a crystalline, non-hygroscopic compound. The salt was also obtained by the addition of an alcoholic solution of calcium chloride to a quaternary ammonium salt of *d*(+)-pantothenic acid.

Experimental

A. **Calcium *d*(+)-Pantothenate.**—A mixture of 26 g. (0.2 mole) of *d*(−)α-hydroxy-β,β-dimethyl-γ-butyrolactone, 18 g. (0.2 mole) of β-alanine, 50 cc. of absolute methanol and 25 cc. (0.24 mole) of diethylamine was refluxed overnight. Absolute ethanol (100 cc.) was added to the clear solution, which was then distilled. During the distillation the volume of solution was maintained at 175 cc. by the addition of more ethanol. The distillation was continued until the distillate contained 0.2 mole of amine as indicated by titration. The solution was cooled slightly and filtered through a pad of Norit. The almost colorless filtrate was mechanically stirred while 6.2 g. (0.11 mole) of solid calcium oxide was added. Stirring at room temperature was continued until all the calcium oxide had dissolved (about five hours), and the solution was clarified by filtration through a bed of Supercel. The filtrate was seeded with calcium *d*(+)-pantothenate and mechanically stirred at room temperature for 48 hours. The white solid was then filtered, washed well with absolute alcohol and dried *in vacuo;* yield 40 g. (84%), $[\alpha]^{24}\text{D}$ +27° (water). From the filtrate an additional amount (2.3 g.) of calcium pantothenate was obtained. The total yield was 89%.

Anal. Calcd. for $C_{18}H_{32}O_{10}N_2Ca$: N, 5.88; Ca, 8.41. Found: N, 5.84; Ca, 8.22.

B. **Sodium *d*(+)-Pantothenate.**—A solution of 0.2 mole of sodium ethoxide in absolute alcohol was added to the filtrate from the Norit filtration (A). The solution was seeded with sodium *d*(+)-pantothenate and mechanically stirred for 48 hours. The solid was filtered, washed with isopropyl alcohol and dried at 60° (75% yield).

X. **Calcium Chloride *d*(+)-Pantothenate.**—A mixture of 3.5 g. (0.04 mole) of β-alanine and 100 cc. of absolute methanol containing 0.03 mole of trimethylphenylammonium methoxide was refluxed until all the β-alanine had dissolved. The solution was cooled to room temperature and filtered. *d*(−)α-Hydroxy-β,β-dimethyl-γ-butyrolactone (3.9 g., 0.03 mole) was dissolved in the filtrate, which was then kept at room temperature for 48 hours. A solution of 3.3 g. (0.03 mole) of anhydrous calcium chloride in absolute ethanol was added to the solution of the pantothenate salt. A white crystalline material began to separate almost immediately. The reaction mixture was kept three days at room temperature. The solid was then filtered and washed with absolute alcohol; yield 4.6 g. (58%), $[\alpha]^{24}\text{D}$ +25.3° (water).

Anal. Calcd. for $C_9H_{16}O_5NCaCl$: C, 36.79; H, 5.49; Cl, 12.07; Ca, 13.64. Found: C, 36.81; H, 5.63; Cl, 12.28; Ca, 13.37.

The same salt is obtained if the alcoholic solution of calcium chloride is added to the solution from the Norit filtration (procedure A).

PROCESS RESEARCH AND DEVELOPMENT DIV.
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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics of Polymerization of Styrene Initiated by the System Benzoyl-Peroxide–Dimethylaniline

BY THEODORE H. MELTZER AND ARTHUR V. TOBOLSKY

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The rates of polymerization and degrees of polymerization produced in styrene by the initiator–activator system benzoyl peroxide–dimethylaniline were studied at several temperatures. At 0° the initiation of polymer chains appears to result from a bimolecular reaction between peroxide and amine. At higher temperatures the kinetics are more complex.

Introduction

For benzoyl peroxide initiated polymerization of pure styrene, the following relationship obtains[1]

$$R_p = K[M][Bz_2O_2]^{1/2} \qquad (1)$$

where R_p is the initial rate of polymerization in moles per liter per second, [M] and $[Bz_2O_2]$ are the concentrations of monomer and benzoyl peroxide in moles per liter and K is a function of temperature alone tabulated in reference 1.

Horner and Schwenk[2] have noted that the polymerization of styrene by benzoyl peroxide is very much activated by the presence of dimethylaniline.

In this paper we show how the initial rate of polymerization of pure styrene initiated by the catalyst–activator system benzoyl peroxide–dimethylaniline depends on the concentrations $[Bz_2O_2]$ and [DMA]. The experiments were carried out in pure styrene at temperatures of 0, 30, 45 and 60°. The relation between $1/\bar{P}_n$ (reciprocal number average degree of polymerization) and R_p was obtained at all four temperatures. It is important to emphasize that R_P is an *initial* rate of polymerization measured at very low conversions. At higher conversions the rate of polymerization decreases markedly.

Experimental

The experimental procedure for measuring R_p has been described previously.[3] $\bar{P}_n$ was calculated by means of the relationship[4]

$$\bar{P}_n = 1605\,[\eta]^{1.37} \qquad (2)$$

The purification of the dimethylaniline was accomplished as follows.

Eastman Kodak mono-free grade of dimethylaniline was refluxed four hours with 10% of its weight of acetic anhydride. The cooled reaction mixture was poured into an excess of 20% hydrochloric acid. After cooling this mixture was extracted with four 50-ml. portions of ether.

The aqueous layer was cautiously made alkaline to phenolphthalein with 30% NaOH solution, and the amine layer drawn off. The crude amine was dried over KOH pellets prior to fractionation through a Vigreux column. A good middle cut of colorless material was collected under nitrogen at 87° and 14 mm. pressure. It was stored in the refrigerator under nitrogen.

Results.—The results of the experimental work are tabulated in Table I. In this table are presented the values of $[Bz_2O_2]$, [DMA], $[Bz_2O_2]$ [DMA], R_p, $[\eta]$ and $1/\bar{P}_n$.

It was established that R_p was a function only of the product $[Bz_2O_2]$ [DMA], not of the individual concentrations $[Bz_2O_2]$ and [DMA]. Figure 1

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TABLE I

$[Bz_2O_2]$	[DMA]	R_p	$[\eta]$	$1/\bar{P}_n$
		0°		
0.0005	0.0005	6.38×10^{-8}	3.85	1.0×10^{-4}
.001	.001	2.08×10^{-7}	2.95	1.45×10^{-4}
.00123	.00123	1.99×10^{-7}	2.70	1.58×10^{-4}
.00245	.00245	4.67×10^{-7}	1.90	2.64×10^{-4}
.0098-	.00980	1.52×10^{-6}	0.74	9.56×10^{-4}
.020	.020	2.44×10^{-6}	0.51	1.60×10^{-3}
		30°		
0.0005	0.0005	1.15×10^{-6}	3.85	1.00×10^{-4}
.001	.0005	2.34×10^{-6}	3.42	2.08×10^{-4}
.001	.001	2.68×10^{-6}	2.06	2.29×10^{-4}
.001	.002	3.26×10^{-6}	1.85	2.69×10^{-4}
.0025	.0025	4.32×10^{-6}	1.17	5.02×10^{-4}
.005	.005	8.69×10^{-6}	0.88	7.59×10^{-4}
.01	.005	1.35×10^{-5}	.67	1.08×10^{-1}
.01	.01	1.76×10^{-5}	.51	1.58×10^{-3}
.02	.02	2.61×10^{-5}	.42	2.09×10^{-3}
		45°		
0.0005	0.0005	4.77×10^{-6}	3.05	1.37×10^{-4}
.001	.001	7.76×10^{-6}	3.56	1.10×10^{-4}
.00125	.00125	9.02×10^{-5}	1.97	2.51×10^{-4}
.0053	.00133	1.52×10^{-6}	1.21	4.78×10^{-4}
.0025	.0025	1.53×10^{-5}	1.33	4.09×10^{-4}
.0013	.0053	1.36×10^{-5}	1.23	4.79×10^{-4}
.0026	.0053	2.02×10^{-5}	1.05	6.04×10^{-4}
.0053	.0027	2.09×10^{-5}	0.94	6.92×10^{-4}
.0052	.0052	2.90×10^{-5}	.76	9.22×10^{-4}
.0052	.01	3.96×10^{-5}	.67	1.08×10^{-3}
.0053	.01	4.34×10^{-5}	.63	1.21×10^{3}
.01	.005	4.53×10^{-5}	.56	1.38×10^{-3}
.0052	.02	4.27×10^{-5}	.56	1.38×10^{-3}
.0053	.02	4.49×10^{-5}	.50	1.62×10^{-3}
.021	.0052	5.05×10^{-5}	.46	1.82×10^{-3}
.01	.01	4.65×10^{-5}	.62	1.20×10^{-3}
.02	.02	8.35×10^{-5}	.35	2.66×10^{-3}
		60°		
0.0005	0.0005	1.19×10^{-5}	2.34	1.99×10^{-4}
.001	.001	1.85×10^{-5}	1.54	3.46×10^{-4}
.001	.0005	2.08×10^{-5}	1.63	$3.24 \times 10^{-}$
.001	.001	2.14×10^{-5}	1.87	2.63×10^{-4}
.00125	.00123	2.34×10^{-5}	1.57	4.08×10^{-4}
.001	.002	2.60×10^{-5}	1.23	4.78×10^{-4}
.0025	.0025	3.66×10^{-5}	1.01	6.13×10^{-3}
.005	.005	7.10×10^{-5}	0.61	1.24×10^{-3}
.005	.01	1.04×10^{-4}	.54	1.46×10^{-3}
.01	.01	1.08×10^{-4}	.47	1.74×10^{-3}
.01	.005	1.09×10^{-4}	.49	1.66×10^{-3}
.02	.005	1.15×10^{-4}	.46	1.86×10^{-3}
.01	.005	1.16×10^{-4}	.46	1.86×10^{-3}
.005	.02	1.50×10^{-4}	.34	2.76×10^{-3}
.01	.01	1.73×10^{-4}	.38	2.40×10^{-3}
.02	.02	1.74×10^{-4}	.30	3.03×10^{-3}

shows a plot of log R_p *versus* log $[Bz_2O_2]$ [DMA] for the data tabulated in Table I. A straight line is obtained at each temperature. These lines correspond to

$$\begin{aligned}
&(a)\quad R_p = 10^{-3.81}([Bz_2O_2][DMA])^{0.500} \quad \text{at } 0° \\
&(b)\quad R_p = 10^{-3.25}([Bz_2O_2][DMA])^{0.395} \quad \text{at } 30° \qquad (3)\\
&(c)\quad R_p = 10^{-2.84}([Bz_2O_2][DMA])^{0.380} \quad \text{at } 45° \\
&(d)\quad R_p = 10^{-2.54}([Bz_2O_2][DMA])^{0.355} \quad \text{at } 60°
\end{aligned}$$

Plots of $1/\bar{P}_n$ *versus* R_p taken from the data in Table I were made. An example is shown in Fig. 2. These plots, though they show some scatter, are best represented by straight lines corresponding to

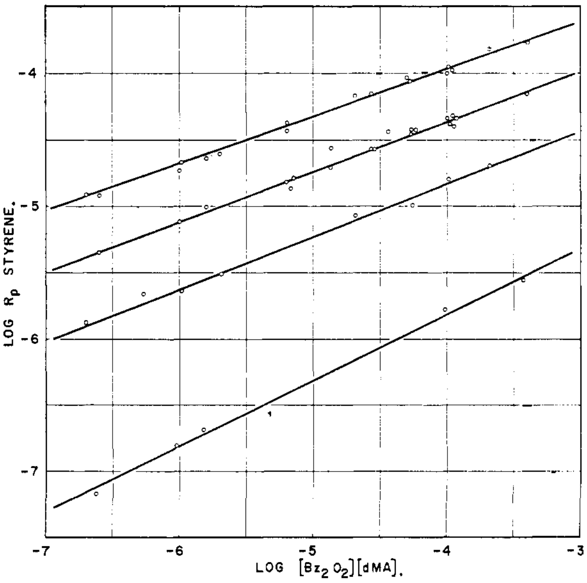

Fig. 1.—Log R_p *versus* log $[DMA][Bz_2O_2]$ for the system styrene–benzoyl peroxide–dimethylaniline at 0, 30, 45 and 60°.

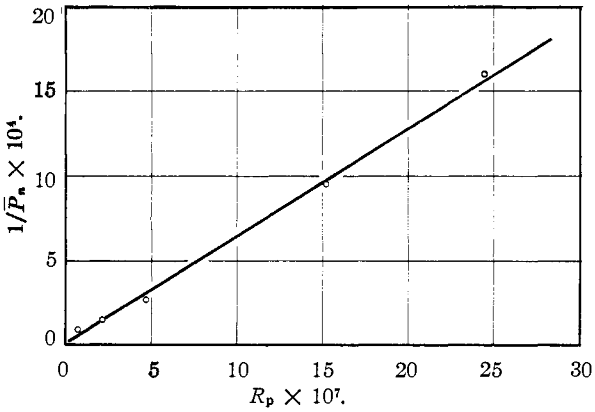

Fig. 2.—$1/\bar{P}_n$ *versus* R_p for the system styrene-benzoyl peroxide–dimethylaniline at 0°.

$$\begin{aligned}
&(a)\quad \frac{1}{\bar{P}_n} = 640 R_p && \text{at } 0° \\
&(b)\quad \frac{1}{\bar{P}_n} = 2 \times 10^{-5} + 79.0 R_p && \text{at } 30° \\
&(c)\quad \frac{1}{\bar{P}_n} = 3 \times 10^{-5} + 29.8 R_p && \text{at } 45° \qquad (4)\\
&(d)\quad \frac{1}{\bar{P}_n} = 6 \times 10^{-5} + 15.2 R_p && \text{at } 60°
\end{aligned}$$

It was also ascertained that moderate amounts of purified dimethylaniline had no effect on the R_p or $\bar{P}_n$ values of 2-azobisisobutyronitrile initiated polymerization of styrene.

Discussion

In references 1 and 3 the following relationship was derived between $1/\bar{P}_n$ and R_p

$$1/\bar{P}_n = C_{tr,m} + C_{tr,s}\frac{[S]}{[M]} + C_{tr,cat}\frac{[Cat]}{[M]} + \frac{A'R_p}{[M]^2} \quad (5)$$

In the above equation, $C_{tr,m}$ is the chain transfer constant to the monomer, $C_{tr,Cat}$ is the chain transfer constant to the catalyst, and $C_{tr,S}$ is the chain transfer constant to any other substance in the system, in this case the activator dimethylaniline.

The results outlined in equation 4 are in reasonably good agreement with those obtained using 2-azobisisobutyronitrile as the catalyst.[1] Since both activator concentration [S] and catalyst concentration [Cat] are non-linear functions of R_p, one would not get the relation given in equation 4 unless the terms $C_{tr,s}$ [S]/[M] and $C_{tr,cat}$ [Cat]/[M] were negligible under the experimental conditions studied.

The fact that small quantities of dimethylaniline did not affect the R_p or $\bar{P}_n$ of a 2-azobisisobutyronitrile initiated polymerization shows that dimethylaniline does not affect the termination or propagation steps of the chain reaction.

The role of dimethylaniline in the Bz_2O_2–DMA initiated systems must therefore be entirely in the initiation step.

The kinetic result for R_p at 0° (see equation 3a) is readily understood. The rate of initiation R_i is related to the rate of polymerization R_p by means of the equation

$$R_i' = \frac{2A'}{[M]^2}R_p^2 \quad (6)$$

Moreover A' is defined in equation 5. $A'/[M]^2$ at 0° is determined by the slope of the straight line defined in equation 4a, namely, 640. Substituting this value and the value of R_p at 0° from equation 3a into equation 6 one obtains

$$R_i'\,(\text{at } 0°) = 3.07 \times 10^{-5}[Bz_2O_2][DMA] \quad (7)$$

Equation 7 is easy to interpret. Assuming that the efficiency of the initiation process is high and that it is independent of the $[Bz_2O_2]$ and [DMA], equation 7 suggests that radicals are produced from dimethylaniline and benzoyl peroxide by a bimolecular mechanism.

At the higher temperatures, however, calculation of R_i from equations 6, 3 and 4 leads to the following result

$$R_i' = K'[Bz_2O_2]^a[DMA]^a \quad (8)$$

where a has the values 0.79, 0.76, and 0.71 at the temperatures 30, 45 and 60°, respectively, and K' also varies with the temperature. There is no obvious kinetic interpretation either of equations 3b, 3c or 3d nor of equation 8, and these equations will have to be regarded as empirical till further explanation is forthcoming.

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PRINCETON, N. J.

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY OF LOUISIANA STATE UNIVERSITY]

The Metal Complexes of Tris-anhydro-*o*-aminobenzaldehyde[1,2]

BY GUNTHER L. EICHHORN AND RASHID A. LATIF

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In a reaction analogous to the conversion of phthalonitrile to phthalocyanine, copper(II), nickel(II) and cobalt(II) ions react with *o*-aminobenzaldehyde to produce complexes of a trimeric condensate, tris-anhydro-*o*-aminobenzaldehyde. This coördinating agent, apparently quadridentate, is also formed by treatment with manganese(II) ion, but in this instance the isolated compound contains no complexed metal ion. Tris-anhydro-*o*-aminobenzaldehyde has the ability to stabilize low oxidation states, bringing about the reduction of copper(II) to copper(I), and preventing the oxidation of cobalt to the +3 state. The copper(I) complex is susceptible to oxidation or disproportionation, depending upon the conditions to which it is subjected.

Introduction

Among the more important developments in the recent history of coördination chemistry has been the increasing recognition that complex formation does not necessarily occur through a simple additive process involving the components of the complex, but that indeed extensive modification may occur in either donor or acceptor as a consequence of coordinate covalent bond formation. A very familiar example of such modification is the tetramerization of phthalonitrile to phthalocyanine[3] under the influence of metals or metallic ions. The metal ion catalysis of the trimerization of *o*-aminobenzaldehyde may be considered analogous to this synthesis of phthalocyanine.

Reaction of Metal Ions with *o*-Aminobenzaldehyde.—The reaction between *o*-aminobenzaldehyde and metal ions has been previously carried out in the presence of ammonia, and has resulted in the formation of complexes of the aldimine derivative of the aldehyde.[4] In the present investigation ammonia was omitted from the reaction mixture in an attempt to secure the complexes of unaltered *o*-aminobenzaldehyde and to study the reaction of the latter with ethylenediamine and other amine derivatives. The nitrates of divalent copper, nickel, cobalt and manganese were employed. Analyses of the products of the reaction did not conform to calculated values for the *o*-aminobenzaldehyde complexes, but were in accord with the theoretical composition of complexes of the trimeric condensate of the molecule. The charge on the metal ion in the complexes was neutralized by uncoördinated

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(1) Presented at the Regional Conclave of the American Chemical Society, New Orleans, December 10–12, 1953.

(2) Taken in part from the Ph.D. thesis of Rashid A. Latif, Louisiana State University, 1953.

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(4) P. Pfeiffer, T. Hesse, R. Pfitzner, W. Scholl and H. Thielert, *J. prakt. Chem.*, **149**, 217 (1937).