the 2-hydroxylated compound has a higher extinction coefficient (log ε, 4.51) than the single peak of the 4-hydroxylated compound (log ε, 4.29), which in turn is lower than the corresponding naphthalazine containing no hydroxyl groups (log ε, 4.48). If the curves that show only a single maximum were composed of two bands lying at the same place, it would be expected that the single peak would have a higher extinction coefficient than those of the peaks found in double peaked curves. Since one of the peaks of the doubly peaked curve is higher, we may assume that we are dealing with single absorption bands in the unsubstituted and *p*-substituted benzalazines.[13]

Acknowledgment.—The authors wish to express their appreciation to Dr. R. B. Woodward for many helpful discussions and to Mrs. D. C. Silverman, Mr. A. S. Makas, and Mr. E. Farmer for their valuable assistance in the determination of most of the absorption spectra recorded herein.

Experimental

The azines were prepared by shaking 2.3 moles of the corresponding aldehyde with 1 mole of 85% hydrazine hydrate in water or dilute ethyl alcohol. In some cases the hydrazone rather than the azine separated, but on addition of a drop of dilute hydrochloric acid to the solvent used in the recrystallization, the hydrazone was decomposed to the azine.

The absorption spectra measurements were made on a Beckmann quartz spectrophotometer model DU using a 1-cm. quartz cell and a hydrogen discharge tube as an ultraviolet source. Absolute ethyl alcohol was used as a solvent throughout.

Summary

The ultraviolet absorption spectra of several substituted aromatic aldazines have been determined. The band splitting noted in 2,2′-substituted benzal- and naphthalazines has been attributed to new absorption bands arising from the non-linearity of such molecules as compared with the unsubstituted and *p*-substituted azines.

[13] We have not neglected to consider that the shorter wave length band in the spectra showing two maxima might be a second order band. 4,4′-Dihydroxybenzalazine is more closely a linear harmonic oscillator than the isomeric 3-hydroxy or 2-hydroxy compound on purely geometric grounds. Thus, assuming that the single absorption band of the 4-hydroxy compound is due to a transition $v = 0 \rightarrow v = 1$ (*i. e.*, a transition from the ground state to the first excited state) it is possible that the double maximum observed in the *o* isomer is actually the result of two transitions, $v = 0 \rightarrow v = 1$ and $v = 0 \rightarrow v = 2$ which are due to oscillations along the same direction in the molecule. The probability of a second order transition occurring in the *p*-hydroxy compound is zero; Lewis and Bigeleisen, THIS JOURNAL, **65**, 2107 (1943). The *o*-isomer has more or less anharmonicity due perhaps to resonance contributions involving charge oscillation non-colinear with the main chromophoric axis. This anharmonicity would make the probability of the transition $v = 0 \rightarrow v = 2$ relatively greater since the electronic levels would lie lower and closer together. An analogous argument would hold for the *m*-compounds with consideration of the fact that the mesomeric effect of the azimethylene chain would not give rise to so great an interaction as that expected for the *o*- and *p*-compounds so that the splitting would be less pronounced. Also the *m*-compound would presumably be a more nearly linear harmonic oscillator than the *o*-compound. But the extinction coefficients for the two bands are nearly equal, and the ratio of their frequencies is << 2, so that it seems unlikely that the shorter wave length maximum is a second order band.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Effects of Temperature on the Polymerization of Styrene

BY SAUL G. COHEN[1]

It now seems probable that the polymerization of vinyl compounds is a chain process involving at least the following types of reactions.[2a,b,c] Active centers are formed, either catalytically (B. p.) or by thermal activation (equations 1a and 1b). In peroxide catalyzed and thermal reactions, these active centers are free radicals. Polymer chains are formed by the successive additions of monomer (M) molecules to the radicals (equation 2). The radicals are capable of undergoing so-called chain transfer reactions in which a growing polymer chain ceases to grow, (P_n), transferring its active center to a monomer or solvent molecule, initiating the growth of a new chain (equation 3). The radicals seem to be destroyed in pairs, either by combination or by disproportionation (equation 4).

$$\text{(1a)}\quad \text{B. p.} \longrightarrow R^*$$

$$\text{(1b)}\quad M + M \longrightarrow 2R^*$$

$$\text{(2)}\quad R_n^* + M \longrightarrow R_{n+1}^*$$

$$\text{(3)}\quad R_n^* + M \longrightarrow P_n + R^*$$

$$\text{(4)}\quad R_n^* + R_m^* \longrightarrow P_{n+m} \text{ or } P_n + P_m$$

With a change in temperature of reaction, the rates of all these processes change, and it is not clear which of these steps is most important in leading to the observed effects of temperature change on polymerization reactions. As the temperature is raised in thermal polymerizations, the rate increases and the molecular weight or degree of polymerization (D. P.) of the product decreases, log D. P. being linear with $1/T$.[2b] This decrease in molecular weight may be explained by two mechanisms.

In one, based on the results of catalyzed polymerizations,[3a,b,c] it may be postulated that D. P. depends solely on the ratio of the rates of steps

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[2a] Price and Kell, THIS JOURNAL, **63**, 2798 (1941). (2b) Flory, *ibid.*, **59**, 241 (1937). (2c) Mayo, *ibid.*, **65**, 2328 (1943).

[3a] Schulz and Husemann, *Z. physik Chem.*, **B34**, 187 (1936); (b) **B36**, 184 (1937); (c) **B39**, 246 (1938).

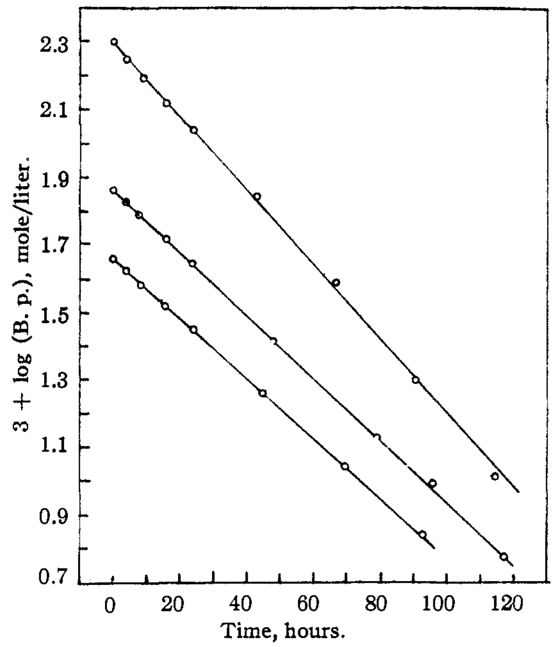

Fig. 1.—Decomposition of B. p. in 3.46 *M* styrene in benzene at 64.02°.

2 and 4, chain propagation and chain termination, $k_2(R^*)(\mathrm{M})/k_4(\mathrm{R}^*)^2$. The rate of step 4 may increase more rapidly than that of step 2 with rising temperature, despite its lower activation energy. This is possible because the concentration of R* rises quite rapidly, the activation energy of step 1b being high. In the alternate explanation,[2b] for which support was obtained from certain photopolymerizations,[4] it was proposed that D. P. depends solely on the ratio of the rates of steps 2 and 3, chain propagation and the postulated chain transfer, and that the activation energy of step 3 is higher than that of step 2.

To obtain more information concerning the effects of temperature on the individual steps, we have studied the benzoyl peroxide catalyzed polymerization of a 3.46 molar solution of styrene in benzene at three temperatures, 53.98, 64.02 and 74.02°. The peroxide concentrations were so selected that the initial rates of decomposition of the peroxide, were equal at the three temperatures. We then made the approximating assumptions that the rates of formation of free radicals were the same, and that the rates of chain initiation were the same at the several temperatures, and that the observed changes in the rates of polymerization and in the molecular weights of the products were due to the effects of temperature change on the rates of steps 2 and 3.

The rates of decomposition of benzoyl peroxide in the solution of styrene in benzene were determined at the three temperatures. The decompositions showed first order kinetics to a fair approximation (Fig. 1). Since the rate constants depended somewhat on the initial concentration of peroxide, the rates were redetermined at about the concentrations at which the polymerizations were to be studied (labelled * in Table I).

TABLE I

DECOMPOSITION OF BENZOYL PEROXIDE IN 3.46 *M* STYRENE IN BENZENE

Temp., °C.	(B. p.), mole/l.	k_1 sec.$^{-1}$ × 10^6
53.98	0.242	1.83*
64.02	.195	7.14
64.02	.0726	5.86*
64.02	.0454	5.69
74.02	.0189	19.3
74.02	.0225	19.3*

Although the concentrations of catalyst may be selected so as to lead to initially equal rates of decomposition, the concentration of peroxide, and thus the rate of decomposition, decreases much more rapidly with time at the higher temperature than at the lower. In order to compare the polymerizations while the rates of formation of free radicals were the same, the reactions were interrupted during the early stages, *i. e.*, after one hour, and the products were isolated and studied. The variations in rates of peroxide decomposition over this period are given in Table II. The average rates were identical within the experimental error.

TABLE II

RATES OF DECOMPOSITION OF BENZOYL PEROXIDE

Temp., °C.	k_1 sec.$^{-1}$ × 10^6	(B. p.), m./l., initial	Rate of decomposition, m./l./sec. × 10^7 initial	after 1 hour	average
53.98	1.83	0.233	4.27	4.23	4.25
64.02	5.86	.0726	4.28	4.18	4.23
74.02	19.3	.0225	4.35	4.06	4.21

The quantity of polymer which was formed in each case by one hour's reaction and the viscosity of its dilute solution (*ca.* 1%) in benzene are given in Table III. Consideration of the products which were formed in the early stages of the reaction minimizes complications due to possible chain transfer reactions with the polymer, and parallels the studies of Schulz and Husemann.[3c]

TABLE III

Temp., °C.	% Polymerization	$-\mathrm{d}(\mathrm{M})/\mathrm{d}t$ m./l./s. × 10^5	η_{sp}/c	log η_{rel}/c	D. P.
53.98	3.97	3.82	1.54 ± 0.03	0.628	82
64.02	5.78	5.55	1.90 ± .06	.763	102
74.02	8.54	8.18	2.28 ± .04	.908	122

From the quantity of polymer which was formed, an average value of the rate was calculated $(-\mathrm{d}(M)/\mathrm{d}t)$. The degree of polymerization, D. P., is that calculated from the Staudinger equation, $\eta_{sp} = K_m M_e$, $K_m = 1.8 \times 10^{-4}$. The rates at 54 and 64° are the averages of four values in which the deviations were ± 1% and ±2%, respectively. The value at 74° is a single value and it is quite consistent with rates found at later times in the same run. The thermal polymerization was negligible compared to the catalyzed reaction. The viscosity values are the averages of three to six samples, the maximum deviations being indicated.

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(4) Taylor and Vernon, THIS JOURNAL, 53, 2527 (1931).

It is of considerable theoretical and practical importance that we find that, when radicals are generated at equal rates at several temperatures, both the rate of polymerization and the molecular weight of the product are greatest at the highest temperature.

In practice, it may be most efficient to carry out vinyl polymerizations at the upper limit of the effective temperature range of the catalyst. The initial catalyst concentration should be low, and additions of catalyst may be made as needed during the reaction.

From these data (Table II and III) the activation energy of chain growth, the addition of a radical to styrene, may be calculated. From equations 1a, 2 and 4, and a steady state expression for the concentration of radicals, the following expression may be derived for the rate at each temperature.

$$-\mathrm{d(M)}/\mathrm{d}t = k_2(\mathrm{R}^*)(\mathrm{M}) = k_2k_1{}^{1/2}(\mathrm{B.\ p.})^{1/2}(\mathrm{M})/k_4{}^{1/2}$$

The values of all the factors in this equation were either fixed or determined except that of the term $k_2/k_4{}^{1/2}$. From the data, and by use of the Arrhenius expression for the rate constants, the value $E_a2 - \frac{1}{2}E_a4$ was calculated, where E_a2 and E_a4 are the activation energies of reactions 2 and 4. We find this to be 8.9 kcal.,[5] about 3 kcal. higher than the currently accepted estimate.[6]

This value, determined in a study of the catalyzed reaction, is confirmed by the fact that it is consistent with the data available from thermal polymerizations. For the thermal reaction, $E_A = \frac{1}{2}E_a1b + E_a2 - \frac{1}{2}E_a4$,[2b] where E_A is the apparent activation energy of the reaction, and E_a1b, etc. are the activation energies of the corresponding steps. Since $E_A = 22 - 24$ kcal.[7a,b,2b] and $\frac{1}{2}E_a1b = 14$ kcal.,[8] our value for $E_a2 - \frac{1}{2}E_a4$ fits quite well, indicating that the assumptions on which our work is based may be justified. Finally, if $E_a4 =$ *ca.* 4 kcal.,[9] we find that $E_a2 = 11$ kcal.

Our calculations are based on the assumption that at equal rates of peroxide decomposition at the three temperatures there are equal rates of chain initiation. Experiments were devised which may allow us to determine the number of chains which are initiated and to investigate the relation between the efficiency of peroxide utilization and the temperature of reaction. However, this work has been interrupted. If it should be found that the catalyst was used with more efficiency at the higher temperature, then the true value of $E_a2 - \frac{1}{2}E_a4$ would be somewhat less than that reported here. If the efficiency was less at the higher temperature, our value of $E_a2 - \frac{1}{2}E_a4$ would be too low.

We have also found that, under the conditions of our experiments, the molecular weight of the product *rises* with rise in temperature of reaction. From this we conclude that, in the peroxide-catalyzed polymerization of styrene, the molecular weight cannot be determined *solely* by a chain transfer reaction (equation 3) of higher activation energy than that of chain growth, and that it is determined in large part in a reaction of lower activation energy which may be, but need not be, the interaction of two growing chains. This is consistent with the conclusions of Schulz and Husemann[2c] and with the results of the work on catalyst fragments in polymer molecules.[10]

The relative values of the rates at the three temperatures are 1:1.45:2.14; the relative values of η_{sp}/c are 1:1.23:1.48 and, if the molecular weights of polymers prepared at the three temperatures are related to the viscosity by the same proportionality constant, then these are the relative values of the molecular weights. If there were no chain transfer reaction, and if equal numbers of chains were started at the three temperatures, then the molecular weights would have to rise in the same proportion as the rates, in order to account for the observed increase in rate. That they do not indicates that chain transfer reactions may take place to some extent.

We can make only an estimate of the activation energy of the chain transfer reaction. The degree of polymerization, or molecular weight (D. P.) is determined by the ratio of the rates of chain propagation and the sum of the rates of chain transfer and chain termination:[2c,11]

$$\mathrm{D.\ P.} = \frac{k_2(\mathrm{R}^*)(\mathrm{M})}{k_3(\mathrm{R}^*)(\mathrm{M}) + k_4(\mathrm{R}^*)^2}$$

Since $k_2(\mathrm{R}^*)(\mathrm{M}) = -\mathrm{d(M)}/\mathrm{d}t$ and $k_4(\mathrm{R}^*)^2 = k_1(\mathrm{B.\ p.})$,

$$\frac{-\mathrm{d(M)}}{\mathrm{d}t}\Big/\mathrm{D.\ P.} - k_1(\mathrm{B.\ p.}) = \frac{k_3}{k_4{}^{1/2}}k_1{}^{1/2}(\mathrm{B.\ p.})^{1/2}(\mathrm{M})$$

Evaluation of the terms on the left at two temperatures, and treatment of the terms on the right in the same way as in the calculation of $E_a2 - \frac{1}{2}E_a4$ leads to a value for $E_a3 - \frac{1}{2}E_a4$.

However, this requires the absolute values of D. P. and k_1(B. p.). Since the proportionality factors relating viscosity and molecular weight are in doubt,[12] calculations based on this equation are crude approximations. Also, it is likely that the rates of chain initiation and destruction are not equal to k_1(B. p.), but are proportional to it, not all peroxide decompositions being

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(5) This is the average of 2 values, 8.3 and 9.4 kcal. based on the rates at 54 and 64°, and 64 and 74°, respectively. The discrepancy between these two values is not particularly serious since the calculations involve the logarithms of the ratios of the rates, 1.45 and 1.48, respectively. An error of 2% in any rate introduces an error of 6% in $E_a2 - {}^1/_2E_a4$.

(6) Mark and Raff, "High Polymeric Reactions," Interscience Publishing Co., New York, N. Y., 1941, p. 214.

(7a) Mark and Raff, *Z. physik. Chem.*, **B31**, 275 (1936). (b) Melville, "Annual Reports of the Chemical Society for 1939," London, 1940, p. 78.

(8) Foord, *J. Chem. Soc.*, 48 (1940).

(9) Rice, THIS JOURNAL, **56**, 284 (1934).

(10) Price, Kell and Krebs, *ibid*, **64**, 1103 (1942).

(11) We omit chain transfer with the solvent since benzene, in the concentration used in our experiments, has little effect on the molecular weight.

(12) Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

necessarily effective. If D. P. is calculated from the Staudinger equation, and the assumption is made that about 90% of the peroxide decomposition are effective, $E_a3 - \frac{1}{2}E_a4$ is found to be about 14 kcal.

It may be noted that the linear relationship between molecular weight and $1/T$, which has been observed in thermal polymerizations,[2b,7b] can be accounted for quantitatively without introduction of chain transfer. Assuming the alternate mechanism, namely, that the molecular weight is determined by the ratio of the rates of steps 2 and 4, from equations 1b, 2 and 4[13]

$$\text{D. P.} = k_2/k_{1b}^{1/2}k_4^{1/2}$$

and from the Arrhenius expressions for the rate constants, and using the value which we have found for $E_a2 - \frac{1}{2}E_a4$

$$\log \text{D. P.} = \text{Const.}\left(\frac{0.4343}{RT}\right)(\tfrac{1}{2}E_a1\text{b} - E_a2 + \tfrac{1}{2}E_a4)$$

in which $\frac{1}{2}E_a1 = 14$ kcal.,[8] and $E_a2 - \frac{1}{2}E_a4 = 8.9$ kcal. This equation is consistent with the experimental observations that log D. P. is a linear function of $1/T$, that D. P. falls with rising temperature, and that the algebraic sum of the activation energies in this expression is about 5.4 kcal.[2b]

The relation between D. P. and temperature observed in thermal polymerizations is consistent with both mechanisms, and cannot be considered as proof for either. The other evidence introduced by Flory[2b] and the interpretation of the relation between molecular weight and dilution[2c] indicate that in thermal polymerizations, because of the absence of peroxides and the low concentration of growing chains, chain transfer reactions do determine the molecular weight of the product. In peroxide catalyzed reactions, however, this mode of molecular weight determination appears to be of secondary importance only.

Experimental

Styrene.—Eastman Kodak Co. styrene was distilled in vacuum under nitrogen before use, b. p. 64° (47 mm.).

Benzene.—Eastman Kodak Co. thiophene-free benzene was distilled, b. p. 78.9–79.8°.

Benzoyl Peroxide.—Eastman Kodak Co. white label benzoyl peroxide was crystallized from chloroform-methanol and dried in vacuum over sulfuric acid and paraffin.

Rate Measurements.—Styrene (36.04 g.) was admitted to a 100-cc. volumetric flask, the desired amount of benzoyl peroxide was dissolved and the solution was made up to volume with benzene at 24.2°. Individual samples were sealed in glass ampoules which had been cleaned in an acid-bath and allowed to stand in sulfurous acid for twenty-four hours before being rinsed with distilled water and dried at 135°. The samples were heated in a thermostat which was kept at constant temperature ±0.02°.

Peroxide Decomposition.—Initial concentrations of benzoyl peroxide in benzene–styrene were determined by titration. Samples, 1.99, 4.98 or 9.98 cc., depending on peroxide concentrations were heated for measured periods of time. The total samples were dissolved in 20 cc. of acetone, 10 cc. of benzene, and 5 cc. of acetic acid, and a small amount of dry-ice was added. One cubic centimeter of 50% aqueous potassium iodide was added and the solutions were allowed to stand ten to fifteen minutes. Water was added and the solutions were titrated against thiosulfate. The data of sample runs follow.

DECOMPOSITION OF BENZOYL PEROXIDE

$T = 53.98°$		$T = 64.02°$		$T = 74.02°$	
Time, hours	(B. p.), m./l.	Time, hours	(B. p.), m./l.	Time, hours	(B. p.), m./l.
0	0.2417	0	0.0454	0	0.01894
12.25	.2261	4.00	.0419	2.00	.01675
24.30	.2114	8.72	.0379	4.00	.01453
44.70	.1836	16.05	.0328	6.00	.01255
68.2	.1555	24.0	.0278	9.60	.00971
114.8	.1113	45.0	.0181	12.00	.00854
162.0	.0801	69.7	.0109	16.02	.00618
		93.0	.0069	24.0	.00358
				44.8	.00085

Rate of Polymerization.—After the rates of benzoyl peroxide decomposition were determined, solutions of the calculated peroxide concentration were prepared. The peroxide concentration was determined by titration. Samples were polymerized for one hour, and cooled. Weighed quantities were added to excess methyl alcohol. Polystyrene precipitated and was allowed to stand at 0° for at least one day. The supernatant liquid was decanted; the precipitate was washed with several portions of cold methyl alcohol, dried first in a vacuum desiccator and then to constant weight in vacuum at 100°.

Viscosity determinations were made in an Ostwald viscometer at 26.95 ± 0.03°. Benzene was used as solvent, and the concentrations of polystyrene were 0.85–1.30%.

Summary

The rates of decomposition of benzoyl peroxide in 3.46 molar solutions of styrene in benzene have been determined at 53.98, 64.02 and 74.02°. The polymerization of the styrene was studied at the three temperatures at equal rates of peroxide decomposition. The rates of polymerization and the molecular weights of the products increased under these conditions with rise in temperature of reaction, the rates rising more rapidly than the molecular weights. The practical implications of these results were noted.

The activation energy of the chain growth reaction was estimated to be 11 kcal. This calculation was based on the approximation that at equal rates of peroxide decomposition at several temperatures there are equal rates of chain initiation.

It was concluded that, in the peroxide catalyzed polymerization of styrene, the molecular weight is determined largely in a reaction of lower activation energy than that of chain growth, and chain transfer reactions are of minor importance. This is in agreement with other investigators' conclusions concerning the mechanism of this reaction.

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[13] Mark and Raff, "High Polymeric Reactions," Interscience Publishers Inc., New York, N. Y., 1941, p. 182.