highest occupied orbital differed from the idealized oxygen lone-pair orbital in having a significant anti-bonding contribution from the adjacent carbon atom. Thus the predicted first transition corresponded very closely to the expected n → π*. The position of the π* nodal plane which is perpendicular to the carbonyl group, plane C of Figure 3, was calculated and found to almost bisect the carbon–oxygen bond. Also, as the n orbital is slightly antibonding between the carbon and the oxygen there is a further nodal surface in this region. In practice, this surface is of little importance as it is almost coincident with C in the region of the carbonyl group.

The calculated rotatory strengths agree well with the observed values in all but one case. A breakdown of the calculated rotatory strength into atomic contributions showed the magnetic moment to be sensibly constant in the series of molecules studied, and to be almost unchanged from the transition magnetic moment of the n → π* system in cyclohexanone. The transition electric moment is mainly induced in the carbonyl group, but there are important contributions from other groups in the molecule. The calculated rotatory strengths were also found to be very dependent upon the configuration of the methyl group.

In the present calculation, the character of the optically active transition was well understood from spectral studies, and the calculation mainly served to confirm the assignment and to illustrate the nature of the optical activity in these molecules. However, the success of this calculation encourages hope that the
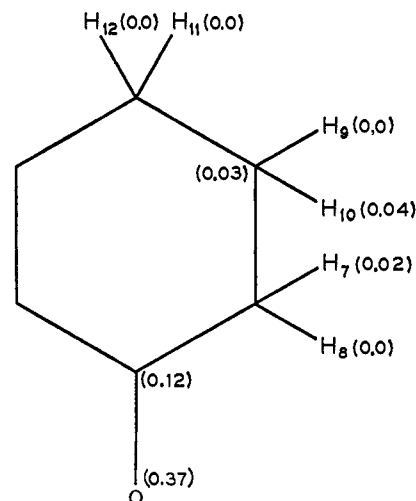

Figure 5. Electron distribution in the π* orbital of cyclohexanone (see note on Figure 4 for the method of calculation). In the case of the carbonyl atoms the dominant contribution is from the $2p_z$ orbitals, although in the case of the carbon there is a very small amount of 2s character.

theory may prove useful in the interpretation of the optical activity of less well understood transitions in other chromophores.

Organic Reactions under High Pressure. X. The Mechanism of Aldehyde Polymerization at High Pressures[1]

Cheves Walling and Thomas A. Augurt[2]

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received December 1, 1965

Abstract: The polymerization of n-butyraldehyde at 6000–8000 atm and 25° responds to none of the usual tests for a radical chain process. It is neither initiated by di-t-butyl peroxyoxalate nor inhibited by galvinoxyl and shows no evidence for copolymerization with methyl methacrylate or diethyl fumarate. Traces of carboxylic acids, however, catalyze the reaction indicating that propagation involves simple acid-catalyzed hemiacetal formation. Contrary results in the literature are ascribed to depolymerization before samples were examined or irreversible conversion to parabutyraldehyde. A striking catalysis is observed by hindered phenols, notably tri-t-butylphenol, which also catalyzes polymerization at −100° and atmospheric pressure. Polybutyraldehyde may be stabilized by end-group acetylation by ketene or by carrying out the pressure polymerization in the presence of acetic anhydride.
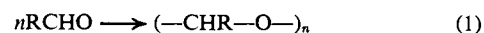
In 1929 Bridgman and Conant[3] reported that n-butyraldehyde and isobutyraldehyde, subjected to a pressure of 12,000 atm for 40 hr, were converted to waxy solids which slowly reverted to aldehyde on standing at atmospheric pressure. Further study by

Conant[4,5] indicated that the polymer had the structure of a polyacetal

$$n\text{RCHO} \longrightarrow (\text{—CHR—O—})_n \qquad (1)$$

with the nature of the end groups undetermined, and that the rate of polymerization depended markedly on aldehyde purity. Thus, freshly distilled aldehyde gave little or no polymer, while samples exposed to ozone or

(1) Taken from the Ph.D. Dissertation of T. A. Augurt, Columbia University, 1965. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) DuPont Teaching Fellow, 1962–1963; Trubeck Fellow, 1963–1964.

(3) P. W. Bridgman and J. B. Conant, *Proc. Natl. Acad. Sci. U. S.*, 15, 680 (1929).

(4) J. B. Conant and G. O. Tongberg, *J. Am. Chem. Soc.*, 52, 1669 (1930).

(5) J. B. Conant and W. R. Peterson, *ibid.*, 54, 628 (1932).

oxygen polymerized readily. Polymerization rate appeared to parallel oxygen absorption, and the highest rate was observed with an extensively autoxidized sample containing 14% butyric acid. However, Conant and Peterson concluded that peroxide rather than the acid was the actual catalyst, since benzoyl peroxide was an effective catalyst, while they observed no polymer from purified aldehyde to which butyric acid had been added. Accordingly, it has been generally assumed that they were dealing with a free-radical process.[6]

Subsequently, several groups have also observed the polymerization. In particular, Novak and Whalley[7] have confirmed the polyacetal structure of the polymers (which can be obtained from a variety of aldehydes) on the basis of infrared spectra, and Gonikberg and Zhulin[8] have studied the effect of variables on the n-butyraldehyde polymerization in an attempt to further establish the reaction mechanism. They found polymerization at 5200–6300 atm and room temperature, and, in addition to a complicated dependence on the composition of the reaction vessel, catalysis by benzoyl peroxide, but not by azobisisobutyronitrile. Carboxylic acids were also ineffective, leading to para-butyraldehyde formation, and addition of large amounts (7–18%) of parabutyraldehyde was claimed to inhibit the polymerization. On the basis of these results, Gonikberg and Zhulin also concluded that they were dealing with a radical chain reaction. They explained the catalysis by benzoyl peroxide, but not by azobisisobutyronitrile, on the basis that decomposition of the peroxide is accelerated by pressure,[9] while that of the nitrile is retarded.[10] Actually, their argument is questionable, since the large pressure acceleration originally reported[6] has proved[11] to be an experimental artifact, and any increase in rate with pressure which actually occurs appears to be an induced decomposition which generates no new radicals.[11,12]

In the meantime, the role of pressure on aldehyde polymerization has been developed in terms of the ceiling temperature concept of Dainton and Ivin.[13] Regardless of mechanism, the propagation steps of any addition polymerization are potentially reversible, and, since ΔH and ΔS for propagation are both negative, above a certain ceiling temperature polymerization cannot occur. This ceiling temperature is given by

$$T_c = \frac{\Delta H_0 + \int \Delta V dP + \int \Delta C_p dT}{\Delta S_0 + R \ln [M]/[M]_0 + \int (\Delta C_p/T) dT} \quad (2)$$

where all quantities refer to the propagation process. Since ΔV (the major correction term) is a negative quantity (a volume decrease accompanies polymerization), pressure will raise the ceiling temperature as has been demonstrated by Kilroe and Weale[14] for the anionic polymerization of α-methylstyrene and by

Busfield and Whalley[15] for the base-catalyzed polymerization of chloral. The low-temperature polymerization of simple aldehydes by various ionic catalysts is well known,[16] but the ceiling temperature at atmospheric pressure lies close to −100° for pure n-butyraldehyde as shown below,[17] so that depolymerization occurs readily on standing a room temperature. If the high-pressure polymerization of butyraldehyde were indeed a radical process it would be of considerable interest since few radical additions to carbonyl groups are known, radical attack on aldehydes usually occurring at the aldehyde hydrogen. In short, in the hypothetical competition pressure would (quite plausi-

$$R\cdot + C_3H_7C\overset{O}{\underset{H}{\diagdown}} \quad \overset{A}{\nearrow} C_3H_7CH\!-\!OR$$
$$\overset{B}{\searrow} C_3H_7\overset{O}{C\cdot} + RH \quad (3)$$

bly) be more effective in shifting the equilibrium A than in facilitating the usual displacement reaction B, suggesting that a variety of other radical additions to carbonyl groups might be achieved under high-pressure conditions. Accordingly we have here reinvestigated the evidence for a radical process. Although our results are negative, they include other interesting observations on the high-pressure reaction including an incompletely explained catalysis by hindered phenols and techniques for producing relatively stable polymers.

Results and Discussion

Mechanism of the High-Pressure Reaction. Our preliminary experiments readily confirmed most of the observations of Conant and subsequent workers. Freshly purified n-butyraldehyde, exposed to 8000 atm for 20 hr, was recovered unchanged. Shelf samples which had been exposed to air were converted to a waxy white polymer in varying yield in a few hours at 6000–8000 atm. The polymer, on purification by precipitation from chloroform with methanol, was obtained as a white powder, soluble in aromatic and chlorinated solvents, and stable almost indefinitely in the solid state at −20°, although it depolymerized rapidly in solution. Its infrared spectrum in CCl₄ was identical with that reported by Novak and Whalley.[7] A prominent feature is a C–O stretching band at 915 cm⁻¹, absent in butyraldehyde and parabutyraldehyde and useful accordingly in detecting polymer in solution.

The usual tests for the existence of a radical chain process are the demonstration of initiation, inhibition, and involvement in other radical processes. Each of these was applied in turn to the butyraldehyde system. Benzoyl peroxide and azobisisobutyronitrile leave something to be desired as room temperature initiators, since their thermal decomposition is very slow. In addition, benzoyl peroxide yields some benzoic acid as

(6) Cf. C. Walling, "Free Radicals in Solution,'" John Wiley and Sons, Inc., New York, N. Y., 1957, p 284.

(7) A. Novak and E. Whalley, Can. J. Chem., 37, 1718 (1959).

(8) M. G. Gonikberg and V. M. Zhulin, Vysokomolekul. Soedin., 3, 262, 268 (1961).

(9) C. Walling and J. Pellon, J. Am. Chem. Soc., 79, 4786 (1957).
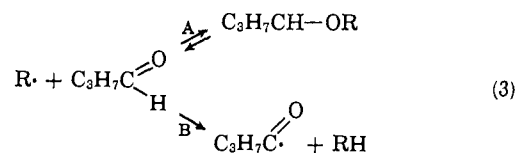
(10) A. H. Ewald, Discussions Faraday Soc., 22, 97 (1956).

(11) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, J. Am. Chem. Soc., 87, 518 (1965).

(12) A. E. Nicholson and R. G. W. Norrish, Discussions Faraday Soc., 22, 97 (1956).

(13) F. S. Dainton and K. J. Ivin, Nature, 162, 705 (1948); Quart. Rev. (London), 12, 61 (1958).

(14) J. G. Kilroe and K. E. Weale, J. Chem. Soc., 3849 (1960).

(15) W. K. Busfield and E. Whalley, Trans. Faraday Soc., 59, 679 (1963).

(16) Low-temperature polymerization of aldehydes has a voluminous literature which will not be reviewed here. Cf. M. W. Letort and P. Mathis, Compt. Rend., 241, 1765 (1955); O. Vogl, J. Polymer Sci., 46, 261 (1960).

(17) This is the value for formation of amorphous, presumably atactic polymer, and systems yielding crystalline stereoregular polymers show higher ceiling temperatures.[16] The exact effect of pressure on ceiling temperature is discussed in the following paper: Y. Ohtsuka and C. Walling, J. Am. Chem. Soc., 88, 4167 (1966).
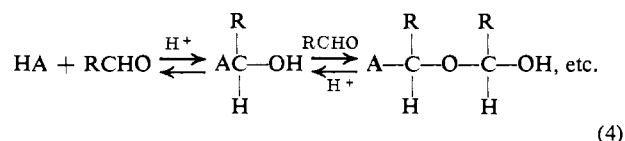
a product. A better choice appeared to be di-*t*-butyl peroxyoxalate (DBPO), which Bartlett[18] has shown to decompose with a half-life of about 3 hr at 35°. Further, no acidic products are formed and *t*-butoxy radicals effective in initiating chain processes are produced in essentially quantitative yield. After preliminary experiments showed that DBPO decomposes completely in 18 hr at 25° and 7000 atm and was an effective catalyst for the polymerization of methyl methacrylate under the same conditions, several samples of pure butyraldehyde containing 0.5% DBPO were held at 7000 atm for 16–48 hr. In no case was any methanol-insoluble product formed, nor could polymer be detected by infrared spectra. Inhibition experiments were carried out using galvinoxyl,[19] a well-known radical trap.[20] At 7000 atm a sample of aldehyde containing 3 mole % acetic acid and 3 mole % galvinoxyl was almost quantitatively converted to polymer. Since (as discussed below) this much acid normally gives only a small yield of polymer, it appears that galvinoxyl actually facilitates the polymerization. This phenomenon is most unlikely for a radical-chain process and is discussed below in connection with the effect of phenols on the polymerization.

Involvement of other species in the postulated radical polymerization of butyraldehyde was investigated by attempting the copolymerization of butyraldehyde with typical carbonyl-conjugated olefins where a strong polar effect would be expected to facilitate copolymerization and possibly even the formation of an "alternating" product.[21] However, subjecting a mixture of methyl methacrylate and butyraldehyde containing 0.5% DBPO to 7000 atm pressure for 18 hr yielded only polymethyl methacrylate, infrared spectrum identical with authentic material. A similar experiment using diethyl fumarate gave no methanol-insoluble products, and the reaction mixture showed no ether bands in its infrared spectrum. Gas–liquid partition chromatography indicated a mixture of higher boiling products, presumably the normal addition product[22] (diethyl α-butyrylsuccinate) plus higher telomers.

Since all our attempts to demonstrate a radical mechanism yielded negative results, we next reinvestigated the hypothesis that the high-pressure polymerization of "old" samples of butyraldehyde is in fact an acid-catalyzed process, usually brought about by traces of butyric acid in the aldehyde. A sample of pure butyraldehyde to which 2.7 mole % butyric acid had been added was held at 8000 atm for 22 hr. The quickly opened reaction vessel was found filled with a viscous liquid. Precipitation of a portion with methanol yielded polymer which had an identical infrared spectrum with that obtained from "old" aldehyde. Another portion of the reaction mixture was placed in a Cannon–Ubbelohde viscosimeter. Three measurements in immediate succession gave flow times of 570, 490, and 380 sec in that order, and it was evident that the polymer was rapidly decomposing. Many similar experiments were carried out; other weak acids, *e.g.*, acetic,

were effective catalysts, but, while larger amounts of acid gave more rapid polymerization, depolymerization (and competing formation of parabutyraldehyde, discussed below) was also accelerated. Under the circumstances, we conclude that the high-pressure polymerization of butyraldehyde is normally an acid-catalyzed process brought about by acidic impurities in the aldehyde. Previous investigators' failure to observe the reaction when large amounts of acid were deliberately added presumably resulted from depolymerization in the reaction vessel after pressure was released and before it could be opened or by the slower, irreversible formation of parabutyraldehyde.[23]

If this interpretation is accepted, the propagation step in high-pressure polymerization of aldehydes is simply an example of acid-catalyzed hemiacetal formation

$$HA + RCHO \underset{\longleftarrow}{\overset{H^+}{\rightleftharpoons}} A\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH \underset{H^+}{\overset{RCHO}{\rightleftharpoons}} A-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH, \text{ etc.}$$

(4)

where HA is a carboxylic acid or other hydroxylic impurity. The successive equilibria lie to the left at atmospheric pressure but are shifted to the right above the critical ceiling pressure, and, as might be anticipated, a comparable base-catalyzed process also exists.[15,23]

The Butyraldehyde–Parabutyraldehyde–Polybutyraldehyde Equilibrium. Treatment of an aldehyde with acid leads to slow equilibration with the corresponding cyclic trimer or paraldehyde. Since this product is an acetal, the reaction shows only acid catalysis, and, since it occurs at room temperature and atmospheric pressure, the ceiling temperature is evidently much higher than for polymerization. In agreement with Gonikberg and Zhulin[8] we find that parabutyraldehyde formation also competes with polymerization under pressure
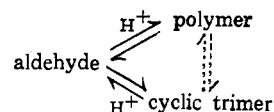
and it was of interest to determine whether equilibrium also exists directly between trimer and polymer. Accordingly, a solution of polybutyraldehyde was treated with a small amount of acetic acid. As soon as depolymerization was complete, the infrared spectrum of the solution was examined, showing butyraldehyde, but no parabutyraldehyde. In a second experiment, pure parabutyraldehyde was held at 8000 atm for 24 hr in the presence of acetic acid and also stronger Lewis acids, BF₃ and SnCl₄. In order to avoid possible reaction before pressure was applied, the catalyst was introduced in a small glass ampoule which crushed on application of pressure. In no case was any polymer observed. Accordingly, we conclude that direct interconversion of paraldehyde and trimer does not take place in our system, and that both products arise from free aldehyde. The situation thus differs from the polymerization of trioxane, which is believed to occur without reversion to monomer.[24]

(18) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).
(19) G. M. Coppinger, *ibid.*, **79**, 501 (1957).
(20) P. D. Bartlett and C. Reuchardt, *ibid.*, **82**, 1756 (1960).
(21) *Cf.* ref 6, Chapter 4.
(22) T. Patrick, *J. Org. Chem.*, **17**, 1009 (1952).

(23) This reversible polymerization–depolymerization can easily be observed in the high-pressure system by following pressure changes above and below the ceiling pressure: Y. Ohtsuka, unpublished results.
(24) H. W. Kohlschutter, *Ann.*, **482**, 75 (1930); W. Kern and V. Jaacks, *J. Polymer Sci.*, **48**, 399 (1960).
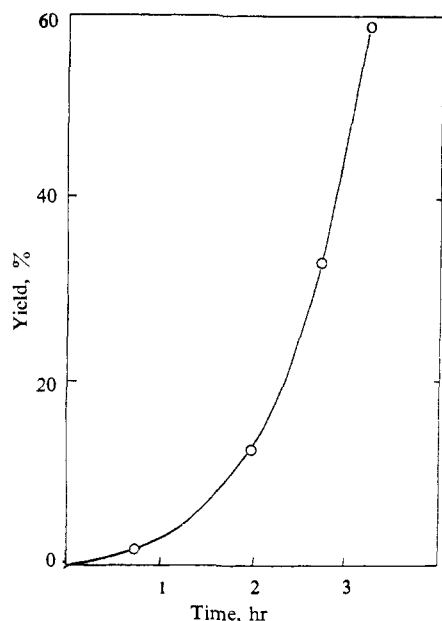
Figure 1. Polymerization of butyraldehyde at 8000 atm, catalyzed by tri-*t*-butylphenol.

acidity. Second, certain highly hindered phenols (notably 2,4,6-tri-*t*-butylphenol (TTBP) and galvinoxyl or its phenolic reduction products) are strikingly effective catalysts for the polymerization. Since they also produce considerable parabutyraldehyde, it seems plausible that they are acting as acidic catalysts, although they fail to trimerize butyraldehyde on standing at atmospheric pressure.

Although we have no detailed interpretation of this striking and unexpected phenomenon, additional observations serve to characterize the process in more detail. First, galvinoxyl-catalyzed polymer, on repeated reprecipitation, shows no ultraviolet absorption characteristic of the galvinoxyl residue, so catalyst is not incorporated in the polymer chain.

Second, TTBP-catalyzed reactions are autocatalytic, Figure 1. Evidently rate is proportional to the amounts of polymer present, suggesting both slow initiation of chains and slow chain growth, so that the number of growing chains increases as reaction progresses.

Third, polymerization rate increases rapidly with TTBP concentration, Table II. At very high catalyst concentration, however, the reaction shifts to irreversible formation of parabutyraldehyde.

Phenol Catalysis. The rapid polymerization of butyraldehyde in the presence of acetic acid and galvinoxyl encouraged us to look into the polymerization of pure butyraldehyde in the presence of phenols alone. Results of a series of survey experiments are listed in Table I and lead to two generalizations. First, phenols in general are catalysts for the trimerization to parabutyraldehyde, effectiveness roughly paralleling phenol

Table II. TTBP Catalysis of Butyraldehyde Polymerization[a]

TTBP, mole %	Polymer, %	Mol wt
0.1	0.5	...
0.2	1.4	...
0.3	60	21,000
0.6	>80	14,500
1.0	>80	...
30	Trimer	...

[a] Conditions: 20 hr at 8000 atm, 25°.

Finally, and perhaps most remarkable of all, highly hindered phenols are also effective catalysts for the polymerization of butyraldehyde at atmospheric pressure below its ceiling temperature. One mole % TTBP leads to polymerization at −196 or −100°, but not at −80°, although propionaldehyde is polymerized at −80°. Products are amorphous and presumably atactic, and evidently the ceiling temperature for butyraldehyde is slightly above −100°, with propionaldehyde somewhat higher. Tetrachlorohydroquinone is also effective, but *p*-*t*-butylphenol is not, paralleling high-pressure results. On the other hand, we observe no low-temperature polymerization with acetic acid.

Stabilization of Polybutyraldehyde. The facile depolymerization of polybutyraldehyde is readily brought about by traces of acids and bases and radical sources[8] and makes the material difficult to handle. The acid-catalyzed depolymerization, at least, requires the presence of a free hemiacetal end group, and should be retarded by introduction of a suitable blocking group.[25] Attempted acylation of polymer in solution at atmospheric pressure with acetyl chloride led only to depolymerization. However, passing ketene into a benzene solution of polymer yielded an undegraded product

Table I. Phenol Catalysis of Butyraldehyde Polymerization[a]

Phenol	% reaction	% polymer
Phenol	13.8	1.6
p-Methyl-	2.1	None
p-*t*-Butyl-	2.6	None
p-Amino-	56[b]	None
p-Methoxy-	2.0	None
p-Chloro-	3.2	None
p-Nitro-	2.6	None
2,6-Dimethyl-	3.0	None
2,6-Di-*t*-butyl-	1.6	None
2,4,6-Trimethyl-	2.1	None
2,4,6-Tri-*t*-butyl-	59[c]	40[d]
2,6-Di-*t*-butyl-4-methyl-	40	10
2,4,6-Tribromo-	2.5	None
2,4,6-Trinitro-	96[c]	None
Pentachloro-	7.3	1.8
1-Naphthol	5.0	None
2-Naphthol	3.0	None
Hydroquinone	2.0	None
Tetrachlorohydroquinone	21[c]	16
Catechol	2.0	1.7
Tetrachlorocatechol	80[c]	None
4-*t*-Butylcatechol	Some	Some[e]
4,4'-Biphenol	2.0	None
Pyrogallol	2.6	1.5
Galvinoxyl	~100	~100[f]
2-Hydroxypyridine	5.1[b]	None

[a] Conditions: 1 mole % phenol, 4 hr at 8000 atm, 25°; % reaction represents total nonvolatile products, trimer, polymer, etc., % polymer, methanol-insoluble products. [b] Probably aldol condensation products. [c] Methanol-soluble product identified as parabutyraldehyde. [d] Mol wt, 35,000. [e] Yield not determined quantitatively; mol wt, 7000. [f] Mol wt (estd), 80,000.

(25) Such reactions, known as "end-capping," are of critical technical importance in the stabilization of formaldehyde polymers. For references and discussion, cf. F. M. Berardinelli, T. J. Dolce, and C. Walling, *J. Appl. Polymer Sci.*, 9, 1419 (1965).

showing disappearance of any —OH peak at 3500 cm^{-1} in its infrared spectrum and appearance of a carbonyl group at 1720 cm^{-1}. Polymer stability was followed by molecular weight change in a vapor osmometer. The acetylated polymer showed no degradation in 30 min, conditions under which unacetylated polymer decomposed completely.

A simpler way of preparing stable polymer proved to be polymerization using TTBP catalyst in the presence of acetic anhydride. After 22 hr at 8000 atm polymer was isolated similar in infrared spectrum and stability to that resulting from the ketene treatment. Evidently in the presence of an effective catalyst polymerization proceeds quite rapidly to equilibrium, after which slow acetylation of the end groups takes place, effectively freezing the equilibrium even after pressure is released.

Experimental Section

Materials. "Pure" n-butyraldehyde was prepared by washing commercial material with bicarbonate, drying over magnesium sulfate, and fractionating through a packed column, bp 75.3–75.5°, and storing in a dark bottle over Drierite in a drybox. Before use it was "prepolymerized" at 8000 atm for 16–20 hr and unreacted aldehyde distilled on a vacuum line into sealable ampoules. These in turn were opened in a drybox under nitrogen immediately before filling reaction vessels. "Old" butyraldehyde was commercial material used without purification. Parabutyraldehyde was prepared by adding 2 ml of concentrated H$_2$SO$_4$ to 100 ml of butyraldehyde. The mixture was allowed to stand 24 hr, washed free of acid with water and bicarbonate solution, dried, and distilled, bp 114–115° (19 mm), n^{25}D 1.4258. Di-t-butyl peroxyoxalate was prepared as described by Bartlett[18] and stored as a 10% frozen

solution in benzene at —20°. Galvinoxyl was prepared as described by Coppinger.[19] Other reagents were commercial materials, purified as necessary by conventional means and purity checked by melting point or other physical properties.

High-pressure techniques were essentially those described previously.[26] Large-scale (5–30 ml) experiments were run in collapsible Teflon vessels as in previous work. For some runs, notably survey experiments on phenol catalysis, smaller vessels were employed constructed of Teflon "spaghetti tube" approximately 36 mm long and 3 mm in internal diameter, the ends closed with Teflon plugs protected in turn from the hydraulic fluid by Neoprene serum caps. These had a capacity of 0.2 ml, and as many as 24 could be placed simultaneously in the pressure system.

Polymer Characterization. Polymer was precipitated with methanol, dissolved in chloroform, and reprecipitated as necessary followed by drying in a vacuum desiccator. It was obtained as a white powder, soluble in aromatic and chlorinated solvents. Infrared spectra were run in CCl$_4$ and molecular weights, when reported, were obtained in benzene or CCl$_4$ solution at approximately 50° using a commercial vapor pressure osmometer (Mechrolab, Inc., Mountain View, Calif.). In the experiments listed in Table I, total product was determined by evaporating a weighed aliquot of the reaction mixture to constant weight under vacuum in a rotary evaporator at room temperature. Polymer was determined as methanol-insoluble material, and it and parabutyraldehyde were confirmed by infrared spectra.

Acetylation of polymer with ketene was accomplished by passing ketene from a ketene generator into a stirred benzene solution of polymer at room temperature. Reaction was continued until samples showed complete disappearance of –OH absorption at 3500 cm^{-1}. Acetylation under pressure was achieved by carrying out normal TTBP-catalyzed polymerizations in the presence of a few per cent acetic anhydride.

(26) C. Walling and J. Pellon, J. Am. Chem. Soc., 79, 4777, 4786 (1957).

Organic Reactions under High Pressure. XI. The Butyraldehyde–Polybutyraldehyde Equilibrium[1]

Yasuji Ohtsuka and Cheves Walling

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received December 1, 1965

Abstract: The equilibrium between n-butyraldehyde and its linear polyacetal has been investigated at 0–20° and pressures of 7000–10,000 atm, and results have been interpreted in terms of a ceiling temperature for the polymerization process. For the equilibrium, with 1 M monomer in hexane $\Delta S_p = -29.1 \pm 1$ cal/deg mole and $\Delta V_p = -8.0 \pm 1$ cc/mole in this pressure range. Direct measurement at atmospheric pressure at 20° gives $\Delta V = -15.5$ cc/mole and $\Delta H = -5.07$ kcal/mole. Extrapolation to atmospheric pressure indicates a ceiling temperature of —75° for 1 M aldehyde in fair agreement with experiment. The importance of this low value on the polymerization properties of aldehydes and the stabilities of their polymers is discussed.

As shown in the preceding paper of this series,[2] the high-pressure polymerization of n-butyraldehyde to a linear polyacetal is a simple acid- (or base-) catalyzed process in which propagation occurs by successive addition of aldehyde to free hydroxyl end groups of a growing polymer chain. Accordingly, propagation steps are freely reversible, and this paper describes a study of the effect of pressure and temperature on the monomer–polymer equilibrium. Our treatment of the results is based upon the concept of ceiling temperature,

developed by Dainton and Ivin,[3,4] which they express in the form

$$T_c = \frac{\Delta H_0}{\Delta S_0 + R \ln [\text{M}]/[\text{M}]_0} \qquad (1)$$

Equation 1 defines a ceiling temperature T_c at which propagation and depropagation of the growing chains in an addition polymerization occur at equal rates. Thermodynamic quantities refer to either the propagation process or the over-all polymerization reaction

(2) C. Walling and T. A. Augurt, J. Am. Chem. Soc., 88, 4163 (1966).
(3) F. S. Dainton and K. J. Ivin, Nature, 162, 705 (1948).
(4) F. S. Dainton and K. J. Ivin, Quart. Rev. (London), 12, 61 (1958).