Anal. Calcd. for C_3H_9IS: C, 17.7; H, 4.4; I, 62.3; S, 15.7. Found: C, 17.8; H, 4.3; I, 60.5; S, 15.2.

β-Methylmercaptopropiophenone and Methyl Iodide. Formation of (2-Benzoylethyl)-dimethylsulfonium Iodide.—β-Methylmercaptopropiophenone (III, $R_1 = CH_3$) (5.0 g., 0.029 mole) was dissolved in methyl iodide (10 ml.). Crystals began to form almost immediately. After 18 hr., the solids were filtered and air-dried to give 9.3 g. (100%) of (2-benzoylethyl)-dimethylsulfonium iodide as platelets melting at 131–132° (gas evolution). Several recrystallizations did not change the melting point. The corresponding bromide salt, prepared from β-methylmercaptopropiophenone and methyl bromide in 53% yield, has been reported.[22]

Anal. Calcd. for $C_{11}H_{15}IOS$: C, 41.0; H, 4.69; I, 39.4; S, 9.95. Found: C, 41.1; H, 4.71; I, 38.4; S, 10.1.

PEARL RIVER, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

Organic Reactions Under High Pressure. I. The Polymerization of Styrene[1]

BY CHEVES WALLING AND JOSEPH PELLON[2]

RECEIVED MARCH 25, 1957

The free radical polymerization of styrene has been studied under hydrostatic pressures up to 6000 kg./cm.². By measuring the effect of pressure on the rate of polymerization of styrene emulsions, $\Delta V^{\ddagger}_{p}$ (the volume change in going from reactants to transition state in chain propagation) has been obtained as −11.5 cc./mole. Comparison of this pressure coefficient with literature data on benzoyl peroxide initiated bulk polymerization indicates that here the increase in k_p with pressure accounts for most of the acceleration but that k_t is also slightly decreased. In the thermally initiated reaction, there also appears to be an increase in the rate of chain starting. The chain transfer constant for styrene–carbon tetrachloride is almost pressure independent, and it is concluded that, in the peroxide-initiated reaction at high pressures, $\overline{P}$ is determined by chain transfer with initiator and monomer, the transfer constants again having almost their atmospheric pressure values.

The application of high pressures, roughly 1000 kg./cm.² and above, provides an additional degree of freedom in controlling the rate and direction of chemical reactions, which, since the initial observation by Roentgen[3] that the acid-catalyzed inversion of sucrose is retarded by pressure, has received rather sporadic but increasing attention in laboratories throughout the world.[4]

A theoretical interpretation of the effect of pressure on reaction velocity was first given by Van't Hoff, in 1901,[5] who proposed the relation

$$\mathrm{d}\ln k/\mathrm{d}P = -\Delta V_c/RT \qquad (1)$$

where ΔV_c represents the volume change in going from reactants to the active molecules at the moment of reaction. The equivalent expression in the more specific terms of transition-state theory

$$\mathrm{d}\ln k/\mathrm{d}P = -V^{\ddagger}/RT \qquad (2)$$

where $\Delta V^{\ddagger}$ represents the volume change in going from reactants to transition state was introduced by Evans and Polanyi,[6] in 1935, and is the form in which the relation is usually expressed. Evans and Polanyi pointed out that the value of $\Delta V^{\ddagger}$ depends upon volume changes both of the reactants and the surrounding solvent. Recent work, notably by Hamann[7] and Laidler,[8] has shown that in reactions between ions or in reactions involving ionic transition states the latter effect is very important. In general, reactions in which the transition states are more ionic than the reactants show large negative values of $\Delta V^{\ddagger}$ (and thus are strongly accelerated by pressure) due to the electrostriction of solvent produced by ion solvation. Because of this complication and because of our interest in non-polar processes, our investigations of reactions under high pressures have been directed initially at radical and "molecular" processes where solvation is relatively unimportant.

The accelerating effect of pressure on (what is now recognized as the free radical) polymerization of olefins was first noted by Bridgman and Conant[9] and has subsequently proved to be a rather general phenomenon. Styrene, as a tractable monomer which undergoes a well-understood and reproducible polymerization at atmospheric pressure, has received particular study. Its thermal polymerization under pressure has been investigated by several groups.[9–12] The benzoyl peroxide initiated reaction has been described by Merrett and Norrish[13] in an important paper which is considered further below. These workers found that the polymerization rate rises almost exponentially with pressure, increasing approximately 12-fold at 5000 kg./cm.². Polymer molecular weight also increases with pressure, but levels off at about 3000 kg./cm.². These high pressure polymers have subsequently been investigated by Trementozzi and Buchdahl,[14] who concluded from light scattering measurements that they show no detectable dif-

---

[1] Taken from a portion of the dissertation of Joseph Pellon, submitted in partial fulfillment of the requirements for the Ph.D. degree, 1957.

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

[3] W. C. Roentgen, *Ann.*, **45**, 98 (1892).

[4] For reviews of early work *cf.* (a) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 2nd Ed., The Clarendon Press, Oxford, 1947, Chapter XI; (b) M. G. Gonikberg, "Chemical Equilibrium and Reaction Velocity at High Pressures," Academy of Sciences USSR, 1953.

[5] *Cf.* reference 4a, p. 338.

[6] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).

[7] J. Buchanan and S. D. Hamann, *ibid.*, **49**, 1425 (1953); H. G. and S. D. Hamann, *ibid.*, **50**, 1188 (1954); S. D. Hamann and W. Strauss, *ibid.*, **51**, 1684 (1955).

[8] C. T. Burries and K. J. Laidler, *ibid.*, **51**, 1497 (1955).

[9] P. W. Bridgman and J. B. Conant, *Proc. Natl. Acad. Sci.*, **15**, 680 (1929); J. B. Conant and C. O. Tongberg, THIS JOURNAL, **52**, 1659 (1930); J. B. Conant and W. R. Peterson, *ibid.*, **54**, 628 (1932).

[10] G. Tammann and A. Pape, *Z. anorg. Chem.*, **200**, 113 (1931).

[11] R. C. Gillham, *Trans. Faraday Soc.*, **46**, 497 (1950).

[12] P. P. Kobeko, E. V. Kuvshinskii and A. S. Semenova, *Zhur. Fiz. Khim.*, **24**, 345, 415 (1950).

[13] F. M. Merrett and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A206**, 309 (1951).

[14] G. A. Trementozzi and R. Buchdahl, *J. Polymer Sci.*, **12**, 149 (1954).

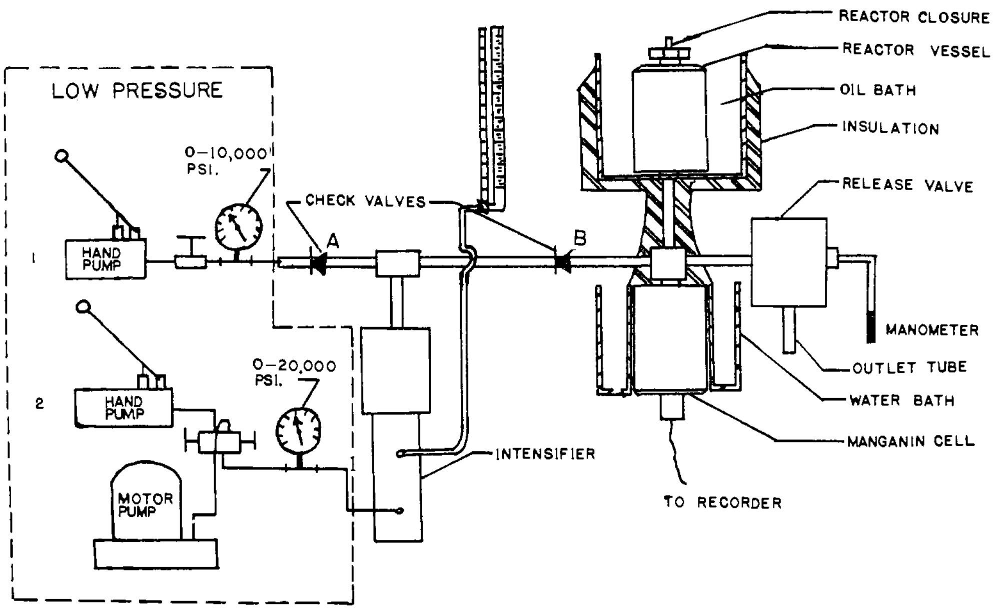

Fig. 1.—Diagram of the high pressure apparatus.

ference in structure from polymers prepared at atmospheric pressure.

Although interpretation of the effect of pressure on a free radical chain reaction such as vinyl polymerization is not complicated by the solvation phenomena accompanying ionic reactions, it is rendered more difficult by the fact that over-all rates are determined by contributions from the rates of several different simultaneous processes. Thus the ordinary homogeneous polymerization of styrene, to a good approximation,[15] obeys the relation

$$R_\mathrm{p} = -\mathrm{d}\,[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{M}]\,(R_\mathrm{i}/2k_\mathrm{t})^{1/2} \qquad (3)$$

where k_p represents the rate constant for chain propagation, R_i the rate of chain starting and k_t the rate constant for chain termination. Accordingly, $\Delta V^\ddagger$ is also made up of three terms, and, from equations 2 and 3, providing the reaction path remains the same under pressure, the pressure dependence of R_p should be given by

$$\mathrm{d}\ln R_\mathrm{p}/\mathrm{d}P = -(\Delta V^\ddagger{}_\mathrm{i} + \Delta V_\mathrm{i}{}^\ddagger/2 - \Delta V_\mathrm{t}{}^\ddagger/2)/RT \qquad (4)$$

where $\Delta V_\mathrm{p}{}^\ddagger$, $\Delta V_\mathrm{i}{}^\ddagger$ and $\Delta V_\mathrm{t}{}^\ddagger$ are the volume changes associated with chain growth, chain initiation and chain termination.

This difficulty was recognized, but not resolved, by Merrett and Norrish.[13] In the work described here we have attacked the problem by determining $\Delta V_\mathrm{p}{}^\ddagger$ directly by measuring the effect of applying pressure to a polymerizing styrene emulsion. By combining this result with data on bulk polymerization, we have been able also to deduce, at least qualitatively, a value of $\Delta V_\mathrm{t}{}^\ddagger$. In addition we have made measurements on the effect of pressure on the transfer constant[16] of styrene with carbon tetrachloride. Here the pressure relationship is

$$\mathrm{d}\ln C/\mathrm{d}P = -(\Delta V_\mathrm{tr}{}^\ddagger - \Delta V_\mathrm{p}{}^\ddagger)/RT \qquad (5)$$

where C is the transfer constant and $\Delta V_\mathrm{tr}{}^\ddagger$ the volume change associated with the attack of a growing polystyrene chain on carbon tetrachloride. Since this paper is the first in a series, we present a rather detailed description of our high pressure apparatus and techniques.

Experimental

High Pressure Apparatus.—The high pressure apparatus which we have employed is essentially a device for placing reaction mixtures (in an internal reaction vessel described further below) under hydrostatic pressures up to 13,000 kg./cm.^{2} and is shown schematically in Fig. 1. It consists basically of a pressure intensifier, a reactor vessel, pressure gage and auxiliary equipment, and since all components are standard high pressure fixtures manufactured by the Harwood Engineering Co. of Walpole, Mass., they will not be described in detail.

In operation an internal reaction vessel containing the system under study is placed in the reactor vessel which is filled with pressure-transmitting fluid (a kerosene fraction, Bayol D, supplied by the Esso Standard Oil Co.) and the reactor closure put in place. A pressure of approximately 500 kg./cm.^{2} is applied directly by the hand pump 1 and then increased to the desired pressure *via* pumps 2 and the intensifier. The pressure on the low-pressure side of the intensifier is next released, and the system becomes isolated by the closing of check-valve B. During a run the temperature of the reaction vessel is held constant by the oil-bath which is thermostated to ±0.2°, and the pressure gage is also thermostated by a water-bath to prevent random drifts in pressure with changes in room temperature. Application of pressure produces a small temperature rise in the system due to adiabatic compression, but measurements of pressure changes on the system containing only the pressure-transmitting fluid indicate that equilibrium is restored within 5–10 minutes. Because of this and because of the few minutes required to open and close the reactor, rate measurements are only feasible on reactions with half-lives of an hour or more. Selection of conditions under which reactions are slow is also important for strongly exothermic reactions, since the viscosities of most liquids rise rapidly with pressure so that heat dissipation becomes very slow.

When a reaction is completed, pressure is relieved *via* the release valve, the closure opened and the sample removed. The pressure gage consists of two balanced manganin wire coils, one of which is within the pressure system but isolated from the pressure-transmitting fluid by a flexible metal bellows. The difference in electrical resistance of the two coils varies linearly with pressure and is determined by a Wheatstone bridge circuit. The manufacturer's calibration

---

(15) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 4.

(16) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943).

was checked by a determination of the freezing point of mercury at 0° and, with a suitable potentiometer, pressure changes in the system can be read to less than 1.7 kg./cm.^{2} in any pressure range, while absolute values of pressure are probably accurate to less than 1%.

Since the entire system beyond the check valve B is isolated and the closure and pipe connections show no detectable leakage, the high pressure system is actually a dilatometer (although operating at constant volume) and the rates of reaction involving volume changes can be followed by the very sensitive readings of the pressure gage. Although this technique was not used in our styrene work (except to check the constancy of reaction rates during individual runs), it has proved very useful in other investigations.

A final property of our high pressure system deserves mention. The free-space between the large and small pistons of the intensifier may be filled with oil and connected to a manometer. After suitable calibration, the oil level in the manometer then gives an accurate measure of the piston positions and the volume of the system under pressure (during a pressure-increasing cycle, so that check-valve B is open). This in turn permits the measurement of pressure–volume relations—for example for the comparison of the compressibilities of reactants and products in a system with variations in $\Delta V^{\ddagger}$ with pressure.

The necessity of isolating reaction systems from the hydraulic fluid in our apparatus requires some sort of internal reaction vessel which is chemically inert and which can change its capacity without damage since compressions of liquids of 10–20% occur at the pressures at which we work. We have employed several devices for this purpose, but for the work described here, we have used a simple open glass vessel of approximately 8-cc. capacity inverted over mercury held in a stainless steel cup, Fig. 2. In filling, the vessel was first filled with mercury and inverted and the sample introduced through a fine capillary or hypodermic syringe. After the capillary was withdrawn, the vessel was warmed slightly to bring the meniscus of the remaining mercury even with the mouth of the vessel and then lowered into a small amount of mercury in the cup. This technique made it possible to avoid any exposure of samples to air, an important precaution in obtaining reproducible rates in radical reactions.

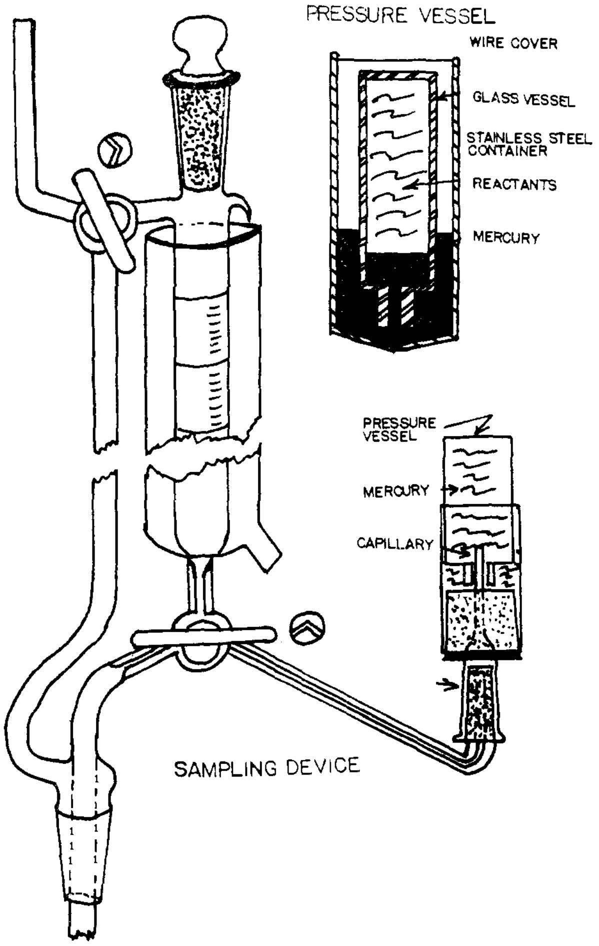

Fig. 2.—Mercury sealed pressure vessel and sampling device for emulsion polymerization experiments.

Emulsion Polymerizations.—Two basic emulsion formulations were employed in this work and are shown in Table I. Formulation A was used in preliminary work, and B, which gave lower polymerization rates, was used in order to extend our study to higher pressures. All experiments were run at 40.0° as higher temperatures gave too high rates to handle in our pressure systems, while at lower temperatures the emulsions tended to coagulate under pressure.

TABLE I

STYRENE EMULSION FORMULAS

All amounts in grams

	A	B
Water	180	180
Styrene	100	75
K palmitate	1.0	1.0
$K_2S_2O_8$	0.3	0.1
$NaHSO_3$	0.05	...

Our basic techniques involved starting a polymerization at atmospheric pressure, determining the polymerization rate by periodic sampling and, at approximately 40% conversion, transferring a portion of the polymerizing emulsion to the high pressure apparatus. The initial polymerization was carried out in a stirred 500-cc. flask under a slight positive pressure of prepurified nitrogen and the transfer accomplished by the device shown in Fig. 2. Emulsion was forced by nitrogen pressure into the measuring buret and then a portion allowed to flow out, rinsing and filling the capillary tube. The mercury-filled reaction vessel was next lowered over the capillary tube and filled as previously described. Experiments in which emulsion was transferred to the reaction vessel and allowed to polymerize further at atmospheric pressure showed that the transfer or the presence of mercury neither interrupted the polymerization nor affected its rate, and our rates at atmospheric pressure using formulation A are in good agreement (14%/hr. *vs.* 13.3%/hr.) with those reported by Morton, Salatiello and Landfield[17] on the same system.

Extents of reaction were determined in a conventional manner by transferring 5–10-g. samples to tared aluminum dishes (*via* the sampling device) which contained 0.005 g. of hydroquinone as a short-stop. After weighing, most of the volatile material was evaporated off on a steam-bath and the dishes dried by heating overnight at 105°. The amount of polymer was then determined by weighing.

Solution Polymerization.—Solutions of benzoyl peroxide in styrene or styrene–carbon tetrachloride mixtures were made up in volumetric flasks and transferred with a hypodermic syringe to empty reaction vessels. These were attached to a high vacuum system, degassed twice at −78° and brought to atmospheric pressure with prepurified nitrogen. Mercury was added to fill the vessels and they were inverted and placed in the pressure apparatus (or in a thermostat at atmospheric pressure for comparison runs). After a run, polymer was isolated by diluting the sample with 10–20 cc. of methyl ethyl ketone and pouring into 200–300 cc. of methanol with vigorous stirring. After standing overnight most of the methanol was decanted and the polymer determined by filtering onto a sintered glass filter and drying under vacuum at 40°. Polymer molecular weights were determined by viscosimetry, using the relation of Mayo, Gregg and Matheson[18]

$$\bar{M}_N = 167{,}000[\eta]^{1.37} \qquad (6)$$

Results and Discussion

Application of Emulsion Theory.—Typically, an

---

[17] M. Morton, P. P. Salatiello and H. Landfield, *J. Polymer Sci.*, **8**, 279 (1952).

[18] F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

emulsion polymerization occurs in three stages which can be kinetically distinguished: (1) an initial period, up to a few per cent. reaction, during which the reaction rate rises to a constant value; (2) a prolonged period of closely zero order reaction to 50–60% conversion; (3) a final stage in which the rate dies off as monomer is exhausted. Harkins[19] has shown that in stage 2 the system consists of three phases: water, relatively large droplets of monomer which decrease in volume as reaction proceeds and a large number of very small particles of polymer which are swollen with dissolved monomer and on the surfaces of which essentially all of the soap (or other surface active agent) is adsorbed. The number of these particles remains constant, and it is within them that essentially all polymerization occurs, fresh monomer being supplied as it is consumed by diffusion from the monomer droplets. In an elegant analysis, Smith and Ewart[20] have shown that during this stage the polymerization rate is given by

$$R_p = k_p N[M]/2 \qquad (7)$$

and thus depends only upon k_p, the monomer concentration in the particles and N, their number per unit volume. Equation 7, which has been shown by extensive experiments[21] to apply very satisfactorily to the polymerization of styrene emulsions of the sort used here, provides the basis for our treatment, for, if an emulsion in this stage is divided into two portions which are allowed to continue to polymerize at atmospheric and high pressures, a comparison of the rates gives directly the effect of pressure on k_p. One experimental precaution, however, needs to be pointed out. As long as a significant quantity of monomer is present in the form of large droplets, emulsions are unstable and require agitation to prevent coalescence and also to ensure monomer equilibrium between droplets and emulsion particles. Accordingly, the separation must be delayed until about 40% reaction when all monomer has passed into the polymer particles and subsequent rate measurements must be made in the rather short period while reaction rate is still closely zero order.

Determination of k_p.—Figure 3 shows a plot of data from typical emulsion experiments. The solid lines give the time–conversion results at atmospheric pressure and the dashed lines the course of reaction of samples subjected to high pressure. From equation 7 it is evident that

$$(k_p)_p/(k_p)_o = t_o/t_p \qquad (8)$$

the ratio of k_p's under pressure and at atmospheric pressure are the inverse of the ratio of the times required for the system to undergo the same change in conversion under pressure and at atmospheric pressure. A summary of all our data obtained in this way is given in Table II. Results obtained with formulation A are subject to the difficulty that polymerization under pressure was so rapid that final conversions were approximately 80% even at 2200 kg./cm.^{2}. This carries the polymerization into a region where it is no longer zero order, and the use of equation 8 requires the assumption that the shape of the resulting rate curve (for which only the end-point is known) is identical with that at atmospheric pressures. Accordingly, although results with the two formulations are in reasonable agreement, only data obtained with formulation B are used in our subsequent calculations.

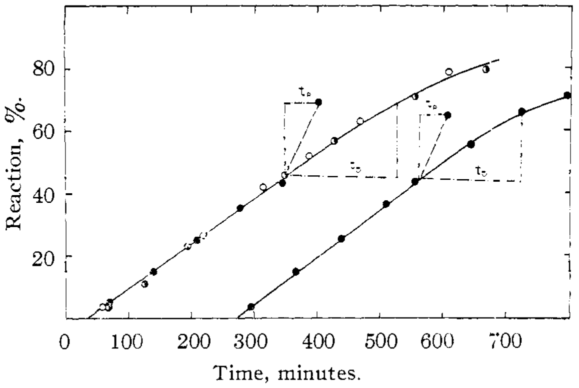

Fig. 3.—Comparison of rates of emulsion polymerization of styrene at atmospheric pressure and at 2150 kg./cm.^{2}. Dashed line indicates course of reaction under pressure and different symbols represent duplicate experiments at atmospheric pressure. Time scales have been displaced to separate two runs.

TABLE II

EFFECT OF PRESSURE ON k_p IN THE EMULSION POLYMERIZATION OF STYRENE AT 40°

Formulation B unless indicated

Run	Pressure, kg./cm.^{2}	$(k_p)_p(k_p)_o$	Run	Pressure, kg./cm.^{2}	$(k_p)_p(k_p)_o$
1[a]	2160	3.35	7	2150	3.8
2[a]	2200	3.25	8	2980	5.4
3[a]	2170	3.17	9	3030	5.4
4	1040	2.4	10	3820	8.5
5	1010	2.2	11[b]	2190	3.9
6	2150	3.6			

[a] Formulation A. [b] Persulfate added (see text).

Our treatment assumes that pressure produces no fundamental change in the mechanism of emulsion polymerization, nor in the number of polymer particles per unit volume in the system.[22] This assumption has been checked in two ways. First, in run 11 additional persulfate (3 times the initial quantity) was added immediately before the pressure sample was withdrawn. Only a small increase in rate was observed in the atmospheric pressure run (about 20%), indicating the validity of equation 7 and the zero order portion of the rate curve was somewhat prolonged, suggesting that some of the final drop in rate in our systems is due to exhaustion of persulfate. However, the pressure coefficient of k_p is in good agreement with other runs. Second, samples of emulsion prepared at atmospheric pressure and at 1000 and 3000 kg./cm.^{2} were examined by electron microscopy. While no detailed determination of particle size and number was made, there were no evident differences. In particular, the pressure runs showed no

---

[19] W. D. Harkins, THIS JOURNAL, **69**, 1428 (1947).

[20] W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

[21] W. V. Smith, THIS JOURNAL, **70**, 3695 (1948); **71**, 4077 (1949).

[22] Actually there is an increase of a few per cent. both in the number of particles per unit volume and in [M], due to the compression of the system, but this is so small compared to the changes in rate which we observe that it has been neglected.

indication of particle coalescence or the formation of new small particles. Accordingly, we conclude our treatment is valid. Figure 4 shows a semilogarithmic plot of $(k_p)_p/(k_p)_0$ from Table II *vs.* pressure, together with data on solution polymerization discussed further below. The plot is linear between 1000 and 3800 kg./cm.^{2} and indicates $\Delta V_p^{\ddagger} = -11.5$ cc./mole. However, the data extrapolate to a point somewhat above unity at zero pressure. This may indicate a somewhat larger negative value of $\Delta V_p^{\ddagger}$ near atmospheric pressure and, indeed, a downward curvature in a plot such as that in Fig. 4 might be anticipated since a small transition state could well be less compressible than the larger reactants so that $\Delta V^{\ddagger}$ becomes a function of pressure. However, it seems to us that at least part of this apparent curvature may arise from an experimental difficulty mentioned earlier. Because of the high rate of polymerization in our systems, pressure experiments were limited to approximately 30 minutes, and during the first 5–10 minutes, due to heating during application of pressure, both temperature and pressure were slightly higher than reported. In consequence all $(k_p)_p/(k_p)_0$ ratios measured must be a little larger than their true values, and, since this effect increases somewhat with pressure, $\Delta V_p^{\ddagger}$ should have an (absolute) value a little smaller than -11.5 cc./mole. Since we have no good way of estimating the magnitude or relative importance of these uncertainties, we shall take the measured value in our subsequent discussion.

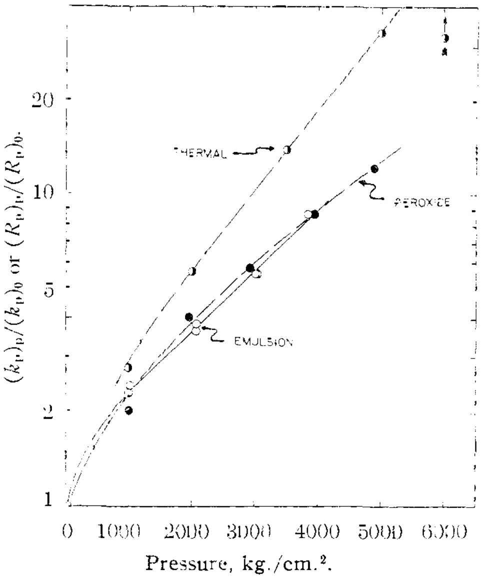

Fig. 4.—Effect of pressure on polymerization of styrene in emulsion and in bulk, initiated with benzoyl peroxide (Merrett and Norrish) and thermally (Kobeko, *et al.*). Values of $(R_p)/(R_p)_0$ for thermal reaction have been divided by 4 to appear on the same scale.

Comparison of Emulsion and Homogeneous Polymerization.—A combination of our data on the effect of pressure on k_p and rate studies on the benzoyl peroxide initiated polymerization of styrene permits us to make an estimate of $\Delta V_i^{\ddagger}$. Figure 4 includes ratios of $(R_p)_p/(R_p)_0$ obtained by Merrett and Norrish for the peroxide-initiated reaction at 60°. Although the points indicate some curvature in a log R_p–pressure plot in the range between 2000 and 5000 kg./cm.^{2} (which best overlaps our emulsion data), they give an over-all value of $\Delta V^{\ddagger} = -11.1$ cc./mole. In order to obtain $\Delta V_t^{\ddagger}$ from equation 4, we need, in addition, an estimate of $\Delta V_i^{\ddagger}$, the activation volume for chain initiation. Since the decomposition of benzoyl peroxide involves the formation of two molecules from one, we would expect it to be pressure retarded and, as is shown in the following papers, such retardation is observed in both allyl acetate[23] and acetophenone[24] solution, although at pressures above 2000 kg./cm.^{2} the situation is complicated by what appears to be a higher order induced decomposition. In acetophenone, $\Delta V^{\ddagger} = 4.8$ cc./mole at 80°. Since the actual rate of unimolecular decomposition of benzoyl peroxide does not vary widely with solvent, this might be a plausible value to use here.[25] However, chain-starting efficiencies of radical sources (which depend upon the amount of wastage of radicals due to primary recombination of initiator fragments within the solvent cage) do vary appreciably with medium, being lowest in dense solvents.[26] Under pressure, where solvent molecules are forced close together, diffusion apart of initiator fragments should be hindered and efficiencies of chain starting reduced. Accordingly, taking the value in acetophenone as a lower limit, we set $\Delta V_i^{\ddagger} \geqslant 4.8$ cc./mole and, from equation 4, obtain $\Delta V_t^{\ddagger} \geqslant 4.0$ cc./mole.

A positive value of $\Delta V_t^{\ddagger}$ is at first surprising since the reaction concerned involves the coming together of two radicals to form a covalent bond, a process which should be accelerated by pressure. Accordingly we conclude that, under pressure, we are in a region where the motion of polymer molecules is so restricted by the compacted solvent that chain termination is diffusion controlled. Such a phenomenon is well known in atmospheric pressure polymerizations at higher conversions[15] in the form of an autoaccelerated reaction, and we may note that such an autoacceleration in styrene polymerization at high pressure was observed by Kobeko[12] and Merrett and Norrish.[13,27]

Kobeko's data on the thermal polymerization of styrene[12] may be used to estimate $\Delta V_i^{\ddagger}$ for the thermal initiation process. Unfortunately, these are only available in the form of a statement that at 6000 kg./cm.^{2} and 72° the polymerization rate is 250 times that at atmospheric pressure, and a rather cryptic graph of ln rate (in fraction/sec.) *vs.* *P* at various temperatures which indicates a reaction rate at atmospheric pressure only one-third to

---

[23] C. Walling and J. Pellon, This Journal, **79**, 4782 (1957).

[24] C. Walling and J. Pellon, *ibid.*, **79**, 4786 (1957).

[25] Throughout this discussion we have ignored small differences in temperature at which $\Delta V^{\ddagger}$'s have been measured, since, unless a significant change in mechanism is occurring, temperature dependence should be a second-order effect, lying well within the experimental error of our measurements.

[26] F. W. Lampe and R. M. Noyes, This Journal, **76**, 2140 (1954); G. S. Hammond, J. N. Sen and C. E. Boozer, *ibid.*, **77**, 3244 (1955); *cf.* also ref. 15.

[27] Although our emulsion experiments were run at 40–80% conversion, this phenomenon is not a complication since k_t does not enter into the emulsion rate equation.

one-half that usually reported. However, we have used these data on the pressure coefficient of the over-all rate to calculate the points for thermally initiated styrene polymerization at 72° shown in Fig. 4. The uncertainty in the atmospheric pressure value means that all points should possibly be displaced downward by a constant amount, but they can still be used to estimate $\Delta V^{\ddagger}_{\text{over-all}}$ as -17.5 cc./mole between 1000 and 6000 kg./cm.^{2}. Substituting this value into equation 4 gives $\Delta V_i^{\ddagger} = -8$ cc./mole for the thermal initiation process, with a somewhat larger negative value below 1000 kg./cm.^{2}. A negative result is certainly plausible since thermal initiation, although its exact course is unknown, is evidently a bi- or trimolecular reaction between styrene molecules[28] which should be pressure accelerated. The result also indicates that thermal initiation processes, in general, should become increasingly important at high pressures.

Effect of Pressure on Chain Transfer.—Our determination of the effect of pressure on k_p in styrene polymerization now permits us to measure the pressure coefficient of radical displacement reactions by a study of chain transfer processes. Table III summarizes data on the styrene–carbon tetrachloride system. Transfer constants were determined by the relation

$$1/\bar{P} = C_s[S]/[M] + C_I[P]/[M] + C_M \qquad (9)$$

where [S] and [P] are concentrations of carbon tetrachloride and benzoyl peroxide. By holding the ratio of peroxide to monomer constant, the last two terms on the right are constant and C_s is evaluated as the slope of the line obtained by plotting $1/\bar{P}$ *vs.* [S]/[M]. Data for [S]/[M] ratios below 0.4 are shown in Fig. 5, and our value of C_s at atmospheric pressure is in good agreement with that reported by Gregg and Mayo,[29] 93×10^{-4}. At higher dilutions of styrene, experimental points begin to fall below the lines of Fig. 5. A similar result was noted by Gregg and Mayo[29] who attributed it to loss of low molecular weight polymer during isolation. At our highest pressure, only such points were available because of too rapid polymerization of high styrene concentration. Accordingly the transfer constant was estimated from these points and compared with a similar estimate at lower pressures. These values, given in parenthesis in Table III, do not represent true values but do indicate that little change occurs.

TABLE III

EFFECT OF PRESSURE ON THE CHAIN TRANSFER OF STYRENE WITH BENZOYL PEROXIDE

0.043 mole % benzoyl peroxide at 60°

Pressure, kg./cm.^{2}	[S]/[M]	$1/\bar{P} \times 10^5$	C_s
1	0	42	
1	.0474	100	
1	.0948	149	98
1	.237	289	
1	1.185	948	
2000	0	16	
1990	0.0474	64	
2000	.0948	110	
2000	.237	233	90
2000	1.185	921	
3950	0	13	
3940	0.0474	63	
3970	.0948	107	
3950	.237	225	84
3930	.5925	496	(67)[a]
3945	1.185	838	
6000	0.237	240	
5980	0.5925	475	(59)[a]
5990	1.185	801	

[a] At high [S]/[M] ratios, see text.

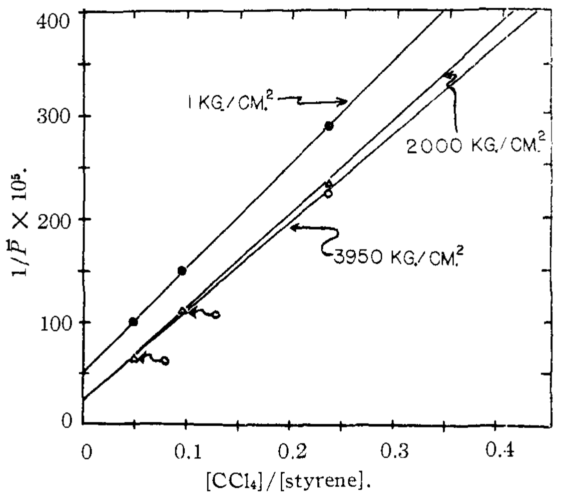

Fig. 5.—Determination of the effect of pressure on chain transfer in the CCl_4–styrene system.

The conclusion which we draw is that, in this system, the transfer constant is almost pressure independent, decreasing about 15% at 3950 kg./cm.^{2}. Accordingly, the radical displacement reaction between a styrene radical and carbon tetrachloride is accelerated by pressure to almost the same extent as the addition to another styrene double bond, and $\Delta V_{tr}^{\ddagger} \cong -11$ cc./mole.

Such acceleration of radical displacement reaction appears to be quite general, and another example appears in our study of allyl acetate.[23] It also provides a plausible explanation of certain observations of Merrett and Norrish.[13] These workers found that the degree of polymerization of polystyrene produced in the presence of benzoyl peroxide increased to a limiting value at above 3000 kg./cm.^{2} which depended upon the amount of peroxide present. At 0.429 and 0.043 mole per cent. of peroxide, these values were 5×10^3 and 2.5×10^4, the latter value being in good agreement with our own, Table III.

At high pressures, with k_p increased and k_t retarded, the factors determining degree of polymerization are presumably chain transfer with initiator and monomer. Taking the values at atmospheric pressure reported by Mayo, Gregg and Matheson[18] of $C_I = 0.055$ and $C_M = 6 \times 10^{-5}$ and assuming these to be pressure independent, we calculate limiting values of $\bar{P}$ of 3.4×10^3 and 1.2×10^4 at the higher and lower peroxide concentrations, with 80 and 29% of the chains being interrupted by transfer with peroxide in the two cases, respectively. The observed values of $\bar{P}$ are some-

---

[28] F. R. Mayo, THIS JOURNAL, **75**, 6133 (1953).

[29] R. A. Gregg and F. R. Mayo, *ibid.*, **70**, 2373 (1948).

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 $[\text{peroxide}]^{1/2}$. 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

---

(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).