ene.[64,65] The colorless precipitate was filtered and washed repeatedly with dry ether under exclusion of moisture. It was then dissolved in 500 ml. of anhydrous ethanol. This solution was treated with a solution of 82 g. (0.35 mole) of anhydrous silver perchlorate in 120 ml. of absolute ethanol. The mixture was filtered. Most of the **N-cyclohexylidenepiperidinium perchlorate** was found with the silver bromide, from which it could be extracted with hot anhydrous acetone. Upon addition of ether to the acetone solution, 39.5 g. of colorless plates was obtained, m.p. 246–249°. Upon cooling of the ethanol solution (above) and addition of ether 2.8 g. additional iminium perchlorate was obtained; total yield 53%, $\nu_{\max}^{\text{Nujol}}$ 1660 cm.$^{-1}$.

A solution of 5.0 g. (0.019 mole) of N-cyclohexylidenepiperidinium perchlorate in 300 ml. of anhydrous methanol was treated at 0° with a solution of diazomethane, prepared from 5.0 g. (0.049 mole) of nitrosomethylurea, in 70 ml. of anhydrous ether. The yellow color of the diazomethane disappeared and gas was evolved. The addition was complete in 5 min., and the solution was allowed to stand in the refrigerator for 4 hr. After concentration to half-volume *in vacuo* at 0° the solution was cooled to −40°. **The 1,1-pentamethylene-2,2-pentamethyleneaziridinium perchlorate** separated as colorless needles and was recrystallized from absolute ethanol, m.p. 236–238° dec., yield 3.8 g. (73%), no infrared maxima corresponding to $-\overset{|}{\underset{|}{\mathrm{N}}}{}^{+}\!-\mathrm{H}$ or $>\mathrm{C}{=}\overset{+}{\mathrm{N}}<$; n.m.r. τ-values ($CDCl_3$): 6.60, 6.68; 7.03 (singlet); 8.00, 8.20.

Anal. Calcd. for $C_{10}H_{22}ClNO_4$: C, 51.51; H, 7.93; N, 5.01. Found: C, 51.24; H, 7.78; N, 5.10.

1-N-Pyrrolidylcyclohexanemethanol.—Formaldehyde condensation with nitrocyclohexane[66] to give 1-nitrocyclohexanemethanol was followed by reduction to 1-aminocyclohexanemethanol according to Noland, Kneller and Rice[67]; b.p. 82–83° (1.3-1.4 mm.), $n^{25}\text{D}$ 1.4951 (reported b.p. 84° (1 mm.), $n^{25}\text{D}$ 1.4959). A mixture of 5.7 g. (0.044 mole) of 1-aminocyclohexanemethanol, 13.8 g. (0.065 mole) of 1,4-dibromobutane and 4.9 g. (0.044 mole) of sodium carbonate in 20 ml. of absolute ethanol was heated under reflux for 84 hr. following the general directions for ring formation.[68,69] After the addition of 50 ml. of water the aqueous ethanolic solution was extracted with ether. The ether extract was washed with dilute aqueous hydrochloric acid. The aqueous layer was strongly basified with sodium hydroxide and extracted with ether. After drying and removal of the ether a pale yellow sludge was obtained. In an attempt to distil it, 1.0 g. of starting material was recovered and the rest solidified. Purification by sublimation at 100° bath temperature and 0.2 mm. yielded 5.3 g. (79% based on unrecovered starting material) of colorless prisms, m.p. 71–72°, $\nu_{\max}^{\text{Nujol}}$ 3400 cm.$^{-1}$ (O–H).

Anal. Calcd. for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.85; H, 11.54; N, 7.35.

The perchlorate of 1-N-pyrrolidylcyclohexanemethanol crystallized as colorless prisms from absolute ethanol; m.p. 92–93°; $\nu_{\max}^{\text{Nujol}}$ 3505 (O–H), 3125 cm.$^{-1}$ ($-\overset{|}{\underset{|}{\mathrm{N}}}{}^{+}\!-\mathrm{H}$).

Anal. Calcd. for $C_{11}H_{22}ClNO_5$: C, 46.56; H, 7.82; N, 4.94. Found: C, 46.72; H, 7.88; N, 4.94.

N.m.r. Model. 1,1-Dimethylpyrrolidinium Perchlorate (XVIII).—A solution of 12.5 g. (0.055 mole) of 1,1-dimethylpyrrolidinium iodide (Aldrich Chemical Co.) in 100 ml. of anhydrous ether was treated with a solution of 12.5 g. (0.060 mole) of anhydrous silver perchlorate in 20 ml. of anhydrous ethanol. Silver iodide was recovered by filtration of the hot solution, ether was added to the filtrate and the precipitate was recrystallized from ethanol as feathery plates, m.p. above 330°, yield 9.5 g. (86%); n.m.r. τ-values (liquid SO_2) at: 6.32, 6.48, 6.65; 6.85 (singlet); 7.70 (broad).

Anal. Calcd. for $C_6H_{14}ClNO_4$: C, 36.10; H, 7.07; N, 7.02. Found: C, 35.98; H, 6.95; N, 7.00.

---

(65) C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936).

(66) We are grateful to Dr. W. F. Jackson of the Explosives Department, E. I. du Pont de Nemours and Co., Inc., for a generous gift of nitrocyclohexane.

(67) W. E. Noland, J. K. Kneller and D. E. Rice, *J. Org. Chem.*, **22**, 695 (1957).

(68) R. C. Elderfield and H. A. Hageman, *ibid.*, **14**, 605 (1949).

(69) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Cationic Catalyzed Polymerization of Styrene at High Conversion[1]

BY G. F. ENDRES, V. G. KAMATH[2] AND C. G. OVERBERGER

RECEIVED APRIL 5, 1962

The cationic polymerization of styrene with stannic chloride catalyst has been studied over the conversion range 9.5-97%, in carbon tetrachloride–nitrobenzene solvent mixture at 0°. The cumulative number average molecular weight appears to decrease with increasing conversion, in accord with the behavior shown on varying the initial monomer concentration at low conversion. However, the weight average molecular weight increases markedly, probably due mainly to chain transfer to the polymer. Owing to the attendant increase of branching in the polymers, their intrinsic viscosities show little dependence on the conversion. The limitations of intrinsic viscosity as a measure of molecular weight at high conversion are discussed, and procedures for obtaining reliable data under such conditions are recommended.

Introduction

In the course of an earlier investigation of molecular termination in the cationic polymerization of styrene with stannic chloride catalyst,[3] it was observed that the intrinsic viscosities of the isolated polymers showed little dependence on the conversion. It was also found that the intrinsic viscosity at a given conversion was quite markedly dependent on the initial monomer concentration. If molecular weights were calculated from these intrinsic viscosities using relationships based on polymers with presumably "most probable" molecular weight distributions, contradictory conclusions could be drawn concerning the dependence of polymer molecular weight on monomer concentration. A possible explanation of this was that it is due to a broadening of the molecular weight distribution with increasing conversion, limiting the validity of these viscosity–molecular weight relationships to low conversions. Such broadening could conceivably be due to at least two causes in the system investigated. The occurrence of "spontaneous" (unimolecular) termination or chain transfer would

---

[1] This is the 20th in a series of papers concerned with ionic polymerization; for the previous paper in this series, see C. G. Overberger and A. Schiller, *J. Polymer Sci.*, in press (1962).

[2] This paper comprises a portion of the Dissertation submitted by V. G. Kamath in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

[3] G. F. Endres and C. G. Overberger, *J. Am. Chem. Soc.*, **77**, 2201 (1955).

lead to a decrease of the instantaneous average degree of polymerization with increasing conversion, resulting in a continuous shift of the maximum in the distribution function (see for example Litt, ref. 4). Further, Atkins and Billmeyer[5] demonstrated that polystyrenes produced at high conversion in the authors' system have a considerable fraction of long chain branches, through comparison of their intrinsic viscosities with those of linear polystyrenes of the same weight average molecular weights.

In several other investigations of the cationic polymerization of styrene with various catalysts, molecular weights have been calculated from intrinsic viscosities at high conversions, and inferences concerning the mechanism have been drawn. The present work was undertaken in the hope of clarifying this situation, and experimentally testing the reliability of such an approach. Styrene has been polymerized to various conversions with stannic chloride catalyst in carbon tetrachloride–nitrobenzene solvent mixture at 0°. The dependence on conversion of the following properties has been determined: (1) intrinsic viscosity in benzene and in butanone solution, (2) number average molecular weight by osmotic and cryoscopic methods, and (3) weight average molecular weight by light-scattering. The data have been compared with theoretical relationships derived from behavior at low conversions.

Experimental

The monomer and solvents were purified, and stannic chloride purified and charged into glass ampoules, essentially by the methods described previously.[6] Polymerizations were carried out using dry-box techniques as described,[3,6] except that monomer and solvents were dried prior to use over molecular sieves (Type 4A) rather than anhydrous silica gel. The polymers were usually isolated by precipitation in methanol, reprecipitated once in methanol from butanone solution, and dried under vacuum. Conversions were estimated from the weights of polymer isolated.

Solution viscosities were measured in benzene and butanone at 30°, using Ubbelohde dilution viscometers. Reduced viscosities were determined at six concentrations from 2.0 to 0.3 g./dl., and intrinsic viscosities estimated by the usual extrapolation to zero concentration.

Osmotic pressure measurements were carried out using a Stabin high speed osmometer[7] at 30°. The half-sum method of Fuoss and Mead[8] was employed, observing the rate of change of the ascending and descending levels. Measurements were made at four concentrations from 0.1 to 1.0 g./dl., and linear extrapolations of π/C to zero concentration were made. The solvent in the outside jacket was evaporated after each measurement to determine the extent of diffusion of polymer through the membrane. As usual with polymers of low molecular weight, considerable difficulty with diffusion and irreproducibility was experienced, and the choice of membrane and solvent was found to be very critical. Very erratic values were obtained when gel cellophane membranes "300," "450" or even "600" were used in benzene, toluene or dioxane solvents, and leakage of 12% of the polymer through the latter two membranes was detected. However, with "Ultracella Allerfeinst" membranes[9] (Carl Schleicher and Schuell Co., "UA-Superdense") in butanone no diffusion was detected and reproducible results were obtained. The values reported in Table I were obtained under these conditions.

Light scattering measurements were carried out in a Brice–Phoenix instrument, with butanone again as solvent. Measurements were made for four polymer concentrations and the pure solvent, at twelve angles from 25° to 140°. The data were treated by the method of Zimm,[10] plotting $Kc/R_{(\theta)}$ *vs.* $Ac + \sin 2\theta/2$, with double extrapolation to zero concentration and zero angle. The best Zimm plots were obtained at the higher polymer concentrations.

For the determination of the low molecular weight fraction lost in methanol during the isolation of the polymer, a large batch was polymerized to about 80% conversion and polymerization stopped as in previous cases by pouring into methanol. The precipitated polymer was filtered off and the filtrate was distilled under vacuum to remove the methanol. The residue was then steam distilled to remove the solvent as well as unreacted monomer, redissolved in pure cyclohexane and again steam distilled. This process of solution in cyclohexane and steam distillation was repeated several times to ascertain that all the solvent and monomer had been removed. The final residue was dried in a vacuum desiccator, yielding a recovery of 2.8%. The molecular weight of this fraction was determined cryoscopically in a Beckmann apparatus using pure cyclohexane as solvent. The apparatus was calibrated using biphenyl, benzoic acid (dimerizes in this solvent) and cholesterol as solutes in cyclohexane solvent. Freezing point depressions were determined at four different concentrations and the molecular weight calculated from these values. The average molecular weight $\bar{M}_n$ of this fraction was found to be 390.

Results and Discussion

In Table I are listed the results obtained for a series of polystyrenes prepared at conversions ranging from 9.5 to 97%. All other conditions of polymerization were identical: initial monomer concentration 1.95 M, stannic chloride concentration 0.023 M, temp. 0°, carbon tetrachloride–nitrobenzene solvent mixture, with nitrobenzene 40% (vol.) of the total charge. Figures 1, 2 and 3 include plots of conversion *vs.* intrinsic viscosity, cumulative number average molecular weight ($\bar{\bar{M}}_n$) and cumulative weight average molecular weight ($\bar{\bar{M}}_w$), respectively.

Table I

Intrinsic Viscosity and Experimental Molecular Weight of Polystyrene at Various Conversions

Conversion, %	[η], dl./g. Butanone	[η], dl./g. Benzene	$\bar{\bar{M}}_n$ (osmotic)	$\bar{\bar{M}}_w$ (Light scattering)
9.5	0.179	0.279	30,000	60,000
25.2	.193	.300	38,000	65,000
29.8	.194	.310	38,900	67,000
34.6	.199	.315	38,000	89,000
35.9	.195	.317	38,600	89,000
59.9	.197	.320	43,500	90,000
64.9	..198	.303	46,300	80,000
93.1	.198	.313	53,000	106,000
97	...	.329	....	103,000

As usual for polystyrene, considerably different values of intrinsic viscosity are obtained in butanone and benzene (the latter is the "better" solvent). In both solvents there appears to be an initial rise in intrinsic viscosity with increasing conversion, leveling off above about 30% to a constant value, although the scatter in benzene could mask a small dependence. These results are in accord with previous findings. On the other hand, the number

---

(4) M. Litt, *J. Polymer Sci.*, **43**, 567 (1960).

(5) J. T. Atkins and F. W. Billmeyer, Jr., *J. Phys. Chem.*, **63**, 1966 (1959).

(6) C. G. Overberger, L. H. Arond and J. J. Taylor, *J. Am. Chem. Soc.*, **73**, 5541 (1951).

(7) J. V. Stabin and E. H. Immergut, *J. Polymer Sci.*, **14**, 209 (1954).

(8) R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).

(9) M. F. Vaughan, *J. Polymer Sci.*, **33**, 417 (1958).

(10) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

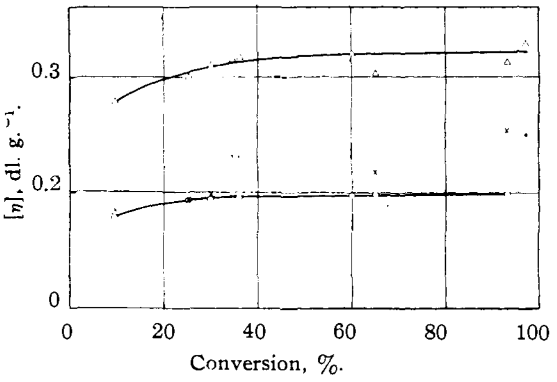


Fig. 1.—Intrinsic viscosity *vs.* conversion: ⊙, butanone solvent; △, benzene solvent; X, calculated from experimental M_w, using eq. 9.

average molecular weights from osmotic pressure measurements (Fig. 2) show a fairly steep rise with conversion, as do the weight average molecular weights obtained from light scattering (Fig. 3). The experimental scatter in the latter measurements is again rather large, but the upward trend seems clear.

The reported results for the dependence of polymer intrinsic viscosity on initial monomer concentration in this system[3] were based on polymers prepared at intermediate conversions (42–62%). Since the viscosities showed little dependence on the conversion (at least at initial monomer concentration 1.95 *M*), they were assumed to be representative of the low-conversion polymers as well, and the following relationship was derived from the data

$$1/\bar{P}_n = k_t/k_p(\text{M})_o + k_m/k_p \qquad (1)$$

where $\bar{P}_n$ is the number average degree of polymerization, $(\text{M})_o$ is the initial monomer concentration, and k_p, k_t and k_m are the rate constants for propagation, spontaneous molecular termination and chain transfer to monomer, respectively. Using molecular weights calculated from the intrinsic viscosities according to the equation of Pepper[11–13]

$$[\eta] = 4.37 \times 10^{-4}\,\bar{M}_n^{0.66}(\text{benzene, } 25°) \qquad (2)$$

the rate constant ratios in eq. 1 were evaluated as

$$k_t/k_p = 5.1 \times 10^{-3} \text{ mole l.}^{-1}, \text{ and } k_m/k_p = 2.4 \times 10^{-3} \qquad (3)$$

The validity of the form of eq. 1 under similar conditions was rigorously confirmed by Ehrig in experiments at low conversion and known co-catalyst (water) concentration, which lead to the relation[14]

$$1/\bar{P}_n = k_{t1}/k_p(\text{M})_o + k_{t2}(\text{H}_2\text{O})/k_p(\text{M})_o + k_m/k_p \quad (4)$$

which is experimentally equivalent to eq. 1 at constant water concentration. The values of the rate constant ratios derived from eq. 4 cannot be used in the present work, since they were measured at a higher temperature and lower dielectric constant, and the water concentration in the present work is unknown (although presumably constant).

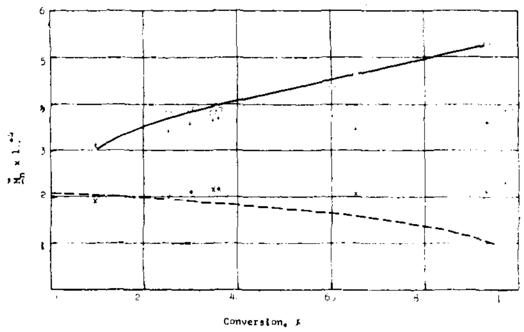


Fig. 2.—Cumulative number average molecular weight *vs.* conversion: ⊙, experimental osmotic data; X, calculated from experimental intrinsic viscosity, using eq. 2; +, calculated from experimental intrinsic viscosity, using eq. 7; dashed curve, calculated from eq. 6.

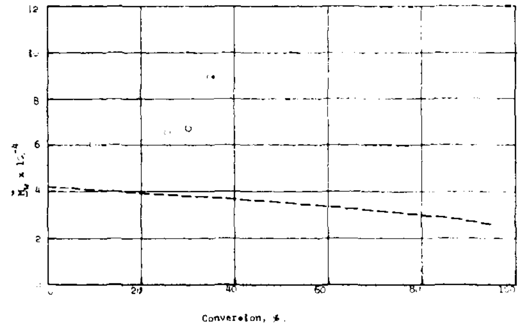


Fig. 3.—Cumulative weight average molecular weight *vs.* conversion: O, experimental light scattering data; dashed curve, calculated from eq. 8.

As pointed out by Schulz and Blaschke,[15] in a chain reaction polymerization where high polymer is being formed, the dependence of the cumulative number average degree of polymerization $\bar{\bar{P}}_n$ on the conversion is given to a close approximation by

$$\bar{\bar{P}}_n = \frac{(\text{M}) - (\text{M})_0}{\int_{\text{M}_0}^{\text{M}} (1/\bar{P}_n)\text{d}(\text{M})} \qquad (5)$$

Substituting from eq. 1 and integrating, there is obtained

$$1/\bar{\bar{P}}_n = \frac{1}{(\text{M})_0 - (\text{M})}\,\frac{k_t}{k_p}\ln\frac{(\text{M})_0}{(\text{M})} + \frac{k_m}{k_p} \qquad (6)$$

which, of course, predicts a decrease in degree of polymerization with increasing conversion. Substituting the values of eq. 3, the expected number average molecular weights as a function of conversion can be calculated, and the corresponding curve is included in Fig. 2. The experimental data are a poor fit, indeed, showing an opposite trend.

Another apparent contradiction can be seen in the data of Table I. The experimental ratio of weight to number average molecular weight $\bar{\bar{M}}_w/\bar{\bar{M}}_n$ remains within experimental error of 2, even at high conversion, which would be consistent with a "most probable" molecular weight distribution. However, as pointed out in the Introduction, a much broader distribution is expected in the present system.

---

(11) D. C. Pepper, *Sci. Proc. Roy. Dublin Soc.*, **25**, 239 (1951).

(12) D. C. Pepper, *J. Polymer Sci.*, **7**, 347 (1951).

(13) M. J. Hayes and D. C. Pepper, *Proc. Roy. Soc.* (*London*), **A263**, 63 (1961).

(14) C. G. Overberger, R. J. Ehrig and R. A. Marcus, *J. Am. Chem. Soc.*, **80**, 2456 (1958).

(15) G. V. Schulz and F. Blaschke, *Z. physik. Chem.*, **51**, 75 (1942).

A clue to the source of these difficulties can be seen in Fig. 2, in the curves for molecular weight calculated from the experimental intrinsic viscosities in benzene, using eq. 2 and also the following equation given by Gregg and Mayo[16,17]

$$\overline{M}_n = 178{,}000\ [\eta]^{1.37}\ (\text{benzene, } 30°) \qquad (7)$$

The two equations yield markedly different results for low molecular weight polystyrenes, as already pointed out by Pepper. The difference has been ascribed[11,12] to the fact that in the derivation of eq. 2 polystyrenes of very low molecular weight were included, and these were unfractionated whole polymers isolated by steam distillation of monomer and solvents. Equation 7 is based on higher polymers isolated by precipitation, where considerable low polymer was known to be lost.[16] Since the experimental osmotic molecular weights at low conversion found in the present work agree more closely with eq. 7 than with eq. 2, it is inferred that such precipitation losses might have occurred in the present work as well.

This possibility was tested experimentally by carrying out a polymerization to high conversion under the conditions of Table I, and precipitating the reaction mixture in methanol as usual, giving an 80% yield of precipitated polymer. An osmotic molecular weight of 50,000 is assumed, from the experimental curve of Fig. 2. The filtrate was subjected to stripping and steam distillation to remove the solvents and unreacted monomer, yielding a further 2.8% of residue, of number average molecular weight 390 (cryoscopic determination). It is readily calculated that combination of these two fractions yields 83% of polymer with number average molecular weight 9,400. This point on Fig. 2 would fall quite close to the theoretical curve calculated from eq. 6, accounting for the observed discrepancies.

It is also possible to compare the experimental cumulative weight average molecular weights with prediction on the basis of eq. 1. Litt[18] has derived the following equation for the dependence of $\overline{\overline{P}}_w$ on conversion, for a system where there is both spontaneous molecular termination and chain transfer to monomer

$$P_w = 2\,\frac{k_p}{k_m}\left[1 - \frac{k_p{}^{\alpha/k_m}}{(\mathrm{M})_0 - (\mathrm{M})}\ln\frac{1 + k_m(\mathrm{M})_0/k_p\alpha}{1 + k_m(\mathrm{M})/k_p\alpha}\right] + 1 \qquad (8)$$

In the case under consideration, where there is assumed to be no chain transfer to solvent, $\alpha = k_t/k_p$. Using again the values of eq. 3, the theoretical curve included in Fig. 3 was calculated. The weight average molecular weight is predicted to fall with increasing conversion, although not quite as steeply as the number average, resulting in a theoretical $\overline{M}_w/\overline{M}_n = 2.68$ at 95% conversion. Again, agreement with experiment is poor, the data showing a strong upward trend. In this case, the loss of a low fraction in the precipitation isolation cannot explain the discrepancy, since weight average molecular weights are not very sensitive to low fractions. However, these polymers are known to be branched.[5] If branching occurs by chain transfer to the polymer, number average molecular weights will be unaffected, but weight average molecular weights will tend to rise, since the distribution is broadened. The upward trend of the data can thus be readily accounted for on this basis. Note that the corrected molecular weight ratio $\overline{M}_w/\overline{M}_n$ is *ca.* 10 at 83% conversion.

The two curves in Fig. 3 should ideally extrapolate to the same intercept at zero conversion. The experimental curve appears to indicate a higher intercept, but the scatter does not permit a reliable extrapolation.

Finally, the dependence of intrinsic viscosity on conversion (Fig. 1) now appears to be rational. In general, the intrinsic viscosity of a linear polymer will tend to reflect its weight average molecular weight rather than its number average. That is, the "viscosity average" molecular weight, to which the intrinsic viscosity is related through the Mark–Houwink equation, is usually considerably closer to the weight average.[19] However, for a given molecular weight, a branched polymer will exhibit a lower intrinsic viscosity than a linear one.[5,20] In Fig. 1 are plotted the intrinsic viscosities in butanone calculated from the experimental weight average molecular weights, using the relation of Atkins and Billmeyer for linear polystyrene.[5]

$$[\eta] = 3.9 \times 10^{-4}\,\overline{M}_w{}^{0.56}\ (\text{butanone, } 25°) \qquad (9)$$

It is seen that the experimental viscosities agree rather well with these at low conversions but show an increasingly negative deviation at higher conversions, as the polymers become more highly branched.

It is evident that, in the system under investigation, the intrinsic viscosity at high conversions does not accurately reflect the changes in either weight or number average molecular weights, and is of little interpretive value. In the present case the principle reason for this appears to be branching through chain transfer to polymer. However, the molecular weight distribution will broaden with increasing conversion in any system where the instantaneous degree of polymerization is a function of the monomer concentration; that is, in any system where the physical chain length is not determined solely by chain transfer to the monomer.

In a study of polymerization mechanism based on kinetics, number average molecular weights of the products are usually desirable. If stationary conditions can be assumed, it will usually be satisfactory to calculate these from intrinsic viscosities if conversions are kept low. If conversions must be high, such as in extremely rapid polymerizations, direct measurement of molecular weights is recommended as the only really safe procedure. This is normally not difficult as far as weight averages are concerned, but if the degrees of polymerization are

---

(16) R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 2373 (1948).

(17) F. R. Mayo, R. A. Gregg and M. S. Matheson, *ibid.*, **73**, 1691 (1951).

(18) M. Litt, private communication. The equation shown as 8 in ref. 4 contains typographical errors.

(19) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 313.

(20) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301 (1949).

moderately low and distributions are broad (as will frequently be the case) there may be no satisfactory method for direct determination of number averages. In such cases, separation into low and high fractions and separate determination by appropriate procedures may be necessary.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASH., AND UTAH STATE UNIVERSITY, LOGAN, UTAH]

Substituent Effects in Pyrolysis. V.[1,2] A ρ–σ^+ Correlation in the Pyrolysis of 1-Arylethyl Acetates

BY ROGER TAYLOR,[3a] GRANT GILL SMITH[3b] AND WILLIAM H. WETZEL[3c]

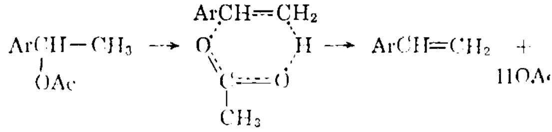
RECEIVED FEBRUARY 5, 1962

A kinetic study of the gas-phase thermal decomposition of a number of 1- and 2-arylethyl acetates has been made between 297.8° and 409.2°. Each ester was pyrolyzed at four different temperatures and over a temperature range of not less than 50° in a static system at reactant pressures of 6 to 200 mm.; the energies and entropies of activation range, respectively, from 41.7 to 44.7 kcal./mole and +0.34 to −2.66 e.u. for the 1-arylethyl acetates, and from 44.8 to 45.9 kcal./mole and −3.24 to −3.67 e.u. for the 2-arylethyl acetates. A plot of log k_{rel} for the effects of the substituents in the 1-aryl series at 600°K. against σ^+-constants (Brown and Okamoto[4]) gives an excellent correlation ($\rho = -0.66$) thus proving that the elimination of acetic acid proceeds *via* a mechanism in which some charge separation occurs, as has recently been suggested.[5] The importance of the breaking of the carbon–hydrogen and single carbon–oxygen bonds in the reaction mechanism has been further evaluated.

It has been recently emphasized by the work of Brown,[4] Bartlett,[6] Lossing[7] and others[8] that reactions which follow a ρ–σ^+ relationship must involve an electron-deficient intermediate, transient or otherwise, which can be stabilized in the rate-determining transition state by electron release from an aromatic ring. If a reaction involves an electron deficient center, such as a fully or partially formed carbonium ion, the correlation between the logarithms of the relative rates and Hammett's σ-constants is unsatisfactory.

In a recent study of the gas-phase thermal decomposition of 1,2-diarylethyl acetates, Smith, Bagley and Taylor[1] showed that substituents in the 1-aryl ring caused a greater change in the rate of pyrolysis than substituents in the 2-aryl ring. A plot of log k_{rel} (log k/k_0) for the effects of substituents in the 1-aryl ring at 600°K. against Hammett's σ-constants gave a poor correlation.[1] However, when the values of log k_{rel} are plotted against σ^+-constants (Brown and Okamoto[4]) a very satisfactory correlation is obtained (see Fig. 1), with $\rho = -0.62$.

A series of 1-arylethyl acetates have been prepared and pyrolyzed in order to evaluate the effects of a large number of substituents in the gas phase for the following three reasons: (a) The small ρ-factor for the reaction permits examination of the effects of substituents with a wide range of reactivities all under identical conditions. (b) The results from this gas phase study can be readily compared with condensed phase electrophilic aromatic substitution since they are all correlated by σ^+-values. (c) The preparation of the 1-arylethyl acetates involve simpler preparative procedures than the 1,2-diarylethyl acetates. For comparative purposes, studies were made on four 2-arylethyl acetates.



The thermal decomposition of esters into olefins and acids has been shown to be a first-order reaction which is unimolecular, homogeneous, and generally has a negative entropy of activation.[5,9] The thermal stability of the esters has been shown to be a function of molecular weight[10] and substit-

---

[1] Part IV, G. G. Smith, F. D. Bagley and R. Taylor, *J. Am. Chem. Soc.*, **83**, 3647 (1961).

[2] (a) This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)616. Reproduction in whole or in part is permitted for any purpose of the United States Government. The project was also supported in part by a grant from the American Chemical Society Petroleum Research Fund. The support is gratefully acknowledged. Presented in part at the Northwest Regional Meeting of the American Chemical Society in Portland, Ore., June 16, 1961. (b) A detailed survey of the literature in table form on the pyrolysis of carboxylates has been deposited with the American Documentation Institute, c/o Library of Congress, Washington 25, D. C., Serial Number 7281, price: Photostat $12.50. Microfilm $4.25.

[3] (a) Postdoctoral Research Associate; now, The Dyson Perrins Laboratory, The University, Oxford. (b) Chemistry Department, Utah State University, Logan, Utah, to whom inquiries should be addressed. (c) Research Assistant.

[4] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

[5] C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

[6] P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960).

[7] A. G. Harrison, P. Kebarle and F. P. Lossing, *ibid.*, **83**, 777 (1961).

[8] (a) D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952); D. E. Pearson and J. D. Burton, *ibid.*, **19**, 957 (1954); (b) J. D. Roberts, J. K. Sanford, F. L. J. Sixma, H. Cerfontain and R. Zagt, *J. Am. Chem. Soc.*, **76**, 4525 (1954); (c) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953); G. S. Hammond, *et al.*, *ibid.*, **80**, 563, 568, 573 (1958); (d) N. C. Deno and A. Schriesheim, *ibid.*, **77**, 3051 (1955); (e) N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957); (f) J. Miller, *Austral. J. Chem.*, **9**, 61 (1956); (g) Y. Tsuno, T. Ibata and Y. Yukawa, *Bull. Chem. Soc. Japan*, **32**, 960, 965 (1959); (h) Y. Ogata and I. Tabushi, *J. Am. Chem. Soc.*, **83**, 3440, 3444 (1961).

[9] (a) C. E. Rudy, Jr., and P. Fugassi, *J. Phys. Colloid Chem.*, **52**, 357 (1948); (b) G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **75**, 2118 (1953); (c) D. Y. Curtin and D. B. Kellom, *ibid.*, **75**, 6011 (1953); (d) D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 1715 (1953); (e) A. T. Blades, *Can. J. Chem.*, **32**, 366 (1954); A. T. Blades and P. W. Gilderson, *ibid.*, **38**, 1401, 1407, 1412 (1960).

[10] (a) F. Krafft, *Ber. deut. chem. Ges.*, **16**, 3018 (1883); (b) G. G. Smith and W. H. Wetzel, *J. Am. Chem. Soc.*, **79**, 875 (1957).