[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Polymerization. V. Molecular Termination in the Cationic Polymerization of Styrene Catalyzed by Stannic Chloride[1]

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The purpose of this work was to obtain quantitative information bearing on molecular termination phenomena in the cationic polymerization of styrene by a metal halide catalyst in organic solvents. Evidence is presented to demonstrate that molecular termination by the monomer itself is a significant factor in the determination of the degree of polymerization, and that certain aromatic "solvents" function as molecular terminating agents. The effects of the latter compounds on the degree of polymerization are correlated by means of the chain transfer equation originally developed for free radical polymerization.

The present status of the theory of the cationic polymerization of olefins to high molecular weight products has been thoroughly reviewed recently.[3] Although it generally is believed that chain transfer processes are important in the determination of the physical chain length in this type of polymerization, little direct quantitative evidence has appeared. The present work was undertaken in order to obtain such evidence concerning molecular termination[4] in a particular system, with primary interest in the question of chain transfer and the mechanism(s) by which it occurs.

The system chosen for study was the polymerization of styrene by the Friedel–Crafts type catalyst stannic chloride, in a carbon tetrachloride–nitrobenzene solvent mixture at 0°. The experimental approaches used here consisted of the determination of the effects on the degree of polymerization of (1) varying catalyst concentration, (2) varying initial monomer concentration, (3) certain added organic compounds and (4) for several representative aromatic compounds, variation of the concentration. In subsequent papers, the effects of aromatic molecular terminating agents on the over-all polymerization rate and the detailed mechanism of the molecular termination process, in particular the effect of the structure of the agent on its activity, will be elucidated.

Experimental

Materials.—Styrene and carbon tetrachloride were purified, and stannic chloride purified and charged into glass ampules, essentially by the methods described previously.[5] The purified styrene always was redistilled under reduced pressure shortly before use.

Nitrobenzene (Matheson) was dried over Drierite and fractionally distilled under reduced pressure, the first and last 20%-portions being discarded, $n^{25.0}\text{D}$ 1.5500.

p-Chlorocumene was prepared according to published directions[6] from chlorobenzene and isopropyl alcohol with boron trifluoride catalyst, and purified by two fractional distillations under reduced pressure through a 20-cm. glass helices-packed column, b.p. 72–73° (11 mm.), $n^{25.0}\text{D}$ 1.5082 (66–72°, 11 mm., $n^{20}\text{D}$ 1.5109).[6]

Isopentane was Phillips Petroleum Co. Pure Grade and was used without further purification.

Benzene (Baker Analyzed reagent) was freed of any traces of thiophene by the procedure recommended by Holmes and Beeman,[7] and fractionally distilled through a 37-cm. glass helices-packed column, a constant-boiling middle fraction being collected, $n^{24.5}\text{D}$ 1.4980 ($n^{24.5}\text{D}$ calcd. 1.4981).[8a]

C.P. Cyclohexane (Fisher) was washed with portions of cold concentrated sulfuric acid until the washings were colorless, washed once with acidified potassium permanganate, then with 5% aqueous sodium hydroxide and finally with water until neutral. The material was dried over phosphorus pentoxide, passed through a column of activated silica gel (28–200 mesh) to remove any benzene and fractionally distilled through a 50-cm. glass helices-packed column, a constant-boiling middle fraction being taken, $n^{25.5}\text{D}$ 1.4232 ($n^{25.5}\text{D}$ calcd. 1.4238).[8b]

Anisole (Eastman Kodak Co. white label) was washed three times with 10% (volume) aqueous sulfuric acid, three times with 10% aqueous sodium hydroxide, and then with water until neutral. After being dried over anhydrous magnesium sulfate, the anisole was fractionally distilled through a 25-cm. glass helices-packed column, $n^{26.7}\text{D}$ 1.5136.

p-Chloroanisole (Matheson) was purified as described above for anisole except that distillation was carried out under reduced pressure, b.p. 79° (11.5 mm.), $n^{25.5}\text{D}$ 1.5326.

Thiophene (Eastman white label) was refluxed for three hours over sodium, decanted, and refluxed for 1.5 hours over fresh sodium. It was decanted once more and fractionally distilled through a 25-cm. glass helices-packed column, $n^{23.7}\text{D}$ 1.5267.

p-Xylene (Matheson) was dried over Drierite and fractionally distilled through a 25-cm. glass helices-packed column, $n^{24.6}\text{D}$ 1.4932, ($n^{24.6}\text{D}$ calcd. 1.4934).[8a]

The Polymerization Method was essentially that described previously,[5] except for somewhat different drying procedures. A dry-box[9] was employed to provide a relatively dry and reproducible atmosphere for the charging of the polymerization bottles and the preparation of the catalyst solutions. It was found necessary, in order to obtain reproducible results,[10] to treat the solvents, monomer and added compounds with a drying agent and to use them directly in the polymerizations. Anhydrous silica gel

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[1] This is the fifth in a series of papers concerned with ionic polymerization. For the fourth paper, see C. G. Overberger and David Tanner, THIS JOURNAL, **77**, 369 (1955). A preliminary report of part of this work was given by C. G. Overberger and G. F. Endres, *ibid.*, **75**, 6349 (1953), and it was presented in part at the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

[2] From the dissertation submitted by Gerard F. Endres to the Graduate School of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] D. C. Pepper, *Quart. Revs.*, **8**, 88 (1954).

[4] Use will be made frequently in this paper of the general term "molecular termination," or formation of an inactive polymer molecular from an active growing chain, intended to include both the case where the active center is deactivated in the process (kinetic termination) and the case where it survives to initiate a new polymer chain immediately (chain transfer).

[5] C. G. Overberger, L. H. Arond and J. J. Taylor, THIS JOURNAL, **73**, 5541 (1951).

[6] G. F. Hennion and V. R. Pieronek, *ibid.*, **64**, 2751 (1942).

[7] H. N. Holmes and N. Beeman, *Ind. Eng. Chem.*, **26**, 172 (1934).

[8] (a) G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946; (b) Vol. II, 1940, p. 78.

[9] C. G. Overberger, R. J. Ehrig and David Tanner, THIS JOURNAL, **76**, 772 (1954).

[10] Using the procedure outlined, data from thirty polymerizations at initial styrene concentration 1.95 *M* and stannic chloride concentration 0.023 *M* gave a mean number average degree of polymerization ($\bar{P}_n$) of 193, with an average deviation of ±7 (4%). These polymers were prepared with several different samples of monomer, catalyst and solvents in sixteen series of experiments. The reproducibility within a given series was generally better.

(Davison Chemical Corp.) was used for this purpose, because of its insolubility, its great effectiveness as a drying agent, and the fact that it causes neither appreciable polymerization of the monomer nor changes in the refractive indices of the solvents and other materials. A coarse grade (6–16 mesh) was used, so that suspended drying agent would not be present in the polymerization solutions. Carbon tetrachloride and nitrobenzene were stored over this material, the monomer was treated with it preferably for about two hours with frequent agitation immediately before use, and the added compounds were treated with it at least overnight before use.

The polymer was isolated by precipitation in methanol and purified, usually by a single reprecipitation in methanol, from methyl ethyl ketone solution. Conversions were estimated from the weights of polymer isolated.

Molecular Weight Determinations.—Intrinsic viscosities were determined at 30° in benzene solution. Modified Ostwald-type viscometers with 104–109 second flow times for the solvent were used and kinetic energy corrections were not applied.

Number average molecular weights and degrees of polymerization were calculated from the intrinsic viscosities, using the relation for unfractionated polystyrene determined by Pepper[11]

$$[\eta] = 4.37 \times 10^{-4}\bar{M}_n\ 0.66 \qquad (1)$$

which is thought to be valid over the molecular weight range 1,000–2,000,000. It can be shown that for approximately the same value of α, different values of K in the Mark–Houwink relation will yield different actual values of the molecular termination constant k_r/k_p in our work, but the relative values of k_r will remain unaffected.

Results

Variation of the Catalyst Concentration.—In Table I are listed the intrinsic viscosities of polystyrenes prepared over an approximately threefold range of stannic chloride concentrations. It is evident that the degree of polymerization is essentially independent of the catalyst concentration over this range.

TABLE I

EFFECT OF CATALYST CONCENTRATION ON DEGREE OF POLYMERIZATION[a]

$SnCl_4$, mole/l.	Conversion, %	$[\eta]$, 100 cc./g.
0.0234	46.0	0.310
.0183	54.1	.31[b]
.0129	41.5	.30[b]
.0070	38.9	.30[b]

[a] Initial styrene concentration 1.95 *M;* solvent, carbon tetrachloride–nitrobenzene (nitrobenzene 40% vol. of total charge); $t = 0°$. [b] Determined by Mr. W. F. Hale.

Variation of the Initial Monomer Concentration.—Degrees of polymerization were determined in the region of 50% conversion over a sixfold range of initial styrene concentrations and the data are given in Table II. Correlation of the apparent degree of polymerization at high conversion with the initial monomer concentration is justified by the fact that the intrinsic viscosity is independent of the conversion, at least at initial styrene concentration 1.95 *M*.[12]

TABLE II

DEPENDENCE OF DEGREE OF POLYMERIZATION ON INITIAL MONOMER CONCENTRATION[a]

$(M)_0$, moles/l.	Convn., %	$[\eta]$, 100 cc./g.	$\bar{P}_n$	$1/\bar{P}_n \times 10^3$
0.488	42.4	0.165	76.9	13.0
0.976	62.0	.238	134	7.45
1.47	51.5	.281	173	5.78
1.95	46.0	.310	200	4.99
2.93	56.7	.343	233	4.28

[a] Stannic chloride concentration 0.023 *M;* solvent, carbon tetrachloride–nitrobenzene (nitrobenzene 40% vol. of total charge); $t = 0°$.

Effects of Added Organic Compounds.—A series of exploratory experiments was performed in order to obtain information concerning the types of organic compounds which might function as chain transfer agents in the styrene–stannic chloride system. The compounds examined were of types which might be expected to interact in this manner with carbonium ions, *i.e.*, compounds containing tertiary hydrogen atoms or aromatic nuclei. Two compounds containing tertiary hydrogen atoms, isopentane and *p*-chlorocumene, had no detectable effect on the degree of polymerization. However, all of the several mono- and dialkyl substituted aromatic hydrocarbons tried distinctly reduced the degree of polymerization at low concentrations, and two other aromatic-type compounds, thiophene and anisole, reduced it drastically. It was evident, therefore, that certain aromatic compounds can function as molecular terminating agents in this system. Plesch[13] has proposed that toluene is a chain transfer agent when used as solvent in the polymerization of styrene by titanium tetrachloride, since infrared analysis suggested the presence of *p*-disubstitution in the resultant polymers.

In order to determine the form of the dependence of the degree of polymerization on the concentration of molecular terminator, precise molecular weight data were obtained for several representative aromatic compounds, anisole, *p*-chloroanisole, thiophene, *p*-xylene and benzene, and these are summarized in Table III. In these experiments the catalyst and initial monomer concentrations were held constant. Since it was known that the degree of polymerization in this system depends to some extent on the dielectric constant of the medium,[14] the volume per cent. of nitrobenzene also was maintained constant. Styrene, carbon tetrachloride, and the aromatic hydrocarbons all have practically identical dielectric constants (*ca.* 2). The dielectric constant of anisole is slightly higher, but the concentrations of anisole (and thiophene) used were very small. In the case of *p*-chloroanisole, this procedure probably resulted in a moderate increase of dielectric constant with concentration.

Usually, the initial molar ratios of added compound to monomer were chosen so as to have about a sixfold variation, and so that the degree of polymerization was reduced to one-half to one-third of the control value at the highest molar ratio. Benzene is seen to have only a very small effect on the degree of polymerization at the relatively high concentrations used, and this effect is within the experimental error.

Discussion

The lack of dependence of the degree of polymerization on the catalyst concentration has been observed previously in the polymerization of styrene

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[11] D. C. Pepper, *Proc. Roy. Dublin Soc.*, (N. S.), **25**, 239 (1951); *J. Polymer Sci.*, **7**, 347 (1951).

[12] Unpublished observation by the authors.

[13] P. H. Plesch, *J. Chem. Soc.*, 1659, 1662 (1953).

[14] J. George and H. Wechsler, *J. Polymer Sci.*, **6**, 725 (1951).

TABLE III

EFFECTS OF ADDED AROMATIC COMPOUNDS ON DEGREE OF POLYMERIZATION

Initial styrene concentration 1.95 *M;* stannic chloride concn. 0.023 *M;* solvent, carbon tetrachloride–nitrobenzene (nitrobenzene 40% vol. of total charge); $t = 0°$.

$(R)_0/(M)_0$, molar ratio × 10³	Conv., %	$[\eta]$, 100 cc./g.	$\bar{P}_n$	k_r/k_p
		R = Anisole		
0	15, 14	0.297, 0.299	187, 190[b]	..
0.738	12	.261	154	1.60
1.54	11	.230	128	1.65
2.29	11	.210	111	1.61
2.83	9	.194[a]	98.6	1.71
2.83	16	.201	104	1.52
3.64	9	.183	90.0	1.60
4.38	10	.170	80.3	1.63
		R = Thiophene		
0	17	0.304	194	..
0.176	67	.293	184	1.58
0.599	83	.281	173	1.08
1.07	83	.264	157	1.15
1.47	92	.254	148	1.09
0	11, 9	0.309, 0.303	199, 193[b]	..
0.490	13	.277	169	1.67
0.978	14	.267	160	1.17
1.97	15	.246	141	1.01
4.89	13	.198	102	0.97
0	6, 7	0.316, 0.313	207, 203[b]	..
12.0	2	.141	60.8	0.96
		R = *p*-Xylene		
R)₀/(M)₀, molar ratio				
0	13, 18	0.311, 0.309	201, 200[b]	..
0.138	19	.264	157	0.0099
.281	14	.227	125	.0107
.417	10	.205[a]	107	.0105
.417	19	.207	108	.0101
.549	12	.186	92.7	.0106
.689	13	.171	81.0	.0107
.829	12	.162	74.8	.0101
		R = *p*-Chloroanisole		
				k_r/k_p × 10³
0	12, 11	0.302, 0.295	193, 186[b]	..
0.106	11	.267	160	9.09
.215	11	.244	140	8.77
.325	21	.230	127	7.95
.431	15	.213	114	8.13
.539	20	.201	104	8.09
.662	17	.190	95.5	7.84
		R = Benzene		
0	17, 12	0.309, 0.301	200, 191[b]	
1.03	14	.301	192	
1.25	14	.300	191	
1.48	15	.295	186	
1.73	16	.299	190	
1.95	31	.299	189	
2.20[c]	32	.305	195	
0	13, 13	0.305, 0.304	196, 195[b]	
2.20[c]	26	.303	193	
2.20[c]	19	.297	188	

[a] Estimated from a value of the reduced viscosity at a single concentration (*ca.* 1 g./100 cc.). [b] The mean of the two controls was taken as $\bar{P}_{n_0}$ in equation 6. [c] No carbon-tetrachloride solvent was present in this solution.

by stannic chloride in other solvents,[15–17] and in fact seems to be quite general for cationic polymerization.[18] This is an indication that mutual termination by active centers (carbonium ions, or more likely carbonium ion-anion pairs) does not ordinarily occur in cationic polymerization, a conclusion which is supported by other evidence.[18] This is in marked contrast to free radical polymerization, where it is well established that mutual termination occurs, resulting commonly in an inverse square root dependence of the degree of polymerization on the catalyst concentration.

The dependence of the degree of polymerization on the initial monomer concentration in the polymerization of styrene by stannic chloride also has been studied previously by Williams[15] in carbon tetrachloride solvent at 25°, by Gantmakher and Medvedev[16] in ethyl chloride at 20° and by Pepper[17] in ethylene dichloride at 25°. There is some apparent uncertainty as to the exact form of the dependence. Williams reported an approximation to a relation of the form $\bar{P}_n = \text{const.} \times (M)_0^{0.5}$, while the other workers reported that the relation was approximately $\bar{P}_n = \text{const.} \times (M)_0$. It should be noted that Gantmakher and Medvedev actually observed that the intrinsic viscosity was proportional to the square root of the initial monomer concentration and apparently arbitrarily assumed the value of 0.5 for the exponent in the Mark–Houwink relation ($[\eta] = K\overline{M}_n^{\alpha}$, where $\overline{M}_n$ is the number average molecular weight), in order that the calculated molecular weights be proportional to the monomer concentration.

All of the available data, including those of the present work, clearly show that the degree of polymerization in styrene–stannic chloride systems is not accurately described by the relation $\bar{P}_n = \text{const.} \times (M)_0$. However, if the data in Table II are plotted as the reciprocal of the degree of polymerization *vs.* the reciprocal of the initial monomer concentration (Fig. 1), a much more nearly linear relationship is observed. In fact, this is true of all of the previously reported data as well (Figs. 1 and 2). (The data of Williams and Gantmakher and Medvedev have been recalculated from their viscosities using equation 1.[19]) This is accounted for readily: suppose that two molecular terminations are operative, one "spontaneous" (unimolecular) and the other involving the monomer. The number average degree of polymerization, which is the ratio of the rate of chain propagation to the total rate of molecular termination (kinetic termination plus chain transfer) is given by

$$\bar{P}_n = \frac{k_p(M_x^{\ddagger})(M)}{k_t(M_x^{\ddagger}) + k_m(M_x^{\ddagger})(M)} = \frac{k_p(M)}{k_t + k_m(M)} \quad (2)$$

where k_p, k_t and k_m are the rate constants for prop-

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(15) G. Williams, *J. Chem. Soc.*, 775 (1940).

(16) A. R. Gantmakher and S. Medvedev, *Zhur. Fiz. Khim.*, **23**, 516 (1949); *C. A.*, **43**, 7295 (1949).

(17) D. C. Pepper, *Trans. Faraday Soc.*, **45**, 404 (1949).

(18) Reference 3, p. 109.

(19) These authors measured viscosities in carbon tetrachloride solution, while equation 1 applies specifically to benzene solutions. However, the intrinsic viscosities of polystyrenes do not differ greatly in the two solvents. The present authors found that samples having intrinsic viscosities 0.323 and 0.171 in benzene gave the values 0.310 and 0.170 in carbon tetrachloride.

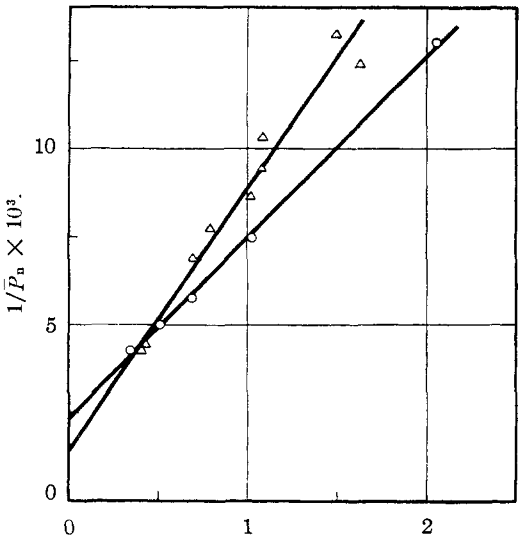

Fig. 1.—Plots of reciprocal degree of polymerization *vs.* reciprocal of initial monomer concentration: ○, present authors, carbon tetrachloride–nitrobenzene solvent, 0°; △, Gantmakher and Medvedev, ethyl chloride solvent, 20°.

agation, spontaneous termination and molecular termination by the monomer, respectively, (M_x^+) represents the concentration of growing active centers, and (M) is the monomer concentration. Upon taking reciprocals

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p} \times \frac{1}{(M)} + \frac{k_m}{k_p} \tag{3}$$

it is seen that a plot of $1/\bar{P}_n$ *vs.* 1/(M) should be linear, with slope k_t/k_p and intercept k_m/k_p.

Pepper as well as Gantmakher and Medvedev postulated only spontaneous unimolecular termination to account for their respective kinetic results and Price[20] has done the same for Williams' results. This can be reconciled with the observed dependence of the degree of polymerization on the monomer concentration simply if it be assumed that the monomer is a chain transfer agent. From Fig. 1 the values $k_t/k_p = 5.1 \times 10^{-3}$ mole/l. and $k_m/k_p = 2.4 \times 10^{-3}$ are obtained from the authors' data. Those of Gantmakher and Medvedev give similar values, while the values obtained from the other data (Fig. 2) are considerably higher. Among the factors possibly contributing toward the differences between the various sets of values are varying temperature and dielectric constant of the solvent and different degrees of dryness. The dominance of chain transfer with the monomer in certain other cationic polymerization systems, such as the polymerization of vinyl octyl ether by silver perchlorate or by iodine,[21] has been inferred from an observed lack of dependence of the degree of polymerization on the initial monomer concentration.

Equation 2 is readily modified to include molecular termination by an added compound

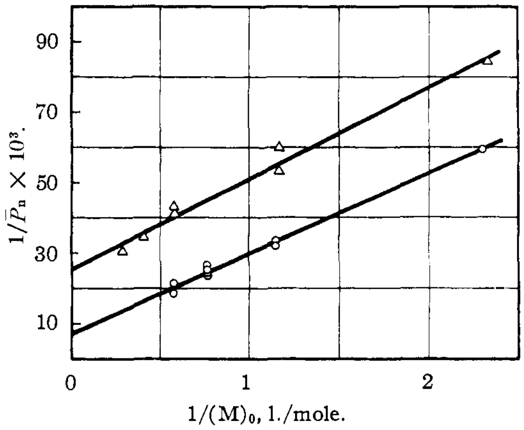

Fig. 2.—Plots of reciprocal degree of polymerization *vs.* reciprocal of initial monomer concentration: ○, Pepper, ethylene dichloride solvent, 25°; △, Williams, carbon tetrachloride solvent, 25°.

$$\bar{P}_n = \frac{k_p(M_x^+)(M)}{k_t(M_x^+) + k_m(M_x^+)(M) + k_r(M_x^+)(R)} \tag{4}$$

where (R) is the concentration of molecular terminator and k_r is the rate constant for its interaction with active centers. Upon cancelling (M_x^+) and taking reciprocals as before there results

$$\frac{1}{\bar{P}_n} = \frac{k_t}{k_p} \times \frac{1}{(M)} + \frac{k_m}{k_p} + \frac{k_r}{k_p} \times \frac{(R)}{(M)} \tag{5}$$

or, substituting from equation 3

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_{n_0}} + \frac{k_r}{k_p} \times \frac{(R)}{(M)} \tag{6}$$

where $\bar{P}_{n_0}$ is the degree of polymerization in the absence of added molecular terminator, all other conditions being the same. It is evident that the final form of the equation is independent of the kinetic form or mechanisms of the molecular termination reactions which take place in the absence of added terminator, provided that the presence of the latter does not interfere with their operation. Equation 6 is identical with the familiar chain transfer equation developed for free radical polymerization,[22,23] and k_r/k_p (which will be referred to in general as the "molecular termination constant") is analogous to the chain transfer constant *C*.

Using equation 6, values of the molecular termination constant were calculated for each of the active compounds in Table III, and it is seen from the table that k_r/k_p is indeed independent of $(R)_0/(M)_0$ over the measured range, as required. Plots of $1/\bar{P}_n - 1/\bar{P}_{n_0}$ *vs.* $(R)_0/(M)_0$ for two compounds are shown in Fig. 3. For all of the active compounds in Table III such plots are linear and pass through the origin. It is concluded that equation 6 quantitatively describes the phenomenon of molecular termination by added compounds in the cationic polymerization system studied. The slopes of these plots are taken as the best values of the molecular termination constants, and these are listed in Table IV.

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[20] C. C. Price, "Mechanisms of Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 113.

[21] D. D. Eley and A. W. Richards, *Trans. Faraday Soc.*, **45**, 425 (1949).

[22] F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943).

[23] For a general derivation of the chain transfer equation which illustrates its independence of mechanism, see T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952, p. 213.

TABLE IV

MOLECULAR TERMINATION CONSTANTS OF REPRESENTATIVE AROMATIC COMPOUNDS

Compound	k_r/k_p[a]
Anisole	1.62 ± 0.02
Thiophene	$0.98 \pm .07$
p-Xylene	$(1.05 \pm .01) \times 10^{-2}$
p-Chloroanisole	$(8.2 \pm .2) \times 10^{-3}$

[a] The precision is taken as the indeterminate error of the mean of the values of k_r/k_p calculated for each concentration (Table III), A.D. = $\pm \Sigma(d)/n \sqrt{n}$, where n is the number of values.

The method used to maintain the dielectric constant of the medium in this work resulted in a corresponding decrease of the concentration of carbon tetrachloride as the concentration of added compound or monomer was increased. If carbon tetrachloride itself were a fairly active molecular terminator, this would complicate the effects on degree of polymerization and the observed molecular termination constants might have to be corrected.[24] However, analysis for chlorine[25] of polymers prepared at high ratios of carbon tetrachloride to styrene and comparison of the degree of polymerization obtained in carbon tetrachloride with that obtained in the presumably inert solvent cyclohexane have demonstrated that the molecular termination constant of carbon tetrachloride cannot be greater than 2×10^{-4}.[26] The corresponding correction would be of the order of magnitude of the experimental error of the lowest constants.

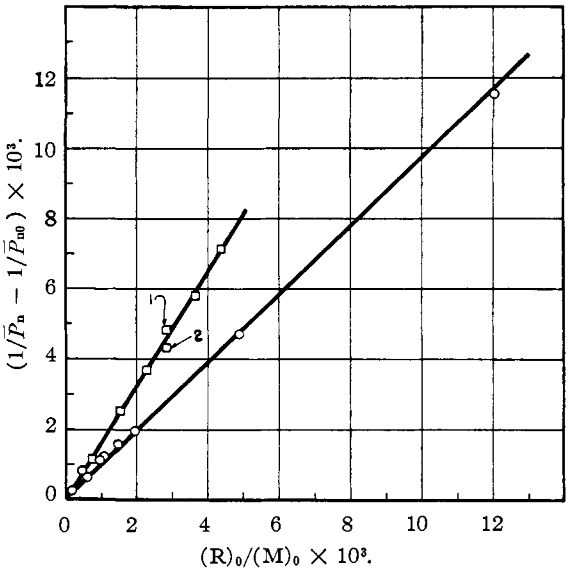

Fig. 3.—Plots according to equation 6: □, anisole, (1) 9% conversion, (2) 16% conversion; ○, thiophene.

Acknowledgment.—The authors gratefully acknowledge the support of this work by the Office of Naval Research, Contract No. Nonr 343(00), Project NR356-262.

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[24] It can be shown readily that in this case equation 6 would have to be modified to:

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_{n0}} + \frac{(R)}{(M)}\left[\frac{k_r}{k_p} - \frac{V_r}{V_s} \times \frac{k_s}{k_p}\right]$$

where k_s/k_p is the molecular termination constant of carbon tetrachloride and V_r and V_s are the molar volumes of the respective substances.

[25] Analyses by Clark Microanalytical Laboratories, Urbana, Ill.

[26] Detailed data may be obtained upon request from the senior author.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

1,3-Shifts. III. The Kinetics of the Thermal Rearrangement of Phenyl Benzanilimino Ethers[1]

BY KENNETH B. WIBERG AND BERTRAM I. ROWLAND

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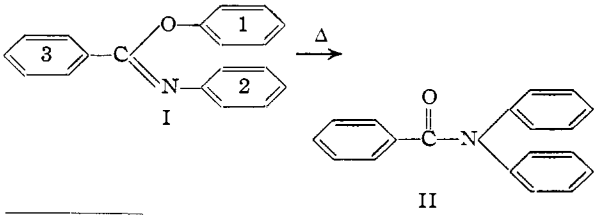
The rate of thermal rearrangement of a number of substituted phenyl benzanilimino ethers was determined in diphenyl ether solution. The rates of reaction for the *para* substituted compounds were found to parallel the rates of a nucleophilic displacement by piperidine on *p*-substituted *o*-nitrochlorobenzenes. It was found that the *ortho* substituted compounds in general gave a higher rate of reaction than the corresponding *para* substituted compounds, and this was shown to be largely an entropy effect by determining the entropy and enthalpy of activation for several compounds. The rearrangement of a mixture of phenyl benzanilimino ether and *p*-chlorophenyl benz-*p*-chloroanilimino ether was found to give no mixed products, indicating the reaction to be intramolecular.

Introduction

The number of rearrangements which appear to involve a cyclic four-membered transition state is very small in comparison to the number of intramolecular 1,2-shifts. In continuing a study of 1,3-shifts, we have chosen to investigate a reaction which is probably of this type, the thermal rearrangement of phenyl benzanilimino ether (I) to N-phenylbenzanilide (II). This reaction was investigated by Chapman[2] who measured the rate of reaction by the comparison of the melting



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[1] Taken from part of a thesis submitted by Bertram I. Rowland to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1954.

[2] A. W. Chapman, *J. Chem. Soc.*, 1992 (1925); 2296 (1926); 1749 (1927).