what higher, indicating that C_I and C_M are both decreased slightly by pressure.

If this interpretation is correct, polystyrene produced under pressures above 3000 kg./cm.^{2} with a non-transfering initiator such as azobisisobutyronitrile should give values of $\bar{P}$ of about 3×10^4 at 60°, independent of initator concentration, and, since the activation energy for transfer with monomer is much larger than that for chain growth, still higher values at lower temperatures.

Acknowledgments.—Thanks are due to several sources for support of this work: to the Union Carbide and Chemical Corporation for a Fellowship, to the Office of Naval Research for a research contract and to E. I. du Pont de Nemours and Co. and to the Higgins Fund of Columbia University for grants from which much of our high pressure equipment was purchased.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Organic Reactions Under High Pressure. II. The Polymerization of Allyl Acetate[1]

BY CHEVES WALLING AND JOSEPH PELLON[2]

RECEIVED MARCH 25, 1957

The benzoyl peroxide initiated polymerization of allyl acetate has been studied at 80° at pressures up to 8500 kg./cm.^{2}. Pressure slightly decreases the rate of unimolecular decomposition of benzoyl peroxide in this system (although a fast induced reaction sets in at above 2500 kg./cm.^{2}) and the degree of polymerization of the polyallyl acetate formed increases only slightly with pressure. On the other hand, the over-all rate of polymerization increases exponentially with pressure (50-fold at the highest pressure) and becomes proportional to [peroxide]$^{1/2}$. It is concluded that pressure has little effect on the competition between polymer chain growth and transfer with allylic hydrogen, although both are strongly accelerated. In addition, the resulting allylic radicals readily start new chains under pressure so the degradative nature of chain transfer becomes unimportant. Some applications of these conclusions to radical chain processes in general are pointed out.

The preceding paper[3] in this series described the effect of high pressures on the polymerization of styrene and gave an analysis of changes in rate and molecular weight in terms of the effect of pressure on the individual rate constants involved. The polymerization of allyl acetate differs from that of styrene in that kinetic chains are relatively short, and the reaction-rate is approximately proportional to the first power, rather than the square root, of initiator concentration (benzoyl peroxide). These results were rationalized by Bartlett and Altshul[4] in terms of degradative chain transfer, and they proposed as the major steps in the reaction chain

$$M\cdot + M \xrightarrow{k_p} M\cdot \qquad (1)$$

$$M\cdot + M \xrightarrow{k_{tr}} A\cdot \qquad (2)$$

$$2A\cdot \longrightarrow \text{inert products} \qquad (3a)$$

$$\text{or } A\cdot + M\cdot \longrightarrow \text{inert products} \qquad (3b)$$

Here (1) represents the usual chain growth step of attack of a growing polymer chain on the double bond of allyl acetate and (2) represents attack on an allylic hydrogen of allyl acetate to yield the radical $CH_2 = \dot{C}H-CHOAc$. The resulting allylic radical is highly resonance-stabilized and unreactive and was considered to disappear by reactions 3 rather than carrying on the kinetic chain. Subsequent evidence for (2) was obtained by Bartlett and Tate[5] who showed that higher polymerization rates and molecular weights are obtained with deuterated allyl acetate $CH_2{=}CH-CD_2OAc$, although Gaylord and Eirich[6] have suggested that some transfer occurs as well at other C–H bonds in the molecule.

The sequence of reactions given above predicts a first-order dependence of polymerization rate on initiator concentration [P] and also a constant value of d[M]/d[P]. Bartlett and Altshul observed such a relation for individual runs. However, d[M]/d[P] increased somewhat with decreasing initial peroxide concentration (between 10 and 1 wt. %), although molecular weights remained constant ($\bar{P}$ = 13.7). Apparently, as radical concentrations are decreased and radical lives are prolonged, there is some restarting of kinetic chains by A· radicals *via*

$$A\cdot + M \longrightarrow M\cdot \qquad (4)$$

Our own work below indicates that (4) becomes increasingly significant at still lower initiator concentrations. The work reported here was directed toward elucidating the effect of pressure on the competition between (1) and (2), which determines $\bar{P}$, and between (3) and (4) which largely determines kinetic chain length. Our results, combined with those obtained with styrene, lead us to a number of conclusions as to the utility of the use of high pressures as a tool in directing the course of free radical chain processes in general.

Experimental

High Pressure Techniques.—The high pressure apparatus was that described in our previous paper,[3] and polymerizations were carried out using approximately 5-cc. samples in glass internal reaction vessels over mercury. The make-up of samples and filling of the reaction vessels were the same as in our experiments on the styrene-carbon tetrachloride system. The presence of mercury and our filling technique was shown to have no effect on the polymerization rate at atmospheric pressure, since samples in our reaction vessels showed 13 and 24% polymerization in 1.25 and 2.5 hr., respectively, at 80° in the presence of 6.10 wt. % benzoyl

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[1] Taken from a portion of the dissertation of Joseph Pellon, submitted in partial fulfillment of the requirements for the Ph.D. degree, 1957. This work was also supported in part by the Office of Naval Research.

[2] Union Carbide and Carbon Corp. Fellow, 1955–1956.

[3] C. Walling and J. Pellon, THIS JOURNAL, **79**, 4776 (1957).

[4] P. D. Bartlett and R. Altshul, *ibid.*, **67**, 812, 816 (1945).

[5] P. D. Bartlett and F. A. Tate, *ibid.*, **75**, 91 (1953).

[6] N. G. Gaylord and F. R. Eirich, *ibid.*, **74**, 337 (1952).

peroxide, compared with 13 and 23% polymerization for samples polymerized similarly in sealed, degassed glass tubes. Bartlett and Altshul[4] report 11.3 and 20.6% polymerization under the same conditions. All high pressure polymerizations were carried out at 80.0°, and rates were determined by following the small pressure change in the system (held at constant volume) due to reaction. Since the total change never exceeded 100 kg./cm.² and was usually under 50 kg./cm.², the variation had no significant effect on the measured rate. The relation between pressure change and % reaction was determined from the total pressure change during a run and the amount of polymer isolated at the end of a run. The relation was assumed to be linear, as has been found in a number of other systems, and the assumption checked by polymer isolation from experiments run to different conversions.

The pressure change–conversion relation obviously changes with sample size, so (although this can be corrected for) identical size samples were used in each run in a series. The change in pressure per % reaction was also found to be independent of total pressure between 5500 and 8500 kg./cm.² and about 10% less than at 2500 kg./cm.².

Figure 1 shows a plot of our data at 8500 kg./cm.². Pressure is recorded in arbitrary scale readings on the slide wire of the potentiometer measuring the resistance of our manganin gage, and increased values indicate a decrease in pressure. The initial rapid drop arises from the rapid cooling of the sample which has been heated almost adiabatically during compression, so the zero reading is obtained by extrapolation of the flat portion of the curve. Since the potentiometer may be read to 0.1 scale division, the sensitivity of the method is approximately 0.5% reaction.

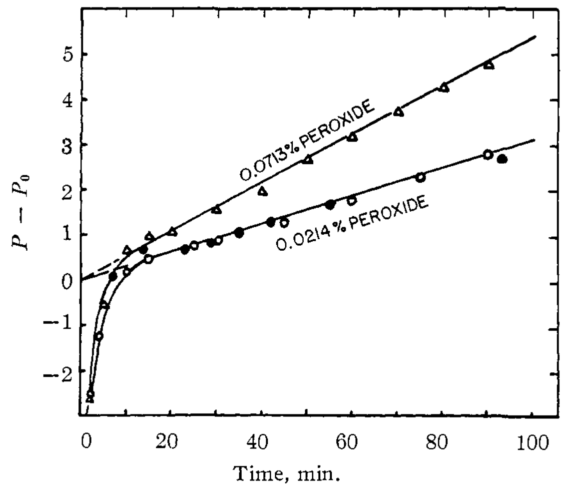

Fig. 1.—Polymerization of allyl acetate at 8500 kg./cm.² and 80°. Ordinate indicates pressure change in arbitrary units of potentiometer slide-wire scale, 1 unit = 4.53% reaction.

Treatment of Polymer.—Polyallyl acetate was isolated by cooling the reaction vessel in ice-water to stop polymerization, and transferring to a tared Petri dish. Most of the volatile monomer was evaporated off in a stream of air and the residue brought to constant weight by vacuum drying for 1–3 days at room temperature. Since our yields at atmospheric pressure were consistently slightly higher than those reported by Bartlett and Altshul,[4] who determined unreacted monomer by titration (*cf.* Fig. 2), our products may have contained a few per cent. of unreacted monomer.

Polymer molecular weights were determined by viscosity measurements in benzene at 30° using the relation employed by Bartlett and Altshul, $\bar{P} = 300\ [\eta]$.

Peroxide Decompositions.—The effect of pressure on the rate of decomposition of benzoyl peroxide in allyl acetate was determined by heating 1.01% peroxide solution at 80° under pressure essentially as described for the polymerization experiments and determining the remaining peroxide by titration of iodine, liberated from iodide in acetic acid, with standard thiosulfate. For reactions at 5500 kg./cm.² it was found necessary to add 3 cc. of carbon tetrachloride to the system before titration to dissolve the considerable amount of polyallyl acetate present and prevent its occluding iodine and interfering with the titration.

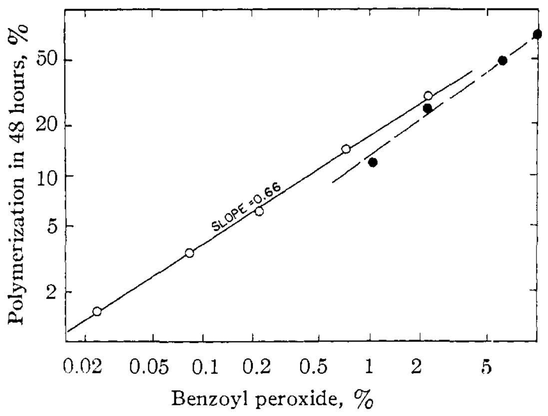

Fig. 2.—Initial peroxide concentration *vs.* total (48 hr.) polymerization of allyl acetate at atmospheric pressure, 80°: open circles, this paper; solid circles, Bartlett and Altshul.

Results and Discussion

Polymerization of Allyl Acetate at Atmospheric Pressure.—In order to interpret our polymerization experiments at high pressures, it was necessary to demonstrate that the presence of mercury had no effect on polymerization rate and to extend atmospheric pressure experiments to lower peroxide concentrations than had previously been reported. The mercury experiments were discussed in the Experimental part of this paper, and the low peroxide runs are summarized in Table I. For comparison with Bartlett and Altshul's data, all experiments were run for 48 hr. at 80° (to essentially complete consumption of initiator). It will be seen that the ratio of d[M]/d[P] increases steadily with decreasing initial peroxide concentration, indicating a rate dependence on peroxide concentration, measured in this way, of less than unity. This relation is shown further in Fig. 2 which gives a logarithmic plot of yield *vs.* initial peroxide concentration and indicates an empirical relation

TABLE I

48-HOUR POLYMERIZATION OF ALLYL ACETATE AT 80° AND ATMOSPHERIC PRESSURE

Wt. % peroxide	Yield, %	Δ[M]/Δ[P]
2.14	30	34
0.713	14	47.5
.214	6.2	70
.084	3.4	98
.023	1.5	158
.00	0.22	...

$$\Delta[M]/\Delta[P] = k[P]_0^{0.66} \qquad (5)$$

The figure also shows the extent of agreement between our data and those of Bartlett and Altshul, and Table I indicates that polymerization due to thermal initiation or adventitious initiators present is negligible.

From Table I it is evident that, at low peroxide concentrations, most acts of chain transfer with allylic hydrogen do not lead to chain termination, since kinetic chain lengths become progressively longer without any increase in $\bar{P}$. Since Bartlett and Altshul's initial suggestion, there have been several attempts to account for this sort of phenomenon. In particular, Sakurada and Takahashi[7] have set up a kinetic scheme to determine the relative rate constants for "effective" and "degradative" chain transfer, considering these as distinct processes and their treatment has been used further by Gaylord.[8] Unfortunately, this treatment involves a limiting value of d[M]/d[P] at zero initiator concentration, and both groups have used values of this ratio for allyl acetate which are much smaller than we actually observe. Furthermore, their kinetic scheme takes no account of what seems to us the most plausible interpretation: the competition between reactions 3, chain termination by allylic radicals, and 4, the restarting of polymer chains; so we regard it as invalid. This competition would lead to an over-all rate expression of mixed first and half order in initiator[9] which is well approximated by an empirical relation such as (5).

The Effect of Pressure on Polymerization Rate.—Results of our high pressure experiments appear in Table II, and in Fig. 3 initial rates are plotted against peroxide concentration using a logarithmic scale. The points at atmospheric pressure are taken from Bartlett and Altshul and are extrapolated to a slope of 0.66 at lower peroxide concentrations on the basis of our own results. Two results are immediately evident from Fig. 3. First, polymerization rate is greatly increased by pressure and, second, the order of reaction in respect to initiator approaches 0.5.

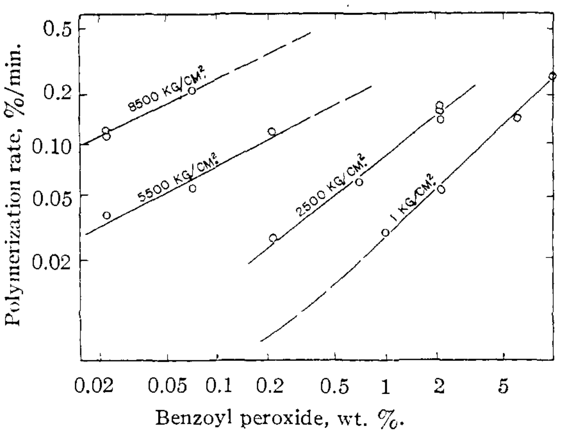

Fig. 3.—Effect of pressure on the polymerization of allyl acetate. Data at atmospheric pressure (1 kg./cm.²) from Bartlett and Altshul.

Since degree of polymerization increases only slightly with pressure, while, as is seen below, the rate of chain starting is actually decreased, both these results indicate that kinetic chain lengths become longer and chain transfer becomes decreasingly "degradative" as pressure increases.

TABLE II

EFFECT OF PRESSURE ON THE POLYMERIZATION OF ALLYL ACETATE AT 80°

Kg./cm.²	[P], wt. %	t, min.	Yield, %	Init. rate, %/min.	$\bar{P}$
2510	2.14	75	15	0.17	..
2440	2.14	150	23	.17	18.8
2430	2.14	265	35	.14	..
2450	0.214	440	10	.027	..
2500•	.713	280	18	.060	..
5510	.214	120	15	.12	21.2
5400	.0214	185	7	.038	21.2
5470	.0713	120	8	.054	..
8520	.0214	90	11	.12	23.6
8490	.0214	150	15	.12	23.6
8520	.0713	90	19	.21	19.4
8500	0	1140	11	...	24.2

In short, at high pressures, the rate of addition of allylic radicals to allyl acetate is accelerated relative to their rate of bimolecular disappearance. This parallels our conclusions about the effect of pressure on the relative rates of k_p and k_t in styrene polymerization. Also, by analogy to styrene, we would expect k_p (the rate constant for reaction 1) to increase with pressure, and this is suggested by the further increase in rate between 5500 and 8500 kg./cm.² where the polymerization rate is already half order in initiator, and chain transfer is no longer degradative.

At 0.3% peroxide concentration to which all rates can reasonably be extrapolated, the rate increases exponentially with pressure, the change being approximately 50-fold at 8500 kg./cm.². This corresponds to $\Delta V^{\ddagger}_{\text{over-all}} = -13.4$ cc./mole. Although the complications in interpreting such a composite quantity were pointed out in the previous paper, the value is close to that for styrene.

Finally, the last run in Table II represents a run carried out at 8500 kg./cm.² in the absence of any added initiator. Although the yield of polymer corresponds to a polymerization rate 150 times that of the parallel experiment at atmospheric pressure (Table I), it is still less than 10% of that in any of the initiated runs.

Effect of Pressure on Degree of Polymerization.—Degrees of polymerization of representative polymer samples prepared at different pressures are indicated in the last column of Table II. In spite of the large increase in k_p evident from our rate measurements, the ratio of $C_M = k_{tr}/k_p$ is relatively insensitive to pressure, decreasing by less than 40%, a result in keeping with our previous observations on the effect of pressure on chain transfer reactions in styrene polymerization. As would be anticipated from our kinetic scheme, there is also no significant variation with peroxide concentration.

Effect of Pressure on Chain Initiation.—Decompositions of 1.01% solutions of benzoyl peroxide in allyl acetate at 1, 2500 and 5500 kg./cm.² are plotted as first-order reactions in Fig. 4. The rate constant derived from our data at atmospheric pressure, $k_d = 5.0 \times 10^{-5}$ sec.$^{-1}$, is in good agreement with that of Bartlett and Altshul (5.3×10^{-5} sec.$^{-1}$). The data at 2500 kg./cm.² also give a good first-order plot, $k_d = 3.3 \times 10^{-5}$ sec.$^{-1}$.

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(7) I. Sakurada and G. Takahashi, *Chem. High Polymers (Japan)*, **11**, 266 (1954).

(8) N. G. Gaylord, *J. Polymer Sci.*, **22**, 71 (1956).

(9) The exact form of the rate equation depends upon the particular bimolecular termination involved. Thus if (3b) is the major termination step, the form is $R_p = a[M]R_i^{1/2} + bR_i$.

This 33% reduction in rate corresponds to $\Delta V^{\ddagger} = 4.7$ cc./mole, a plausible value for a unimolecular process in which one molecule dissociates into two fragments. The effect of pressure on chain initiation depends both upon this change in k_d and any effect on the efficiency of radicals in initiating chains. As we pointed out in our discussion of styrene polymerization, if anything, a decrease in efficiency with pressure should be anticipated, so there is evidently an appreciable decrease in the rate of chain initiation with pressure. Accordingly, the increase in kinetic chain length is even greater than the increase in over-all rate discussed above. At 5500 kg./cm.^{2} the rate of peroxide decomposition is markedly increased and is now higher than first order. This we attribute to the onset of a fast induced decomposition which is discussed further in our following paper, but which we believe represents simply wastage of initiator, and not any increase in radical formation which could lead to the initiation of new radical chains.

Some Generalizations about the Effect of High Pressures on Radical Chain Processes.—At this point we feel it is possible to arrive at some general conclusions about the effect of high pressures on radical chain processes on the basis of our results on the styrene and allyl acetate systems. These are as follows: 1. Radical formation by unimolecular decomposition of initiators is slightly repressed by pressure, but polymolecular processes (such as the thermal initiation of styrene polymerization) are accelerated. 2. Both radical addition to unsaturated molecules and radical displacements are strongly accelerated by pressure, $\Delta V^{\ddagger} = -10$ to -15 cc./mole. 3. Bimolecular radical destroying reactions are relatively unaffected by pressure and may even be retarded as they become diffusion controlled. 4. Degradative chain transfer becomes increasingly unimportant under pressure, since the relatively stable radicals produced are now able to initiate fresh chains.

Since the success of a great number of radical chain processes depends upon the successful competition between chain-carrying steps involving radical additions and displacements and chain termination by degradative chain transfer or bimolecular reactions between radicals, our conclusions suggest that the use of high pressures should be a powerful tool in extending the scope and efficiency of radical chain reactions involving such steps. However, in reactions where the yield of a particular product depends upon the competition between radical addition and displacement (as in the formation of 1:1 and 2:1 products in radical additions to olefins) pressure should have little effect on product distributions.

Radical chains are also known which involve radical rearrangements and decompositions. The effect of pressure on rearrangements is difficult to predict, but decomposition chains (as in the decarbonylation of aldehydes) should be inhibited by pressure. Similarly, radical additions which are reversible should show unusually large increases in rate with pressure.

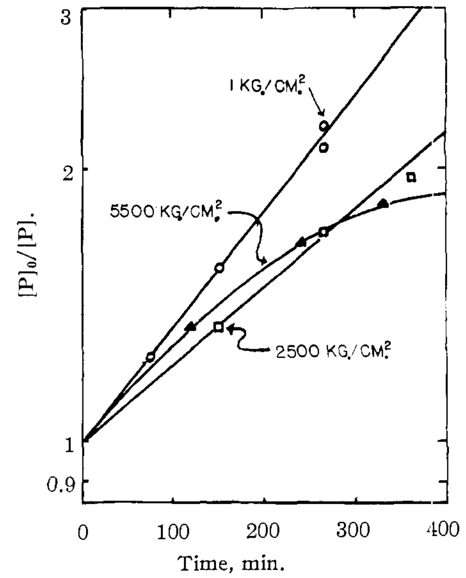

Fig. 4.—Effect of pressure on the rate of decomposition of 1.01% benzoyl peroxide in allyl acetate at 80°.

At present, only a few reactions have been investigated at pressures high enough to produce significant changes in rate *constants* (as distinguished from changes in *rate* due to changes in concentration of a gaseous reagent). However, aside from studies of polymerizations mentioned in our previous paper,[3] the technical radical polymerization of ethylene is conducted at pressures of 1000 kg./cm.^{2} and above,[10] and rates increase significantly with pressure in this region where the gas is no longer significantly compressible. The composition of ethylene–carbon monoxide copolymers proves to be dependent on total pressure at 10–1000 kg./cm.^{2},[11] presumably because of reversibility of the reaction of the growing chain with carbon monoxide,[12] but the effect may arise chiefly from changes in the solubility of carbon monoxide in the reaction system. On the other hand, a very interesting terpolymer of ethylene, carbon monoxide and alcohols formed at 2000–8,000 kg./cm.^{2} has been described[13] which requires the reaction of a $-\dot{R}C{=}O$ radical with another molecule of carbon monoxide and may well require an increased rate of chain propagation for formation. Finally, Weale[14] has reported that, in the polymerization of 1,2-dichloroethylene, the ratio of polymer to dimer increases at high pressures. The dimer has the structure $CHCl_2CHClCl{=}CHCl$ and is possibly formed by the sequence

$$Cl\cdot + CHCl{=}CHCl \longrightarrow CHCl_2\dot{C}HCl \qquad (6)$$

$$CHCl_2\dot{C}HCl + CHCl{=}CHCl \longrightarrow CHCl_2CHClCHCl\dot{C}HCl \qquad (7)$$

$$CHCl_2CHClCHCl\dot{C}HCl \longrightarrow CHCl_2CHClCH{=}CHCl + Cl\cdot \qquad (8)$$

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(10) For a general discussion *cf.* R. A. V. Raff and J. B. Allison "Polyethylene," Interscience Publishers, Inc., New York, N. Y., 1956.

(11) M. M. Brubaker, D. D. Coffman and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952).

(12) C. Walling, *J. Polymer Sci.*, **16**, 315 (1955).

(13) T. L. Cairns, D. D. Coffman, R. Cramer, A. W. Larchar and B. C. McKusick, THIS JOURNAL, **76**, 3024 (1954).

(14) K. E. Weale, *J. Chem. Soc.*, 2223 (1952).

If so, reaction 8 should be retarded by pressure, while the addition of the dimer radical in (8) in another molecule of dichloroethylene would be facilitated, leading to the observed result.

We are currently investigating the effect of pressure on a variety of radical chain processes, and the results will be reported in due course.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Organic Reactions under High Pressure. III. The Decomposition of Benzoyl Peroxide[1]

BY CHEVES WALLING AND JOSEPH PELLON[2]

RECEIVED MARCH 25, 1957

The rate of decomposition of benzoyl peroxide in acetophenone solution at 80° is retarded 22% by a pressure of 1500 kg./cm.^{2}, corresponding to a value of $\Delta V^{\ddagger} = 4.8$ cc./mole for the unimolecular decomposition. At higher pressures a fast decomposition sets in which is apparently higher than first order and believed to represent a rapid induced radical chain reaction, although it is not affected by the presence of methyl methacrylate. At atmospheric pressure, the decomposition in cumene containing styrene is significantly accelerated by mercury.

In 1946, Bartlett and Nozaki[3] and Cass[4] proposed that the decomposition of benzoyl peroxide in organic solvents proceeds by both a spontaneous unimolecular decomposition and a subsequent induced chain, and this formulation is now generally accepted.[5] The initial decomposition is apparently into two benzoyloxy radicals

$$C_6H_5COO{-}OCOC_6H_5 \longrightarrow 2C_6H_5COO\cdot \qquad (1)$$

which either lose CO_2 or attack reactive substrates in the decomposition medium. In aromatic solvents or other relatively inert media, the subsequent chain appears to involve attack on peroxide molecules by peroxide fragments,[3] while in solvents such as ethers and alcohols (where the chain reaction is much more rapid) radicals derived from solvent act as chain carriers.[4,6]

The analysis of the effect of pressure on organic free radical processes which we have developed in preceding papers[7] suggests that reaction 1 should be slightly pressure retarded but that subsequent induced decompositions should be strongly accelerated since they involve chains of radical displacement or addition processes. In this paper we will see that, in acetophenone solution at 80°, both of these expectations are realized, although the nature of the induced chain has not been worked out. Acetophenone was chosen as a solvent since it has been studied in some detail by Blomquist and Buselli,[8] and it is a medium in which there appears to be little induced decomposition at atmospheric pressure.

Experimental

Preliminary Experiments.—Since in our previous work on polymerization samples had been isolated from the pressure-transmitting fluid by carrying out the reactions in glass vessels over mercury, we first undertook to see if mercury had any effect upon the rate of decomposition of relatively concentrated solutions of benzoyl peroxide. Decomposition rates of benzoyl peroxide were compared for samples in sealed degassed glass tubes and in similar tubes containing mercury. The solvent chosen for this preliminary work was cumene containing 0.2 molar styrene to eliminate any induced decomposition.[9] With 0.01 *M* peroxide at 85°, identical first-order rates were observed, although peroxide titrations on the samples run in the presence of mercury were consistently 2–3% lower than the others. With 0.10 molar peroxide, the initial rate in the presence of mercury was approximately 17% faster than in its absence and the decomposition appeared somewhat autocatalytic. In addition, a heavy white precipitate of what was presumably an organomercury compound appeared in the tubes.[10] For this reason the use of mercury as a sealing fluid was abandoned, and series of very inert, flexible vessels developed as shown in Fig. 1. For the work described here, the glass and Teflon (polytetrafluoroethylene) vessel A was employed, but subsequently design B[11] constructed of Teflon or Kel-F (polytrifluorochloroethylene) has been found more satisfactory. Such vessels have a capacity of 11 cc. and with a wall thickness of 0.014 in. will withstand several atmospheres internal pressure, so that low-boiling liquids can be introduced into the pressure system well above their boiling-points. Neither design showed detectable leakage on exposure to pressure cycles of 8000 kg./cm.^{2} and can be used repeatedly without damage.

Technique of Pressure Experiments.—Solutions of benzoyl peroxide[12] were degassed and a slight excess transferred to the Teflon vessel with minimum exposure to air. The plug was inserted so that no gas bubble was left in the vessel, the top screwed on and the vessel and container placed in the pressure apparatus and brought to pressure as previously described. Comparison experiments at atmospheric pressure were run in sealed degassed glass tubes. At the end of a run peroxide was titrated by iodimetry essentially as described by Blomquist and Buselli.[8]

Results and Discussion

First-order plots of typical experiments are shown in Figs. 2 and 3. Considering first the experiments at 1500 kg./cm.^{2} and below where first-

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[1] Taken from a portion of the dissertation of Joseph Pellon, submitted in partial fulfillment of the requirements for the Ph.D. degree, 1957. This work was also supported in part by the Office of Naval Research.

[2] Union Carbide and Carbon Corp. Fellow, 1955–1956.

[3] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

[4] W. E. Cass, *ibid.*, **68**, 1976 (1946).

[5] For more extensive references than those given here, *cf.* A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

[6] P. D. Bartlett and K. Nozaki, THIS JOURNAL, **69**, 2299 (1947).

[7] C. Walling and J. Pellon, *ibid.*, **79**, 4776, 4782 (1947).

[8] A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

[9] C. G. Swain, W. T. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5429 (1950).

[10] The formation of phenylmercuric benzoate from the reaction of benzoyl peroxide with mercury in refluxing benzene has been described by G. A. Razuvaev, Y. A. Ol'dekop and L. N. Grobov, *Doklady Akad. Nauk S.S.S.R.*, **88**, 77 (1953); *Zhur. Obshchei Khim.*, **23**, 589 (1953).

[11] Designed by Mr. J. Peisach of this Laboratory.

[12] In general freshly distilled and carefully fractionated acetophenone was used as our solvent. However, no significant difference in rate was observed using commercial material as received.