperature by the application of very high pressure (3000–12,000 atm.)<sup>1</sup> In the case of isoprene the product is rubber-like; in the case of *n*-butyraldehyde the final polymer is a hard solid which reverts to the original aldehyde on standing at room temperature and atmospheric pressure. The previous work<sup>1</sup> showed that peroxides and ozonides were effective catalysts for both types of polymerization. However, it was concluded that peroxide catalysis was not essential since a sample of isoprene distilled in nitrogen and compressed without exposure to air polymerized at a rate only slightly less than that of material freshly distilled in air. The results of the experiments recorded in this paper have led us to revise this conclusion. We are now strongly inclined to the opinion that peroxide catalysis is essential to the polymerization and the effect of increased pressure is only to accelerate the catalytic reaction.

The evidence that peroxide catalysis is essential to the pressure polymerization of isoprene is as follows. Peroxides and ozonides have a strong positive catalytic action. Freshly distilled isoprene polymerizes at a rate only one-fifth to one-tenth of that of isoprene which has stood in the air for some days. This increased tendency to polymerize on standing is almost certainly due to the formation of peroxides from the dissolved oxygen. If peroxides (or dissolved oxygen which will form a peroxide) are essential to the polymerization, we must assume that when the isoprene was distilled in nitrogen some trace of oxygen or volatile peroxides was in the distillate. We have now strong evidence for this assumption since we have found that by adding hexaphenylethane (which reacts rapidly with oxygen) to isoprene in nitrogen and distilling, the rate of polymeriza-

<sup>1</sup> THIS JOURNAL, 52, 1659 (1930).

tion of the distillate is reduced ten-fold. The material thus prepared still polymerizes under pressure (14% at 12,000 atm. in forty-eight hours); it can be argued that this represents the uncatalyzed reaction but it seems equally probable that traces of oxygen or peroxide are still present adsorbed to the glass. That very minute amounts of peroxide are sufficient for catalysis is demonstrated by the work with aldehydes which is described below.

The pressure polymerization of the aldehydes has proved to be of particular interest from the point of view of the elucidation of the mechanism of the reaction, since it is possible to prepare samples of *n*-butyraldehyde which show no evidence of polymerization after twenty-four hours at 12,000 atmospheres.<sup>2</sup> This is done by minimizing the time of contact of the redistilled aldehyde with the air. The aldehyde is purified through the bisulfite addition product in the usual way and then distilled carefully in nitrogen through an efficient fractionating column directly into the tube which is subsequently rapidly inserted in the press. If such a sample of carefully purified *n*-butyraldehyde is placed in an apparatus in contact with air and the oxygen absorption measured, the rate of autoxidation is found to be considerable, as shown by the results given in Table I. Samples were withdrawn from time to time and subjected to a pressure of 12,000 atmospheres for twenty-four hours at 28°; the results are given in the last column of the table. It is clear that the rate of polymerization

TABLE I  
OXYGEN ABSORPTION AND RATE OF POLYMERIZATION OF *n*-BUTYRALDEHYDE

Time, hrs.	O <sub>2</sub> absorbed per 100 cc. of aldehyde, cc.	Polymerization of sample at 12,000 atm. for 24 hr.
0	0	No polymerization
21	12.6	Liquid, viscous as glycerin
50	24	Very viscous liquid
73	36	Too viscous to pour
145	73	Thick paste
170	94	Soft solid

parallels the oxygen absorption. Material which had stood several years in a loosely corked bottle polymerized at the fastest rate of any sample of aldehyde we were able to obtain. The butyric acid content of this aldehyde was high (14%) but this was not the effective catalyst since butyric acid added to freshly distilled butyraldehyde was without catalytic effect.

The only conclusion that can be drawn from the foregoing facts is that a very small portion of the absorbed oxygen forms some substance which has a very strong catalytic effect on the pressure polymerization. We

<sup>2</sup> The degree of polymerization of the aldehydes is estimated by the viscosity of the product if still liquid or roughly judged by the consistency of the paste if sufficient polymerization has occurred; quantitative results cannot be obtained.

shall designate this substance a peroxide without attempting to propose a structure for it; the amount of this catalytic substance increases with oxygen uptake parallel to the increase in butyric acid; it can therefore hardly be an intermediate between the aldehyde and the acid. One may estimate the amount of peroxide formed to correspond to not more than 1% of the absorbed oxygen, since the correlation of increased acidity and absorbed oxygen was within 1%. The minute amount formed in the absorption of 12 cc. of oxygen per 100 cc. of aldehyde would be approximately  $0.12/24,500$  of a mole per 100 cc. or a mole fraction of  $5 \times 10^{-6}$ ; this amount is sufficient to bring about polymerization at an appreciable rate at 12,000 atmospheres.

Extremely sensitive tests are available for the detection of peroxide. The most sensitive involves the use of 10% ammonium thiocyanate to which a crystal of ferrous ammonium sulfate (free from the ferric salt) has been added (a peroxide develops a red color).<sup>3</sup> The best sample of aldehyde we could prepare distilled in nitrogen gave this test strongly. A less sensitive test is to shake the organic compound with neutral aqueous potassium iodide, a yellow to red-brown color appearing if peroxide is present. Our best samples of aldehyde freshly distilled in nitrogen gave a faint yellow on the initial shaking with the aqueous iodide solution; samples which had stood for several days and had absorbed oxygen (Table II) gave a distinctly darker color under the same conditions while older samples gave a still stronger test. The acidified potassium iodide test with starch (giving a blue color) is less sensitive (at least in the presence of aldehyde) than the test just described, samples are easily prepared which do not give this test; material which has stood for some time in the air does show peroxide by this test, however. These tests thus bear out our assumption that increasing amounts of peroxide are formed when butyraldehyde absorbs oxygen. It must be pointed out, however, that the tests are very delicate and to some extent uncertain; they must be performed under strictly comparable conditions. Even the best samples of aldehyde liberate relatively large amounts of iodine from neutral potassium iodide solution, if the mixture is shaken a few minutes in the air.

These conclusions in regard to the role of absorbed oxygen in catalyzing the polymerization of *n*-butyraldehyde are supported by the fact that other peroxides were found to be catalysts though larger amounts are necessary. Five per cent. of benzoyl peroxide dissolved in the aldehyde was sufficient to cause the formation of a hard solid in twenty-four hours at 12,000 atm. Benzaldehyde which had stood in the loosely-stoppered bottle for some days and contained 0.75 millimole of peroxide per 100 cc. (by titration), when added to the extent of 5% to freshly distilled butyral-

<sup>3</sup> We are greatly indebted to Mr. Edward Mallinckrodt, Jr., for calling our attention to these tests and the possibility of their application to this problem.

dehyde caused appreciable polymerization at 12,000 atm. for twenty-four hours.

**The Mechanism of the Reaction.**—In view of the facts just presented it seems to us that a peroxide is essential to the pressure polymerization of isoprene or the aliphatic aldehydes, although very minute quantities of peroxide are sufficient. We suggest that the mechanism is a series of chain reactions in the liquid initiated by the spontaneous decomposition from time to time of the peroxide. The accelerating effect of great pressures is due, according to our theory, to the orientation of the molecules of the isoprene or aldehyde into a more compact bundle in which longer reaction chains would be propagated by the spontaneous decomposition of a single peroxide molecule. It seems quite certain that as the volume of a liquid is diminished by the application of pressure, a definite orientation of the molecules is approached and we assume that this orientation is very similar to that existing in the polymer itself. This explanation corresponds with the fact that the polymer is considerably more dense than the original material (in the case of isoprene the change is from a density of 0.68 to about 0.9) and that in the polymerization of isoprene at 18,000 atmospheres, there was very little volume change during the polymerization, *i. e.*, the isoprene had been compressed very nearly to the density of the polymer before the chemical reaction started. It seems reasonable to suppose that the spontaneous decomposition of a peroxide molecule would be more effective in producing long reaction chains, the less the random motion of the molecules and the more compact and oriented they were assembled. We imagine that as each molecule becomes in turn activated by the energy originally coming from the peroxide, it unites with its neighbor, which in turn becomes active by virtue of the exothermic nature of the polymerization process. The pressure polymerization is thus to be thought of as chain reaction in which the energy is passed on in a chain and all the reacting molecules actually unite. The accelerating effect of temperature is easily explained as being due to the more frequent initiation of peroxide decompositions and hence of reaction chains. The efficiency of a given peroxide as a catalyst would depend on its instability; thus relatively large amounts of the stable benzoyl peroxide are required. The effect of negative catalysts mentioned in the previous paper would be to break the reaction chain.

The mechanism just suggested would lead to the conclusion that if a sample of aldehyde stood out of contact with air at atmospheric pressure, the spontaneous decomposition of peroxide would continue but would not result in polymerization (particularly in the case of the aldehyde since the polymer is metastable at atmospheric pressure). The decomposition of the peroxide, however, removes some of the catalyst and after long standing out of contact with air the rate of pressure polymerization

should decrease. Such was found to be the case. A sample of *n*-butyraldehyde which had taken up sufficient oxygen to polymerize to a solid after twenty-four hours at 12,000 atm. was kept in a tube with the tip under mercury and was introduced in the press without the admission of air after sixteen days. After twenty-four hours at 12,000 atm. only a thick paste resulted, showing a decrease in the rate as compared with the original material. After four months' standing out of contact with air, the same material showed no signs of polymerization after being subjected to 12,000 atm. for twenty-four hours.

The spontaneous decomposition of the peroxide at atmospheric pressure was greatly accelerated by an increase in temperature, as would be expected. Heating for twenty-eight hours at 60° out of contact with air was sufficient to destroy completely the ability to polymerize of a sample of butyraldehyde which had absorbed sufficient oxygen to polymerize to a hard solid under the usual application of pressure. A similar effect was obtained when the catalyst was an added peroxide instead of the butyraldehyde peroxide. Freshly distilled aldehyde containing 5% of benzoyl peroxide polymerizes to a hard solid under our usual conditions but after heating out of contact with air for one hundred fifteen hours, a sample showed no signs of polymerization at 12,000 atm. for twenty-four hours; after eighty-eight hours there was a very slight polymerization, while after seventy hours the polymer was a thin paste. It is interesting that oxygen was evolved during the first seventy hours of heating; this oxygen was removed before continuing the heating, the further heating was apparently necessary to decompose the aldehyde peroxide formed from the gaseous oxygen previously evolved. All these facts seem to us strong evidence in support of the mechanism just suggested.

The addition of other liquids to the aldehyde greatly diminishes the rate of polymerization, as would be expected from the point of view of our mechanism, since the chance of producing long reaction chains would be diminished. Thus, the addition of 10% by volume of absolute ethyl alcohol to butyraldehyde which had absorbed considerable oxygen perceptibly diminished the rate (a paste instead of a solid after twenty-four hours at 12,000 atm.) and 15% inhibited the polymerization to such an extent that none could be detected after twenty-four hours at 12,000 atmospheres. The amount of *n*-butyric acid necessary to produce a similar effect was 28%. With isobutyraldehyde 30% by volume of alcohol was necessary to inhibit any appreciable polymerization under our usual conditions and about 50% of isobutyric acid. Somewhat less amounts of diluents yielded pastes instead of the usual solid. Mixtures of *n*-butyraldehyde and isobutyraldehyde (both having absorbed sufficient oxygen to give high rates of polymerization) in all proportions polymerized to pastes at 12,000 atm. for twenty-four hours. The material was more

nearly solid, however, if one or the other aldehyde was present to the extent of at least 70%. These facts indicate that mixed polymers are probably formed, the aldehyde molecules being nearly interchangeable in the polymer molecule and in the reaction chains.

In addition to the pressure polymerization of the two butyraldehydes we have also found that *n*-valeric aldehyde and *n*-heptaldehyde, after distilling in the air without precautions, polymerized to thick pastes after twenty-four hours at 12,000 atm. These polymers reverted to the aldehyde on standing at room temperature and pressure as in the case of the butyraldehyde.

**Structure of the Aldehyde Polymers.**—When prepared at 12,000 atmospheres, the aldehyde polymers are hard transparent solids, if the polymerization is complete. When benzoyl peroxide is used as a catalyst or the polymerization is carried out at 4000 to 6000 atmospheres (many days being required) the polymer is not transparent but white. The completely polymerized *n*-butyraldehyde is insoluble in all the common solvents (carbon tetrachloride, chloroform, pyridine, acetophenone and cyclohexanone appear to dissolve the material very slightly). The polymer swells in benzene and toluene much as does rubber in the same solvents, but does not dissolve. The material has no melting point, since raising the temperature merely accelerates the decomposition to *n*-butyraldehyde. The spontaneous depolymerization of the polymer at atmospheric pressure is strongly catalyzed by aqueous acids or alkalis, which cause the complete depolymerization in a few minutes at 25°. The rate of decomposition of the solid itself is a function of the temperature and is greatly increased by the presence of the butyraldehyde; the process is thus autocatalytic. The material may be kept *in vacuo* over calcium chloride at 5° for considerable periods of time. The rate of decomposition of the polymer of *n*-butyraldehyde suspended in dioxane was determined by noting the change in freezing point of the solvent (11°). The results are summarized in Table II.

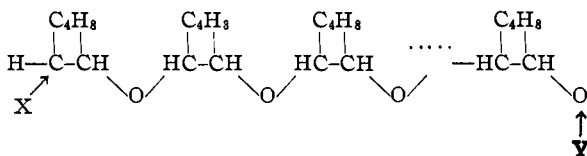
TABLE II  
RATE OF DEPOLYMERIZATION OF *n*-BUTYRALDEHYDE POLYMER SUSPENDED IN  
1,4-DIOXANE

Temperature 50°			Temperature 60°			Temperature 70°		
Time, minutes	Decomposed, %	Decomposed per min., %	Time, minutes	Decomposed, %	Decomposed per min., %	Time, minutes	Decomposed, %	Decomposed per min., %
20	4.37	0.22	20	10.05	0.50	20	16.71	0.84
40	8.72	.22	40	15.30	.38	40	25.35	.63
60	12.24	.20	60	21.85	.36	60	36.27	.60
90	17.48	.19	90	28.41	.32	90	42.83	.48
165	26.22	.16	120	32.78	.27	120	50.26	.42
	Average	.198		Average	.366		Average	.594

The percentage of decomposition was calculated on the assumption that the decrease in freezing point from time to time was due to the libera-



two hours the polymerization was hardly appreciable. The solid was obtained by evaporating off the unpolymerized material *in vacuo* at 100°. Thus prepared, the solid is a hard clear resin showing no tendency to depolymerize. It is quite soluble in benzene, chloroform, ethyl ether and amyl ether at room temperature. It is insoluble even at the boiling point in ethyl alcohol, acetone, glacial acetic acid and acetic anhydride. It did not sublime even at a pressure of  $10^{-3}$  mm. of mercury and a temperature of 100°, although it was perfectly stable at this temperature. This behavior points to a high molecular weight, although by the freezing point method the apparent molecular weight in *p*-chlorotoluene was 565 and in dioxane 168. These low values are probably due to the same difficulties which have been met with in recent years in the attempts to use the freezing point method with natural products of high molecular weight. The material was unattacked by boiling concentrated hydrochloric acid or 25% alcoholic potassium hydroxide. The analyses of the most carefully dried material were as follows: calcd. for  $C_6H_{10}O$ : C, 73.4, H, 10.28. Found: C, 72.6, 72.2, 72.7; H, 10.1, 10.3, 10.5. It seems probable that the polymerization of this derivative of ethylene oxide is very similar to that of the aldehydes except that the polymer is stable at atmospheric pressure. The structure would be written as



### Summary

A further study has been made of the polymerization of aliphatic aldehydes and isoprene under very high pressures. It has been established that peroxides are essential to the reactions. A chain mechanism has been suggested which seems to account for all the observed facts. Attempts to stabilize the polymeric aldehydes were not successful. Cyclohexene oxide has been polymerized but with great difficulty.

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