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DIMERIZATION OF BUTYRALDEHYDE AT ULTRAHIGH PRESSURES

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In 1929 P. W. Bridgman and J. B. Conant ([1]) discovered the phenomenon of reversible polymerization of butyraldehyde at room temperature and a pressure of 12,000 atm. Subsequent studies ([2,3]) established that this reaction is initiated by small amounts of oxygen and peroxides. The polymers obtained have a consistency ranging from a viscous liquid to a wax-like substance and gradually depolymerize at atmospheric pressure with formation of the original aldehyde. The rate of depolymerization depends to a considerable extent on temperature. According to the data of ([3]), the polymers can be stored in vacuo over calcium chloride at 5° for a long time. The polymers proved to be insoluble in organic solvents, which made it impossible to determine their molecular weights. Nor did the addition to the polymerizing aldehyde of various reagents for establishing the nature of the end groups of the polymer molecules lead to positive results.

Thus, up to the present time the structure of the polymers of butyraldehyde and the reasons for their extreme instability remain unclear. It seemed to us that, in order to resolve these questions, one should first attempt to obtain, under conditions of ultrahigh pressure, the lower polymers of butyraldehyde, which might prove accessible to physicochemical investigation. The present communication sets forth the results of work that led to the preparation of an unstable dimer of butyraldehyde.

Experimental Part

In the experiments, butyraldehyde was used which, after drying with calcium chloride, was distilled on a rectification column with an efficiency of 30 theoretical plates (in an atmosphere of nitrogen purified from oxygen); b.p. 74.3–74.7° (748 mm), n_D^{20} 1.3793–1.3801. The corresponding literature data are contradictory (b.p. 73–77°, n_D^{20} 1.38433 ([4]); b.p. 73–74°, n_D^{20} 1.37875 ([5]); b.p. 74.7° ([6]), etc.). Butyraldehyde purified by preparation of the bisulfite compound and its subsequent decomposition possessed the same constants as those indicated by us above; however, its yield was extremely low owing to the occurrence of condensation processes during decomposition of the bisulfite compound by solutions of caustic soda and sodium carbonate.

Fig. 1. Sealed ampoule

Figure 1: Fig. 1. Sealed ampoule

Fig. 2. Evaporation curve of the polymerizate

Figure 2: Fig. 2. Evaporation curve of the polymerizate

Procedure for carrying out the experiments. Freshly distilled butyraldehyde was introduced by means of a syringe, under nitrogen, into a brass ampoule of about 2 ml capacity, fitted with a long outlet tube which, after filling the ampoule, was pinched in two places (Fig. 1). The ampoule was then immersed up to the upper bend of the tube in ice water, and the opening of the outlet tube was soldered with tin. The sealed ampoule was placed in a multi-

plier (see (7)); isopentane was used as the pressure-transmitting medium. The pressure was measured with a manganin manometer placed in the channel of the high-pressure vessel of the multiplier, with an accuracy of ±100 atm. The ampoule with aldehyde was kept under pressure at room temperature for a specified time, after which the pressure was reduced and the ampoule was removed from the multiplier.

Method for determining the polymer yield. The reaction product, in an amount of about 1.5 g, was poured into a cylindrical duralumin cup (cup weight 2.70 g, height 80 mm, inner diameter 10 mm), which was suspended from a spring balance. The balance consisted of a spiral of tungsten wire placed in a high glass tube, sealed at one end and provided with a side arm for creating a vacuum. The accuracy of weight measurements on the spring balance was ±0.005 g. A vacuum was then produced in the tube (residual pressure 13–18 mm Hg). As a result of the rapid evaporation of the remaining unpolymerized butyraldehyde, the cup cooled to a temperature of about -5° (which prevented depolymerization of the polymer formed (3)). In this process an approximately constant value of weight loss per unit time was established, persisting until the monomer had almost completely evaporated; then the slope of the "weight*—time" curve began to decrease rapidly and reached a new constant value. A typical evaporation curve is shown in Fig. 2. The ordinate of point A on the "weight—time" curve, corresponding to the beginning of establishment of a constant evaporation rate after removal of the initial monomer, was taken by us as the value of the polymer yield in the given experiment.

Fig. 1. Sealed ampoule

Fig. 2. Evaporation curve of the polymerizate

To estimate the error of the method, we determined the composition of artificial binary mixtures of butyraldehyde (n_D^{20} 1.3798) and butyl ester of butyric acid (corresponding in its empirical formula to the dimer of butyraldehyde) with n_D^{20} 1.4063; n_D^{25} 1.4043 (according to literature data (8), n_D^{25} 1.4045). The results of these experiments are given in Table 1.

Examination of Table 1 leads to the conclusion that the use of the method described above makes it possible to carry out an approximate determination of the composition of a mixture consisting of components with widely differing saturated-vapor elasticities and molecular weights. The values obtained for the content of the high-molecular component proved to be somewhat overestimated (by 2.5–5%).

Results of the study. The experiments we carried out showed that at pressures of 5500–6000 atm a liquid polymer can be obtained from butyraldehyde. For this it is necessary to adhere to the procedure described above for obtaining the aldehyde, filling the ampoule with it, and sealing the latter. Experiments conducted under conditions that permitted contact of the aldehyde with air led in a number of cases to the formation of a wax-like product. At 3000 atm polymerization was not observed. The liquid polymers obtained dissolved in benzene, which made it possible to deter-

* Expressed as a percentage of the polymer weighed out.

divide their molecular weight. The results of some experiments are summarized in Table 2.

Examination of Table 2 permits the conclusion that, under the conditions studied, polymers are formed from butyraldehyde whose molecular weight is close to the molecular weight of the dimer (144).

Table 1

Analysis of a mixture of $C_4H_8O + C_8H_{16}O_2$

Content of $C_8H_{16}O_2$ in the mixture, wt. %, true	Content of $C_8H_{16}O_2$ in the mixture, wt. %, found	Absolute error, %
20	22.5	+2.5
40	45	+5
60	65	+5

Figure 3 shows the dependence of the refractive index of the polymerizate on its dimer content (experiments Nos. 2, 4–8*). The straight line in this graph is drawn in accordance with the assumption of additivity of n_D^{20} for the monomer and dimer (by weight fractions; n_D^{20} of the dimer was taken as 1.4150). As can be seen from the figure, the experimental points obtained lie to the right of this straight line, the deviations reaching 5% in the direction of higher dimer content.

In air at atmospheric pressure, the polymers obtained gradually depolymerize. However, in a dilute solution of the polymer in benzene near the solidification point of the latter, the rate of depolymerization is insignificant. Thus, in experiment No. 2 the molecular weight decreased in 47 min from 142 to 135, and in experiment No. 6 in 33 min from 143 to 134, which in fact is almost within the limits of the error of the determinations.

Table 2

Results of experiments on the dimerization of butyraldehyde

Experiment No.	P, atm	Duration of experiment, h	n_D^{20} of aldehyde	n_D^{20} of polymer**	Mol. wt. of polymer
1	3000	25	1.3795	Polymerization was not observed	Polymerization was not observed
2*	5500	24	1.3801	1.4145	142
3*	5500	48	1.3801	1.4221	164
4	6000	23	1.3801	1.4143	137
5	6000	24	1.3793	1.4178	–
6	6000	23	1.3707	–	143
7	6000	21	1.3795	1.4121	–
8	6000	9	1.3800	1.4141	–

* Experiments Nos. 2 and 3 were carried out in parallel in two multipliers with one and the same initial aldehyde.

** After evaporation of the unpolymerized aldehyde.

We also carried out an experiment to determine whether any significant depolymerization of the butyraldehyde polymer occurs at the moment of its dissolution in benzene.

We mixed the dimer from experiment No. 5 (n_D^{20} 1.4178) with benzene (n_D^{20} 1.5010). The resulting mixture, containing 32 wt. % dimer, was characterized by n_D^{20} 1.4728; calculated according to the additivity scheme, n_D^{20} 1.4744. Taking into account some

* The yields of polymer in the various experiments differed considerably from one another, apparently because we did not ensure complete identity of the characteristics of the monomer and of the experimental conditions.

depolymerization occurring during the weighing of the polymer, and also the possible approximate nature of the additive scheme, it may be asserted that no appreciable depolymerization of the polymer occurs at the moment of its dissolution in benzene and that, consequently, the molecular weights of the polymer determined by us are close to the true values.

Fig. 3. Dependence of the refractive index of the polymerizate on the dimer content. The points indicate the dimer content according to the evaporation curves.

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Thus, in the present work, an unstable dimer of butyraldehyde has been obtained for the first time (at pressures of 5500–6000 atm.). The structure of the dimer obtained and the reasons for its instability are the subject of further investigation.

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REFERENCES

1. P. W. Bridgman, J. B. Conant, Proc. Nat. Acad. Sci., **15**, 680 (1929).
2. J. B. Conant, C. O. Tongberg, J. Am. Chem. Soc., **52**, 1659 (1930).
3. J. B. Conant, W. B. Peterson, J. Am. Chem. Soc., **54**, 628 (1932).
4. J. W. Brühl, Lieb. Ann., **203**, 1 (1880).
5. J. Timmermans, Bull. Soc. Chim. Belg., **36**, 506 (1927).
6. H. Adkins, A. E. Broderick, J. Am. Chem. Soc., **50**, 500 (1928).
7. V. P. Butuzov, G. P. Shakhovskoi, L. G. Gonikberg, Tr. Inst. Crystallography, Acad. Sci. USSR, No. 11, 233 (1955).
8. J. C. Munch, J. Am. Chem. Soc., **48**, 997 (1926).

Note: Figure translations are in progress. See original paper for figures.