[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

The Polymerization of Styrene in Phenolic Solvents[1]

BY CHEVES WALLING

The polymerization of styrene is generally recognized as a chain reaction which may proceed through at least two types of active center. The thermal reaction in the absence of catalysts is sensitive to oxygen[1a,2,3] and numerous inhibitors,[4] approximates second order kinetics and proceeds at the same rate in several solvents,[5,6] and polymerization apparently proceeds through a free radical[7] intermediate. The same type of center is considered to be involved in the polymerization catalyzed by catalysts known to liberate free radicals on decomposition: benzoyl peroxide, nitrosoacetanilides,[8] tetraphenylsuccinonitrile,[9] triphenylmethylazobenzene,[10] etc. In the presence of strong electrophilic reagents such as stannic chloride, the polymerization is of third or higher order,[11] and the reaction is probably best explained as involving a carbonium ion.[11,12]

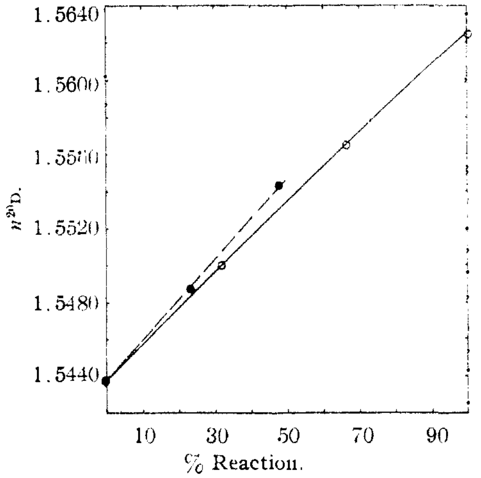

Fig. 1.—Variation of index of refraction with % reaction for 3.68 molar styrene polymerized in *m*-cresol at 131°: O "synthetic" reaction mixtures; ● actual reaction mixtures.

Moore, Burk and Lankelma[13] have studied the polymerization of styrene in thymol and have found the reaction to be third order in respect to styrene. Because of the order of the reaction, the low molecular weight of the product, and their failure to detect thymol in the polymer, they have concluded that the polymerization in this medium is of the carbonium-ion type, catalyzed by the acid, thymol.

This paper presents a further study of the polymerization of styrene in phenolic solvents. The results, which extend those of Moore, Burk and Lankelma,[13] seem better interpreted if the polymerization of styrene in these solvents is considered to involve a radical rather than a carbonium ion type of active center.

Experimental

Materials.—Styrene employed was obtained from the Dow Chemical Company, and was of better than 99% purity. Shortly before use, it was distilled to remove inhibitor and stored in a refrigerator. Further purification seemed unnecessary as no difference in results was obtained from a sample purified by repeatedly recrystallizing to constant melting point (−30.6°). Thymol was U. S. P. material from the Givaudan Delawanna Corporation, and other solvents were the best commercial materials redistilled before use. Sodium cresolate was prepared by dissolving sodium in excess cresol under nitrogen. Under nitrogen such solutions could be kept as clear viscous liquids, but they darkened rapidly if exposed to air.

Kinetic Experiments.—Kinetic experiments were carried out in sealed tubes on 2–4 cc. of solution, of which the index of refraction was measured before and after heating in a constant temperature bath for various lengths of time. Experiments *in vacuo* were carried out by attaching the tubes, before sealing, to a high vacuum line, freezing in liquid nitrogen, connecting to the line and degassing to 10^{-4} mm. of mercury, disconnecting from the line, bringing to room temperature, and refreezing. This cycle was carried out at least twice before the tubes were sealed off.

The relation between index of refraction and extent of reaction was determined by measuring the index of refraction of "synthetic" reaction mixtures of low molecular weight polystyrene, styrene and solvent made up to correspond to several extents of reaction for each initial concentration of styrene and solvent studied. The indices of refraction of these mixtures gave good checks with the indices of larger runs in which the polystyrene was actually isolated by distilling off the monomer and some of the solvent under vacuum, taking up the residue in benzene, extracting phenolic materials with sodium hydroxide, and drying to constant weight at 100° and 1 mm. pressure. The relation between extent of reaction and index of refraction appeared generally to be linear to at least 50% reaction, and a sample result, for 3.68 molar styrene in *m*-cresol, is shown in Fig. 1.

Viscosities of polymers were determined on samples isolated as just described, or, in the case of polymerization in thymol, on a sample isolated by precipitating the polymer with methanol, dissolving it in benzene, extracting with potassium hydroxide in 30% methanol, removing the solvent, and drying the product overnight at 100° and 1 mm. pressure. Since a portion of the supernatant liquid from the methanol precipitation, when added to 5%

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(1) Most of the material of this paper was presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Cleveland, O., April 3, 1944.

(1a) Thompson and Burk, THIS JOURNAL, **57**, 711 (1935).

(2) Dostal and Jorde, *Z. physik. Chem.*, **179A**, 23 (1937).

(3) Breitenbach, Springer and Horeischy, *Ber.*, **71**, 1438 (1938).

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

(5) (a) Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **179A**, 361 (1937); (b) Suess and Springer, *ibid.*, **181A**, 81 (1937).

(6) Schulz, Dinglinger and Husemann, *ibid.*, **43B**, 385 (1939).

(7) For a discussion of this point see Mark and Raff, "High Polymeric Reactions," Interscience Publishers Inc., New York, N. Y., 1941.

(8) Blomquist, Johnson and Sykes, THIS JOURNAL, **65**, 2446 (1943).

(9) Schulz and Wittig, *Naturwissenschaften*, **27**, 387, 456 (1939).

(10) Schulz, *ibid.*, **27**, 659 (1939).

(11) Williams, *J. Chem. Soc.*, 775 (1940).

(12) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(13) Moore, Burk and Lankelma, THIS JOURNAL, **63**, 2954 (1941).

aqueous caustic and boiled for a few minutes, gave only a trace of insoluble material, the precipitation of polymer was practically quantitative. This fact is an indication in itself of moderately high molecular weight. Viscosities were measured in benzene, with concentration measured in grams of polymer/100 cc. of solution.

In experiments in the presence of benzoyl peroxide, disappearance of the benzoyl peroxide was followed by adding a few drops of the reaction mixture to an acetone solution of sodium iodide. The peroxide liberates iodine which is detected by color. This test is not only very sensitive, but may be made quantitative by comparing the color with that obtained from known amounts of peroxide.

Discussion of Results

If the polymerization of styrene in phenolic solvents were of the carbonium ion type and catalyzed by the acidic properties of the phenol, the rate might be expected to show at least a qualitative relation to the acid strength of the phenols in water.[14] Figure 2 shows rate curves for 3.68 molar styrene in several phenols and in cresol containing *p*-nitrophenol, acetic acid and sodium cresolate. Although the rates in *m*-cresol (K_a in water 9.8×10^{-11})[15] and in thymol (K_a 3.2×10^{-11})[15] bear the proper relation and the result in the presence of sodium cresolate is plausible if general acid catalysis as well as catalysis by hydrogen ion is important, the other curves are quite anomalous. *o*-Chlorophenol (K_a 3.6×10^{-8})[16] produces approximately the same rate as *m*-cresol, while the addition of 10% of the still stronger acid *p*-nitrophenol (K_a 7×10^{-8})[17] to the cresol solution actually decreases the rate. Still more striking is the effect of acetic acid. Although this acid (K_a 1.86×10^{-5}) is about 50,000 times as strong an acid in water as *m*-cresol, making a *m*-cresol solution of styrene 0.5 molar in acetic acid markedly decreased the rate of polymerization. Accordingly, if the polymerization is to be interpreted as of the carbonium ion type, the formation of carbonium ion must be catalyzed by some property of a phenol other than that which determines its ionization in water; or else *p*-chlorophenol, *p*-nitrophenol and acetic acid must possess chain breaking properties for the carbonium ion polymerization of styrene which are lacking in the more weakly acid phenols.

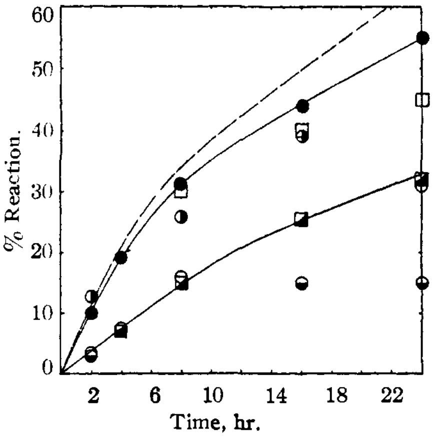

Fig. 2.—Polymerization of 3.68 molar styrene in a number of solvents at 131°, all *in vacuo* unless otherwise noted. Curves are drawn only through experiments in thymol and *m*-cresol. ●, *m*-cresol; ◪, thymol; ⊖, *m*-cresol containing 10% *p*-nitrophenol; ◑, *o*-chlorphenol; ○, *m*-cresol containing 0.1 molar Na cresolate (under nitrogen); □, *m*-cresol containing 0.1 molar acetic acid (air); ----rate in toluene (from data of Schulz, *et al.*).

A mechanism which has been suggested[7,18] for the uncatalyzed radical type polymerization of styrene involves a bimolecular initiation reaction between two styrene molecules to yield a diradical. Each radical then behaves as an independent active center and continues to add styrene molecules until the kinetic chain is terminated by the interaction of two radicals which either unite or disproportionate. These steps are indicated schematically as follows, where M is a styrene molecule, P* a polymer molecule containing an active center, and P an inert polymer molecule

initiation $2M \longrightarrow 2P^*$ (a)[19]
growth $P^* + M \longrightarrow P^*$ (b)
termination $2P^* \longrightarrow 2P$ (disproportionation)
or $2P^* \longrightarrow P\text{-}P$ (combination) (c)

Using the treatment of Breitenbach[20] and Mark,[7] namely, that very early in the reaction a steady state is achieved in which the rates of the initiation and termination reactions are the same, this scheme yields the second order kinetics $-d[M]/dt = k_2[M]^2$ (where $k_2 = k_b\sqrt{k_a/k_c}$), which have been observed in many solvents.[5,6] If to this mechanism is added the concept of chain transfer with the solvent (*i. e.*, that an active center is able to deactivate itself by removing an atom or group from the solvent, and that the resulting solvent radical is then able to start a new chain[18]), it also predicts quantitatively the variation of degree of polymerization with monomer concentration in a number of solvents.[21,22] The reactions of chain transfer with solvent are illustrated by the following equations, where S is a solvent molecule and S* a solvent radical

$$P^* + S \longrightarrow P + S^* \quad (d)$$
$$S^* + M \longrightarrow P^* \quad (e)$$

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[14] Although the absolute values of the dissociation constants of acids as weak as the phenols are in considerable doubt, the K_a's for thymol and *m*-cresol were selected from the same source, and the other constants differ by quantities larger than the uncertainty in their absolute values. Correlation between the strengths of acids in water and their effectiveness as catalysts in other solvents has been established for other reactions: *e. g.*, the diazoamino rearrangement in aromatic amines, by Goldschmidt, *Z. Elektrochem.*, **36**, 662 (1930); the rearrangement of N-bromoacetanilide in chlorobenzene, by Bell, *Proc. Roy. Soc.* (*London*), **A143**, 377 (1934); and the inversion of menthone in chlorobenzene, Bell and Caldin, *J. Chem. Soc.*, 382 (1938).

[15] Boyd, *J. Chem. Soc.*, **107**, 1540 (1915).

[16] Tiessens, *Rec. trav. chim.*, **48**, 1068 (1928).

[17] Lundén, *J. chim. phys.*, **5**, 574 (1907).

[18] Flory, THIS JOURNAL, **59**, 241 (1937).

[19] Actually the two active centers are attached to the same chain, see above.

[20] Breitenbach, *Monatsh.*, 275 (1938).

[21] Mayo, THIS JOURNAL, **65**, 2324 (1943).

[22] Hulburt, Harman, Tobolsky and Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943).

Now, if the solvent radical formed in equation (d) is relatively inert, so that it reacts with styrene only with difficulty, reaction (e) becomes unimportant. Equation (d) is then a termination reaction for the formation of polymer, for an active center undergoing reaction (d) will no longer be able to add monomer. Such a possibility was pointed out by Mayo[21] and a somewhat similar scheme has been advanced by Price[23] to account for the retarding effect of aromatic nitro compounds on polymerization.

If reaction (e) is unimportant and it is assumed that S* does not undergo a transfer reaction with some other species in the reaction mixture to yield a radical capable of starting polymerization chains, the fate of S* is probably described by one of two reactions

$$2S^* \longrightarrow \text{S-S or 2S} \quad \text{(f)}$$
$$S^* + P^* \longrightarrow \text{S-P or S + P} \quad \text{(g)}$$

In either case, (d) becomes an alternative to (c) as a termination reaction for polymer growth, the only difference between (f) and (g) being that (f) indicates that every occurrence of (d) removes one P* and (g) two P*'s (one immediately and one within the fraction of a second that constitutes the life of an active radical in solution). In the case that the rate of (d) is sufficiently large and of (e) sufficiently small, (d) rather than (c) becomes the dominant termination reaction, with a rate in the form $-\mathrm{d}[P^*]/\mathrm{d}t = Ak_\mathrm{d}[\mathrm{P}^*][\mathrm{S}]$ where A lies between one and two depending on the relative importance of reactions (f) and (g).[24] Applying the conventional steady state treatment[7,20] yields, as the over-all rate expression, $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_{3s}[\mathrm{M}]^3/[\mathrm{S}]$ (where $k_{3s} = k_\mathrm{a}k_\mathrm{b}/Ak_\mathrm{d}$); *i. e.*, the rate of polymerization is proportional to the third power of the styrene concentration and inversely proportional to the concentration of solvent.

That such an interpretation may be applied to the polymerization of styrene in thymol is shown in Tables I and II.

TABLE I

RATE CONSTANTS FOR THE POLYMERIZATION OF STYRENE IN THYMOL FROM THE DATA OF MOORE, BURK AND LANKELMA

Temp., °C.	Initial styrene concn. (m./liter)	Rate constants k_3[a]	(In hours) k_{3s}[b]
145	3.24	5.0×10^{-3}	2.0×10^{-2}
145	2.24	3.6×10^{-3}	1.7×10^{-2}
145	1.37	4.3×10^{-3}	2.5×10^{-2}
100	3.24	2.0×10^{-4}	8.6×10^{-4}
100	2.24	1.7×10^{-4}	8.5×10^{-4}

[a] k_3 in equation $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_3[\mathrm{M}]^3$. [b] k_{3s} in equation $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_{3s}[\mathrm{M}]^3/[\mathrm{S}]$.

In Table I the data of Moore, Burk and Lankelma[13] for the polymerization in thymol at 145 and 100° (taken from Table II of their paper) are used to determine both third order rate constants ($-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_3[\mathrm{M}]^3$), and third order constants including the inverse solvent dependence ($-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_{3s}[\mathrm{M}]^3/[\mathrm{S}]$). It will be seen that both constants are quite consistent, and no choice can be made.

TABLE II

POLYMERIZATION OF 3.68 MOLAR STYRENE IN THYMOL *in vacuo* AT 131°, WITH RATE CONSTANT FROM EQUATION $\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_{3s}[\mathrm{M}]^3/[\mathrm{S}]$

Time, hr.	3.72 molar thymol Reaction, %	$k \times 10^3$	1.68 molar thymol Reaction, %	$k \times 10^3$
4	7.6	5.8	16.2	7.2
	8.6	6.7		
	5.1	3.6		
8	15.2	6.7	20.9	5.2
16	27.7	7.7	35.3	6.0
	23.8	6.1		
	24.9	6.5		
24	31.8	6.5	43.6	6.1
32	33.2	5.3	45.0	4.9
48	35.7	4.1	55.7	6.0
		Av. 5.9		Av. 5.9

Table II is a more critical test. Here are given our data for the polymerization at 131° of 3.68 molar styrene in 3.72 molar thymol and 1.68 molar thymol, the balance of the latter solution being made up with chlorobenzene (a solvent in which the radical type reaction proceeds normally). As would be predicted by the mechanism just suggested, the reaction goes twice as fast in the solution containing only half as much thymol; on the other hand, were the reaction of the carbonium ion acid catalyzed type, decreasing the catalyst concentration might reasonably be expected to produce a decreased rate.

If this ability to deactivate growing polymer molecules through the formation of relatively unreactive radicals were a general property of phenols, and providing the phenols were without effect on the rate constants of the initiation and growth reactions, polymerization of styrene in a series of phenols should give a series of rate curves all lying below that obtained in the group of "normal" solvents which affect the rate of polymerization merely by their action as diluents. Figure 2 indicates that the phenols studied behave in this manner and in no case does the rate exceed that in toluene, a typical normal solvent. For phenols in which the rate falls markedly below that in normal solvents, the equation $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_{3s}[\mathrm{M}]^3/[\mathrm{S}]$ should be followed as in the case of thymol, while, for those in which the rate is only slightly lower, termination will occur by both first and second order mechanisms and a mixed order reaction will result approaching second order for high styrene concentrations and third order with inverse solvent dependence for high concentration of solvent. That polymerization in *m*-cresol is

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(23) (a) Price and Durham, THIS JOURNAL, **65**, 757 (1943); (b) Price, *ibid.*, **65**, 2380 (1943).

(24) In the subsequent treatment, it is assumed that in any group of experiments A is essentially constant. Even if this assumption is not valid, the variation in rate constant introduced is small.

such a case is shown in Table III, where the results of experiments at three initial concentrations are summarized. Even here, the rates lie closer to the third order solvent dependent reaction than to the second order reaction.

TABLE III

RATES OF POLYMERIZATION OF STYRENE IN *m*-CRESOL *in vacuo* AT 131°

Initial concn. of styrene, molar	Time, hr.	Yield, %	$k \times 10^2$ $-d[M]/dt = k_2[M]^2$	$k \times 10^2$ $-d[M]/dt = k_{3s}[M]^3/[S]$
3.68	1	7	2.04	3.2
3.68	2	10	1.68	2.7
3.68	4	19	1.60	2.7
3.68	8	31	1.50	3.1
3.68	16	44	1.38	2.9
3.68	24	55	1.43	3.5
	Average		1.61	2.9
2.34	2	10	2.6	7.0
2.34	4	16	2.1	6.0
2.34	8	20	1.3	7.0
2.34	16	23	0.8	2.5
2.34	24	31	0.8	2.7
	Average		1.5	5.0
1.29	24	10	0.36	2.6
1.29	48	25	.78	8.4
	Average		.57	5.5

Another consequence of chain transfer with the solvent will be a lowering of the molecular weight of the polymer below that obtained by the polymerization of styrene in absence of solvent or in a solvent showing little tendency to transfer. We have found the intrinsic viscosity in benzene of the polymers obtained by polymerizing 3.68 molar styrene in thymol and *m*-cresol to be 0.10 and 0.274, respectively. Unfortunately, these values lie in a region in which the correlation between viscosity and molecular weight is particularly difficult to determine, because molecular weight is too high for accurate cryoscopic determinations and low enough so that it is difficult to find an impermeable membrane for osmotic molecular weight measurements. However, very approximate values are obtained by extrapolating to low viscosities the data obtained by Alfrey, Bartovics and Mark[25] on the relation between viscosity and molecular weight for polystyrene polymerized at 120°. This extrapolation yields molecular weights 9500 for the polymer obtained in thymol and 33,000 in *m*-cresol as compared with 150,000 obtained by polymerizing pure styrene at 132°. Extrapolation upward of the data of Kemp and Peters[26] obtained with very low molecular weight polystyrene gives somewhat lower values, but neither method of extrapolation approaches the extremely low molecular weights (600–1200) reported by Moore, Burk and Lankelma for the polymerization in thymol. If our results are correct, and the molecular weight of polystyrene obtained in thymol is of the order of 10,000, inclusion of thymol in the polymer might well have escaped detection by the method employed by Moore, Burk and Lankelma. The observation of these authors that their polystyrene had to be hydrogenated to yield consistent molecular weights is in conflict with results in this Laboratory, where consistent osmotic and viscosimetric molecular weights have been obtained on a large number of polymers without this precaution. It is suggested that hydrogenation may have led to degradation of their polymer, and their failure to obtain consistent results before hydrogenation was due to the great experimental difficulties in obtaining cryoscopic molecular weights above 1–2000.[26]

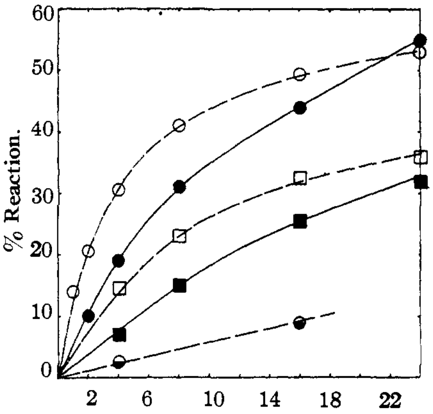

Fig. 3.—Effect of air and benzoquinone on the polymerization of 3.68 molar styrene in phenolic solvents at 131°. Circles: reactions in *m*-cresol; squares, reactions in thymol; dotted lines, in air; solid lines, *in vacuo*; ◒, 0.1 molar benzoquinone in *m*-cresol in air.

Two characteristics of the radical type thermal polymerization of styrene are its sensitivity to oxygen and its inhibition by quinones. Figure 3 shows that the polymerization in both thymol and cresol is initially accelerated by air, and that benzoquinone acts as an inhibitor.[27] Such effects

TABLE IV

INHIBITION OF THE BENZOYL PEROXIDE CATALYZED POLYMERIZATION OF STYRENE BY *m*-CRESOL

All experiments 3.68 molar styrene, 0.1 molar benzoyl peroxide.

Solvent	Temp., °C.	Time, hours	% Polymerized
Chlorobenzene	60	6	24
m-Cresol	60	6	0
Chlorobenzene	100	0.5	48
m-Cresol	100	.5	1
Chlorobenzene	100	1.0	77
m-Cresol	100	1.0	5

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[25] Alfrey, Bartovics and Mark, THIS JOURNAL, **65**, 2319 (1943).

[26] Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1099 (1942).

[27] The reaction in the presence of benzoquinone was followed only by change in index of refraction. It was possible that the small change was due only to the reaction by which benzoquinone removes active centers and even less polymerization occurred than indicated.

have not been found in known carbonium ion type polymerizations. The good third-order rate constants obtained by Moore, Burk and Lankelma are evidence that their technique of flushing with nitrogen was effective in suppressing the effect of air in their experiments.

A puzzling observation, which at first seems difficult to reconcile with the idea that the polymerization of styrene in phenolic solvents is a radical type reaction, is that *m*-cresol, and presumably other phenols, inhibit the benzoyl peroxide catalyzed polymerization of styrene at 60 and 100° (Table IV). The answer, however, is apparently found in the rate of disappearance of benzoyl peroxide. In a number of inert solvents the half life of benzoyl peroxide is fifty-five to seventy-five hours at 60° and thirty-five to forty-five minutes at 100°.[28] In 3.68 molar styrene in cresol at 60°, however, the peroxide can no longer be detected after six hours, while at 100° it is approximately 95% consumed in ten minutes. Whether the cresol liberates the radicals of the peroxide so rapidly that they are consumed by mutual interaction, or destroys the peroxide by another mechanism, is not known; but in either case the catalyst is effectively prevented from promoting the polymerization.

Acknowledgment.—The author extends his thanks to Dr. Frank R. Mayo of this Laboratory for much helpful discussion and advice.

Summary

1. The rate of polymerization of styrene at 131° has been measured in a number of phenolic solvents.
2. The rate is affected by air and by benzoquinone and bears no simple relation to the acid strengths of the phenols as measured in water, and the polymer is of low molecular weight.
3. In thymol the rate is third order in respect to styrene and inversely proportional to the concentration of thymol. In *m*-cresol the rate lies between second and third order.
4. These results are interpreted on the basis that the polymerization is of the uncatalyzed, free radical type, somewhat inhibited by the phenolic solvent; and that this inhibition takes place through a chain transfer reaction yielding relatively unreactive solvent radicals. No evidence is found that the polymerization involves a carbonium ion.
5. Cresol has been found to destroy benzoyl peroxide. This observation has been used to explain the inhibition of the benzoyl peroxide catalyzed polymerization of styrene by this solvent.

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[28] Values obtained by extrapolation of the data of Kamenskaya and Medvedev, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940).

NOTES

Abnormalities in the Willgerodt Reaction

BY RICHARD T. ARNOLD, EVERETT SCHULTZ AND HAROLD KLUG

Very few irregularities have been observed during the course of the Willgerodt reaction. At an early date, Willgerodt[1] showed that with insufficient sulfur *p*-tolyl methyl ketone is converted into 2,5-di-*p*-tolylthiophene and more recently Fieser and Kilmer[2] reported the reduction of 3-acetoacenaphthene under the conditions employed in the Willgerodt synthesis.

In this Laboratory the Schwenk and Bloch[3] modification of the Willgerodt reaction has been used successfully with numerous ketones. When applied to 6-tetralyl ethyl ketone, however, there was obtained not only the normal acid, β-6-tetralylpropionic acid, but a certain amount (about 6%) of 5,6,7,8-tetrahydro-2-naphthoic acid; m. p. 150–152° (uncor.).[4]

The substance which undergoes oxidative degradation to give rise to this unexpected acid may or may not be an intermediate in the normal Willgerodt reaction.

Experimental

A mixture containing 46.9 g. of 6-tetralyl ethyl ketone, 8.0 g. of sulfur, and 24.0 g. of morpholine was heated at a temperature of 120–125° for eleven hours in a 200-cc. round-bottomed flask equipped with a condenser.

The hot mixture was poured onto 300 g. of ice and, after the melting was completed, the water layer was decanted. The semi-solid residue was washed with warm water to remove water soluble impurities, and the water was again separated. The remaining solid was just covered with ethanol and the whole was warmed for several minutes during which time the ethanol boiled gently. After removing the source of heat, the alcoholic solution was decanted from the crystalline precipitate and discarded. When recrystallized twice from ethanol, the solid yielded 25.2 g. of pure thiomorpholide; m. p. 133–135°.

Anal. Calcd. for $C_{17}H_{23}ONS$: C, 70.6; H, 8.0. Found: C, 71.0; H, 7.8.

Saponification of this thiomorpholide gave a quantitative yield of β-6-tetralylpropionic acid.

The mother liquor from the first recrystallization of the above thiomorpholide was evaporated to dryness, and the resulting dark oil was hydrolyzed with boiling 10% potassium hydroxide, cooled and filtered. This alkaline solution was treated with norite, filtered, ether extracted and

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[1] Willgerodt, *J. prakt. Chem.*, **80**, 192 (1909).

[2] Fieser and Kilmer, THIS JOURNAL, **62**, 1354 (1940).

[3] Schwenk and Bloch, *ibid.*, **64**, 305 (1942).

[4] Newman and Zahm, *ibid.*, **65**, 1097 (1943).