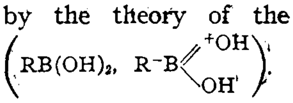
phenylboric acid than in the corresponding benzoic acid derivative. The large ΔpK of groups in boric acid derivatives can also be seen in a comparison of the acid strengths of butyl, benzyl and β-phenylethylboric acids with those of the correspondingly substituted ammonium ions. ΔpK for benzyl minus butyl and for β-phenylethyl minus butyl are -1.63 and -0.73 in the first series and -1.27 and -0.78 in the second.[13] The negativity effects are thus at least as great in the boric acids as in the ammonium ions, though in the former series the dissociating protons are one atom further removed from the compared groups than in the latter. We have chosen the above groups for this comparison because they have no resonance interaction with the rest of the molecule.

The above observations may be explained by the theory of the boric acid resonance,  $\left(RB(OH)_2,\ R^{-}B\begin{matrix} ^{+}OH \\ OH \end{matrix}\right)$. The strength of a boric acid depends on the interaction of the unshared electron pairs of a hydroxyl group with the sextet boron atom. This process imposes a negative charge on the boron atom and is assisted by the negativity of the attached group. This effect is additional to the normal repulsion of the proton by a negative group and enhances the influence of the group. It may be noted that owing to the above resonance the action of a negative substituent is largely on the boron atom in a boric acid but on the hydroxyl group in a benzoic acid derivative, and so acts over a shorter distance in the former than in the latter case.

We wish to express our appreciation to Mr. C. E. Larson of the Biochemistry Department who carried out the glass electrode measurements on the nitrophenylboric acids.

Summary

The dissociation constants of some substituted phenylboric acid derivatives have been measured. These have been discussed and compared on the basis of negativity and resonance.

It is pointed out that the old resonance order assumed for the halogens is wrong and that the true order is F > Cl > Br.

o-Nitrophenylboric acid, unlike other *o*-nitro aromatic acids, is weaker than its meta and para isomers. An explanation for this has been given.

An enhanced effect of the negativity of substituted groups has been noted in boric acid derivatives.

BERKELEY, CALIF. RECEIVED MAY 21, 1934

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[13] These values are calculated from dissociation constants given by Yabroff, Branch and Bettman, Reference 1b; and by Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

[CONTRIBUTION NO. 141 FROM THE EXPERIMENTAL STATION OF THE E. I. DU PONT DE NEMOURS & COMPANY]

Polymerization under High Pressure

BY HOWARD W. STARKWEATHER

Since polymerization reactions involve greater contractions in volume than most reactions in condensed systems, it seemed reasonable to suppose that polymerizations would be more sensitive to pressure than most reactions.

Strange and Bliss claimed[1] that the polymerization of hydrocarbons, such as butadiene, to rubber-like substances was greatly accelerated when they were subjected to high pressure.

Bridgman and Conant[2] reported the polymerization of isoprene, dimethyl-2,3-butadiene-1,3, styrene, indene, isobutyraldehyde and *n*-butyraldehyde at pressures up to 12,000 atmospheres. Conant and Tongberg[3] investigated the polymerization of isoprene, vinyl acetate and *n*-butyraldehyde in greater detail. They showed that the rate of polymerization of isoprene was accelerated by peroxides, was retarded by hydroquinone, and followed the rate for a first order reaction. Conant and Peterson[4] continued this investigation and concluded that peroxide catalysts were essential to the polymerization, and that the effect of increased pressure was only to accelerate the catalyzed reaction. Cyclohexene oxide was polymerized with great difficulty. Tammann and Pape[5] investigated in considerable detail the polymerization of styrene, isoprene, vinyl acetate, dimethylbutadiene and indene at pressures of 720 to 3100 atmospheres and temperatures of 140 to 160°.

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[1] Strange and Bliss, British Patent 3045 (1913).

[2] Bridgman and Conant, *Proc. Nat. Acad. Sci.*, **15**, 680 (1929).

[3] Conant and Tongberg, THIS JOURNAL, **52**, 1659 (1930).

[4] Conant and Peterson, *ibid.*, **54**, 628 (1932).

[5] Tammann and Pape, *Z. anorg. allgem. Chem.*, **200**, 113 (1931).

This paper summarizes an investigation of the effect of high pressure upon the polymerization of various unsaturated compounds. An attempt has been made to arrange these compounds in the order of their ease of polymerization under high pressure.

Apparatus.—The high pressure apparatus was essentially that described by P. W. Bridgman.[6] The sample was placed in a glass tube, the open end of which dipped under mercury contained in a steel tube. By equipping this steel tube with a suitable valve and chilling the tube and contents to within a few degrees of the freezing point of mercury, it was possible to work with samples boiling below 0°. The sample tube was entirely filled with liquid. Kerosene was used in transmitting hydrostatic pressure to the mercury and to the outside of the glass tube. In the experiments above room temperature the heavy-walled steel pressure cylinder was heated by a bank of carbon lamps.

Procedure.—The majority of the samples used in this work were obtained from Dr. Carothers and his co-workers, and the methods of preparation of the newer compounds are described in recent publications from this Laboratory. The samples had been freshly distilled but were exposed to air for at least a few minutes, so they probably contained at least traces of oxygen or peroxides.

After the sample had been placed in the press, the pressure was gradually built up until the electric gage indicated that the desired pressure had been obtained. The piston was then held in place with a lock nut until the pressure was released for removal of the sample. About fifteen minutes were required to insert or to remove the sample. Although the press was shown to be free from leaks, the electric gage indicated that it was necessary to force the piston further into the cylinder from time to time in order to maintain constant pressure, in the case of samples which polymerized. There was a slight but definite decrease in volume of the samples during polymerization even at these high pressures. The compressibilities of the monomers were apparently greater than the compressibilities of the polymers, so the higher the pressure the less was the change in volume during polymerization. The extent of this difference varies with the different compounds.

In a few experiments with bromo-2-butadiene-1,3,-chloro-2-butadiene-1,3 and divinylacetylene, three small glass tubes containing portions of the same sample were placed in the press at the same time and removed at different times in order to follow the rate of polymerization.

Wherever possible the percentage polymerization was determined by evaporating the monomer under reduced pressure from a weighed sample either directly or after precipitation in alcohol. In some cases the entire sample was required for other tests and its approximate polymerization, as indicated, was estimated from the contraction in volume and appearance of the sample.

Product.—The products of polymerization at these high pressures showed no marked difference from those obtained under more nearly normal conditions. Any differences were in degree rather than in kind. In their resemblance to natural rubber, polymerized chloroprene and bromoprene were far superior to any of the other polymers prepared. The polymers of most of the other dienes were more or less rubber-like. Isoprene samples 13a and 13b were plastic and could be vulcanized; the other isoprene samples were too elastic for compounding. The polymers of monovinylacetylene and divinylacetylene were nonplastic and only slightly elastic. Styrene and vinyl acetate gave thermoplastic polymers.

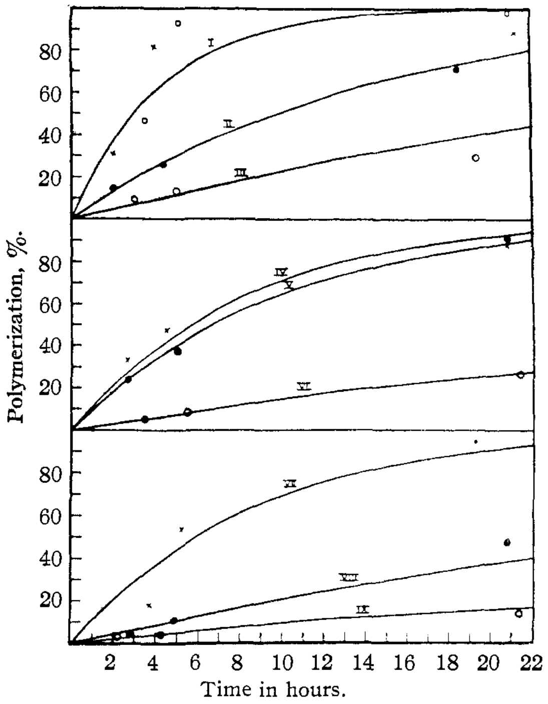

Fig. 1.—Polymerization under high pressure: Bromo-2-butadiene-1,3, I, × 6000 atmospheres, 24°. □, 6000 atmospheres, 22°. II, ●, 3000 atmospheres, 36°. III, ○, 3000 atmospheres, 24°. Chloro-2-butadiene-1,3, IV, × 6000 atmospheres, 22°. V, ●, 3000 atmospheres, 42°. VI, ○, 3000 atmospheres, 22°. Divinylacetylene, VII, × 6000 atmospheres, 43°. VIII, ●, 6000 atmospheres, 29°. IX, ○, 6000 atmospheres, 22°.

Calculation of Results.—In calculating the results given in the table the rates of polymerization are assumed to be first order.

$$k = \frac{2.3}{t} \log \frac{1}{1 - x}$$

in which x equals the fraction polymerized after time t. Earlier conclusions that polymerizations are first order reactions are substantiated in this

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(6) Bridgman, "The Physics of High Pressure," Macmillan Co., New York, 1931.

POLYMERIZATION UNDER HIGH PRESSURE

Compound	Sample	Press., atm.	Temp., °C.	Time, hours	Polymerization, %	k $\frac{2.3}{t}\log\frac{1}{1-x}$	k calcd. for 6000 atm. and 25°		Calcd. hours for 50% polymerization at 6000 atm. at 25°
							Av. for sample	Av. for compound	
Iodo-4-butadiene-1,2	1a	6000	Room		Decomp.				
	1b	2000	Room	16.5	40.0	0.031	0.5	0.5	1.4
Bromo-2-butadiene-1,3	2a	6000	22	3.5	48.8	.191			
				5.25	93.0	.506			
				21.25	96.7	.161	.40		
	2b	6000	24	2.0	31.0	.186			
				4.0	81.0	.414			
				21.5	86.0	.091	.26		
	2c	3000	21	4.3	23.0	.061			
				6.3	23.0	.041			
				20.0	88.0	.106	.87	.39	1.8
	2d	3000	24	3.0	9.7	.034			
				5.0	12.5	.025			
				19.3	28.7	.018	.23		
	2e	3000	36	2.0	14.6	.079			
				4.4	26.0	.071			
				18.5	70.0	.065	.17		
Chloro-2-butadiene-1,3	3a	6000	22	2.75	32.8	.145			
				4.5	47.0	.141			
				21.0	84.0	.087	.17		
	3b	3000	22	3.5	5.0	.0147			
				5.5	8.8	.0167			
				21.5	24.5	.0131	.17	.16	4.3
	3c	3000	42	2.7	24.1	.102			
				5.0	37.3	.093			
				21.0	90.6	.113	.13		
Methyl vinyl ketone	4a	5500	40	16.0	94.0	.176	.049		
	4b	6000	24	23.0	77.6	.065	.073	.051	14.0
	4c	6000	38	2.75	6.9	.026			
				4.9	78.0	.31	.041		
Phenyl-2-butadiene-1,3	5	5500	Room	18.0	30 ±	.020	.028	.028	25.0
Dichloro-1,4-hexatriene-2,3,5	6a	6000	47	24.0	95 ±	.13	.01		
	6b	6000	25	23.0	50 ±	.03	.03	.02	35.0
Divinylacetylene	7a	6000	22	2.17	3.0	.0139			
				4.17	3.6	.0088			
				22.5	12.7	.0060	.014		
	7b	6000	29	2.75	4.0	.015			
				4.8	10.5	.023			
				21.0	47.7	.030	.015		
	7c	6000	41	3.75	11.4	.083			
				6.0	34.4	.072			
				22.25	98.7	.195	.018	.017	40.0
	7d	6000	43	3.7	17.4	.052			
				5.25	53.4	.145			
				19.25	94.6	.152	.017		
	7e	3000	36	21.5	14.0	.0070			
				45.5	38.0	.0105			
				68.3	93.0	(.039)	.022		
Heptyl-2-butadiene-1,3	8a	5500	Room	64.0	46.0	.010	.017		
	8b	5500	54	45.5	97.0	.077	.007	.013	53.0
	8c	5500	40	18.0	58.0	.048	.013		
Styrene	9	5000	58	23.0	92.4	.112	.008	.008	88.0
Chloro-1-butadiene-1,3	10	6000	50	48.0	95 ±	.062	.005	.005	140.0
Dimethyl-1,2-chloro-3-butadiene-1,3	11	6000	40	102.0	90 ±	.023	.005	.005	140.0
Chloro-3-octatetrene-1,3,5,7 and pyrogallol	12	6000	Room	65.0	25 ±	.004	.004	.004	170.0
Isoprene	13a	5500	Room	64.0	6.7	.001	.0014		
	13b	5500	54	45.5	93.4	.093	.0066		
	13c	5500	54	16.0	78.0	.094	.0067	.004	170
	13d	5500	40	18.0	30.0	.020	.0056		
	13e	6000	Room	94.0	4.3	.0005	.0005		
Methylethylvinylethinylcarbinol	14	6000	50	76.0	95 ±	.04	.003	.003	230
Vinyl acetate	15a	6800	45	20.0	61.0	.047	.0032		
	15b	8000	46	23.5	87.6	.089	.0024	.003	230
Butadiene-1,3	16a	7500	62	18.0	50 ±	.039	(0.0003)		
	16b	7000	61	19.0	95 ±	.158	.0021		
	16c	7000	48	46.0	95 ±	.065	.0029	.0025	280
Chloro-2-tetramethylene-3,4-butadiene-1,3	17	6000	38	70.0	50 ±	.01	.0024	.0024	290
Dichloro-1,3-hexadiene-2,4	18	6000	49	93.0	90 ±	.025	.002	.002	350
Monovinylacetylene	19	6000	54	17.0	50 ±	.04	.002	.002	350
Heptyl-1-chloro-2-butadiene-1,3	20	6000	38	96.0	50 ±	.007	.0017	.0017	400
Butyl-1-chloro-2-butadiene-1,3	21	6000	38	96.0	50 ±	.007	.0017	.0017	400
Chloro-2-propene-1	22	5000	Room	16.0	0.03	2×10^{-5}	4×10^{-5}		20000

POLYMERIZATION UNDER HIGH PRESSURE (*Concluded*)

Compound	Sample	Press., atm.	Temp., °C.	Time. hours	Polymerization, %	k $\frac{2.3}{t}\log\frac{1}{1-x}$	k calcd. for 6000 atm. and 25° Av. for sample	k calcd. for 6000 atm. and 25° Av. for compound	Calcd. hours for 50% polymerization at 6000 atm. at 25°
Chloro-1-propene-1	23	5000	Room	16.0	0.01	6×10^{-5}	12×10^{-6}		60,000
Chloro-3-hexatetrene-1,3,4,5	24	6000	Room	Decomposed to C, H_2 and HCl					
Vinyl fluoride, sat. sol. in toluene at −35°	25	6000	67	16.0	Polymerized to some extent.				
Diethyl fumarate + 1% benzoyl peroxide	35	2000	59	22.5	92%				
Formalin	37	6300	74	21.0	Slight turbidity, otherwise unchanged.				

Dipentene, dichloro-1,2-butene-3, dichloro-1,4-butene-2, dichloro-2,4-butene-3,[29] hydroxy-4-butadiene-1,2,[30] phenoxy-4-butadiene-1,2,[31] methoxy-1-chloro-3-hexadiene-2,4,[32] chloro-4-butadiene-1,2,[33] diethyl fumarate, formamide, methyl formate and crude butylene were treated at pressures of 5000–9000 atm., temperatures of 40 to 74° and for times of 15 to 154 hours but were unchanged.

Compound	References
1, 30	Carothers and Berchet, THIS JOURNAL, **55**, 2807 (1933).
2	Carothers, Kirby and Collins, *ibid.*, p. 782.
3	Carothers, Williams, Collins and Kirby, *ibid.*, **53**, 4203 (1931).
5, 8	Carothers and Berchet, *ibid.*, **55**, 2813 (1933).
6, 24	Coffman and Carothers, *ibid.*, p. 2040.
7, 19	Nieuwland, Calcott, Downing and Carter, *ibid.*, **53**, 4197 (1931).
10, 12, 25, 29, 31	Unpublished
11, 17	Carothers and Coffman, *ibid.*, **54**, 4071 (1932).
14	Carothers and Jacobson, *ibid.*, **55**, 1097 (1933).
18, 32	Coffman, Nieuwland and Carothers, *ibid.*, p. 2048.
20, 21	Jacobson and Carothers, *ibid.*, p. 1624.
33	Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932).

case by measurements with bromoprene, chloroprene and divinylacetylene. The results obtained with samples 2a, 2b, 2d, 2e, 3a, 3b, 3c, 7a, 7b and 7d are shown in Fig. 1. The curves were plotted according to the calculated values from the average reaction constants.

Since the various compounds polymerized at widely different rates, it was necessary to use more rigorous conditions with some samples than with others. In order to make an exact comparison of the rates of polymerization of these different compounds it would be necessary, as indicated by the results of Conant and his coworkers, and of Tammann and Pape, to make an extensive series of experiments with each compound, studying the effect of the presence of possible catalysts as well as the effect of temperature and pressure on the rate of polymerization. Since such extended investigation did not appear to be feasible, it was necessary to use an arbitrary method for calculating the different reaction velocities to the same conditions of temperature and pressure. Of the equations considered, the following appeared most nearly to represent the experimental results.

$$\log k_1 = \log k_2 + 3.0 \times 10^{-4} (P_1 - P_2) + 4370 \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

k_1 = First order rate constant at pressure P_1 and temperature T_1.

k_2 = First order rate constant at pressure P_2 and temperature T_2.

For the purposes of this comparison P_1 is taken as 6000 atmospheres and T_1 as 298 Å.

This equation assumes that the reaction velocity in the neighborhood of 6000 atmospheres doubles for every 1000 atmospheres and that the heat of activation is 20,000 calories. This is in approximate agreement with the observations of Conant and Tongberg. The calculated results for k at 6000 atmospheres and 25°, for the compounds for which data are available under different conditions, agree as well as the constants calculated for different determinations under the same conditions. In spite of the many uncertainties involved, it is believed that the results calculated according to the above equation give a semi-quantitative comparison of the rates of polymerization at 6000 atmospheres and at 25° of the compounds listed in the table. The time for 50% polymerization was calculated from the average value for k.

If the chloro-3-octatetrene-1,3,5,7 had been free from pyrogallol, it would have polymerized much more rapidly than the results indicated. With iodo-4-butadiene-1,2, chloro-3-hexatetrene-1,3,4,5, and in some experiments with chloro-2-butadiene-1,3 polymerization occurred so rapidly that the heat of polymerization caused the sample to decompose.

Conclusions that can be drawn from these data as to the influence of substituent groups upon the polymerization of compounds containing conjugated double bonds are in agreement with those recently presented by Carothers.[7]

The presence of substituent groups in the β position increases the rate of polymerization; the effect of halogens, in the increasing order Cl, Br, I, is much greater than that of alkyl groups. It has been pointed out in previous publications that the polymers derived from these haloprenes are radically different from those obtained from diene hydrocarbons. The effect of the phenyl group is intermediate between that of the halogens and alkyl groups. The presence of halogens on the α carbon has less influence than on the β carbon. Alkyl groups on the α carbon inhibit polymerization and repress the activating effect of a group on the β carbon. Butene, dipentene and hydroxy-4-butadiene-1,2 did not polymerize under these conditions.

Miscellaneous Experiments.—In addition to the experiments with pure compounds, the effect of pressure on a number of commercial mixtures was studied. Different samples of cracked gasoline were subjected to pressure—in one case to 9000 atmospheres at 60° for forty-eight hours. There was no indication of resinous products, although the distillation range indicated that 10% of the low boiling material had been converted to higher boiling compounds.

A series of experiments with China wood oil showed that it polymerized at 5000 to 6000 atmospheres and 50° to give products similar to those formed at much higher temperatures and atmospheric pressure. Samples in the press for three hours showed marked increase in viscosity; the longer the sample was subjected to pressure the more gelatinous it became and ultimately it was converted to a waxy gel somewhat drier than those obtained by heating at atmospheric pressure. Castor oil was little if at all changed by pressure.

After a 35% solution of ethylene oxide in water had been maintained at 6000 atmospheres and 60° for nineteen hours the ethylene oxide was found to have been converted to ethylene glycol, even though no catalyst had been added. Attempts were made similarly to combine amylene and water but they were unsuccessful, even when a stable emulsion of amylene and water had been prepared.

Summary

A large number of compounds have been polymerized at pressures up to 9000 atmospheres. Velocity constants are calculated according to the equation for first order reactions. An equation is proposed for calculating all of the rates of polymerization at the same conditions of pressure (6000 atmospheres) and temperature (25°). The compounds investigated are arranged in descending order of their ease of polymerization. With the exception of methoxy-1-chloro-2-hexadiene-2,4 all of the compounds containing conjugated double bonds which were investigated underwent polymerization under pressure. Except iodo-4-butadiene-1,2, which probably rearranges, compounds containing adjacent double bonds, but no conjugated double bonds, were unchanged by pressure.

WILMINGTON, DELAWARE RECEIVED MAY 28, 1934

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[7] Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934).