

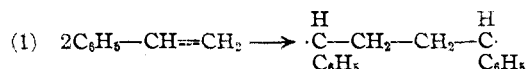
[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Transfer in the Polymerization of Styrene: The Reaction of Solvents with Free Radicals¹

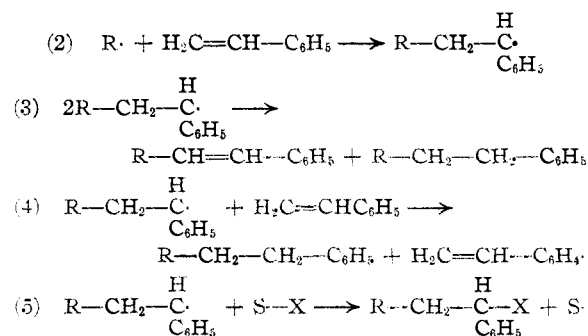
BY FRANK R. MAYO

When styrene is polymerized in a solvent, the resulting polymer has a lower molecular weight than the product prepared in the absence of a solvent; the effect varies with the solvent. This paper has two objects: (1) to show that the molecular weight lowering by solvents can be fully accounted for by chain transfer between the growing polymer and the solvent; (2) to compare the reactivities of solvents in chain transfer and show that they are consistent with their reactivities toward other reagents. The discussion will be confined to the polymerization of styrene in the absence of added catalysts.

The Existence of Chain Transfer.—It is convenient to assume a mechanism for the uncatalyzed polymerization of styrene. The following radical-chain mechanism is simple, is adequate for present purposes, and has experimental support. The first step (to be considered further in the next section) is the interaction of two styrene molecules to give a diradical:²



The two radical ends behave independently, and R· will be used to designate any individual radical. Growth of each radical then continues by successive addition of styrene units (equation 2) until interrupted by one of the chain terminating reactions, (3), (4) or (5)



Reaction (3), disproportionation, is well established and generally accepted.³ Reaction (4) rep-

resents chain transfer with the monomer; its importance has not yet been determined.⁴ Reaction (5), chain transfer with the solvent, is the reaction with which this paper is chiefly concerned. Here, the polymer radical R· removes a univalent atom, X·, from a solvent molecule, S-X, yielding a completed polymer molecule and a new free radical, S·. If the free radical formed in either chain transfer reaction, (4) or (5), adds readily to a styrene molecule, then a new chain is immediately begun. In contrast to reaction (3) in which two active centers destroy each other, these chain transfer reactions then do not affect the over-all rate of polymerization. They simply reduce the average molecular weight of the polymer formed, and the solvent acts as a "regulator" of polymerization. However, if the free radicals formed from the solvent molecule do not add readily to styrene, then they will accumulate in solution, destroy reaction chains by a reaction analogous to (3), and reduce the over-all rate of polymerization.

Flory⁵ was the first to describe the principle of chain transfer, more than six years ago. Very few workers have taken account of chain transfer in interpreting results of liquid-phase polymerizations, although many workers refer to his paper, and although the concept has adequate support from both kinetic and chemical evidence. Cuthbertson, Gee and Rideal⁶ found that toluene reduced the rate constant and degree of polymerization of vinyl acetate; they proposed a mechanism which includes a step corresponding to reaction (5) when the solvent radical formed does not readily start a new chain. Kamenskaya and Medvedev⁷ have accounted quantitatively for the degree of polymerization of vinyl acetate in benzene solution on the basis that all the polymer chains are terminated either by chain transfer with benzene or by interaction of two radicals. Breitenbach and Maschin⁸ carried out the polymerization of styrene in carbon tetrachloride; their data show that their polymer contained about four chlorine atoms per molecule. This finding is readily explained on the basis that, in equation (5), X corresponds to a chlorine atom while S·

(4) Chain transfer with the monomer may also involve transfer of a hydrogen atom from the β -carbon atom of the polymer radical to an unsaturated carbon atom of the monomer, or transfer of a vinyl hydrogen atom from the monomer to the polymer radical. If the nucleus of styrene is as reactive in chain transfer as benzene, then about 10% of the chains are terminated by reaction (4) in the initial polymerization of pure styrene.

(5) Flory, *THIS JOURNAL*, **59**, 241 (1937).

(6) Cuthbertson, Gee and Rideal, *Proc. Roy. Soc. (London)*, **A170**, 300 (1939).

(7) Kamenskaya and Medvedev, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940).

(8) Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

(1) Presented before the Organic Division at the Detroit Meeting of the American Chemical Society, April 12, 1943.

(2) The structures shown for the free radicals are presumed to be more stable and therefore more probable than the isomeric structures because of analogies with the addition of hydrogen bromide, mercaptans, and bisulfite to styrene. In these addition reactions, the attacking radical becomes attached exclusively to the β -carbon atom of the double bond, leaving a free valence on the α -carbon; cf. Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

(3) Cf., e. g., Schulz and Husemann, *Z. physik. Chem.*, **39B**, 246 (1938). No change in treatment is required if some or all of the radicals combine in pairs to saturate each other.

corresponds to $\cdot\text{CCl}_3$ and is capable of starting a new chain.

Suess, Pilch, Rudorfer and Springer⁹ and Schulz, Dinglinger and Husemann¹⁰ have studied the rate and degree of polymerization of styrene in several solvents in the absence of catalysts. Their data are admirably suited to testing the concept of chain transfer which they ignored. The results show that the over-all rate of the uncatalyzed polymerization of styrene is close to second order and that the rate constant is little affected by the solvent. Nevertheless, the degree of polymerization (average number of styrene units per polymer molecule) varies markedly with the solvent. The most plausible interpretation of such results is based on chain transfer.¹¹

Definition and Evaluation of the Transfer Constant.—The following derivation will assume that the mechanism of the uncatalyzed polymerization of styrene is adequately represented by equations (1) to (5), all the steps being second order reactions. The mechanism of chain initiation has not been established but the following evidence indicates that it is second order. Since the over-all rate of polymerization of styrene corresponds to a second order reaction and since chain growth and chain termination are almost certainly of second order, chain initiation must also be of effectively the same order. A bimolecular chain initiation has been suggested by Flory,⁵ who considered the activation energies involved, and is supported by the chemical evidence of Kern and Feuerstein.¹² The latter investigators heated styrene and quinone, obtained compounds containing one quinone and two styrene residues (but none containing one quinone and one styrene residue), and concluded that the original active center in the polymerization of styrene contains two styrene units. It will also be assumed that all growing polymer radicals have the same reactivity, that the radicals formed by chain transfer with the solvent or monomer are not markedly less reactive, and that the conventional steady state approximation can be applied to free radical concentrations over the first few per cent. of polymerization.

If the degree of polymerization of styrene, \bar{P} , is equal to the rate of chain growth divided by the total rate of chain termination (by chain transfer with the solvent, disproportionation, and chain transfer with the monomer), and if we represent the concentrations of monomer and solvent by (M) and (S), respectively, then, over the first few per cent. of polymerization, where the relative concentrations of monomer and solvent remain constant.

(9) (a) Suess, Pilch and Rudorfer, *ibid.*, **A179**, 361 (1937); (b) Suess and Springer, *ibid.*, **A181**, 81 (1937).

(10) Schulz, Dinglinger and Husemann, *ibid.*, **B43**, 385 (1939).

(11) Representative results are clearly summarized in Figs. 1 and 2 of reference (9b). This same conclusion about chain transfer has been reached previously by Kamenskaya and Medvedev, reference (7), p. 585.

(12) Kern and Feuerstein, *J. prakt. Chem.*, [2] **158**, 186 (1941).

$$(6) \quad \bar{P} = \frac{k_2(\text{R}\cdot)(\text{M})}{k_3(\text{R}\cdot)(\text{S}) + k_3(\text{R}\cdot)^2 + k_4(\text{R}\cdot)(\text{M})}$$

Inverting both sides of equation (6), dividing numerator and denominator by $(\text{R}\cdot)(\text{M})$, and inserting the steady state concentration of free radicals, $(k_1/k_3)^{1/2}(\text{M})$, for the only $(\text{R}\cdot)$ which is then left, we obtain

$$(7) \quad \frac{1}{\bar{P}} = \frac{k_5(\text{S})}{k_2(\text{M})} + \frac{(k_1k_3)^{1/2} + k_4}{k_2}$$

In the absence of a solvent, the first term on the right-hand side vanishes, and the second term is the reciprocal of the degree of polymerization in the absence of a solvent (\bar{P}_0). Making this substitution, and defining the transfer constant, C , as k_5/k_2 , we arrive at the simple expression

$$(8) \quad \frac{1}{\bar{P}} = C \frac{(\text{S})}{(\text{M})} + \frac{1}{\bar{P}_0}$$

The transfer constant is thus the rate constant for chain transfer with the solvent divided by the rate constant for chain growth. If $(\text{S}) = (\text{M})$, then the transfer constant represents the probability that any given radical will undergo transfer with the solvent rather than growth by addition of monomer. This probability must be very small if the polymer is to obtain any size. The transfer constant is easily evaluated; it represents the slope of the line obtained by plotting the reciprocal of the degree of polymerization (after a small extent of reaction) against the ratio of solvent to monomer concentrations. The value of the constant should depend upon what monomer, what solvent and what temperature are used, but in a series of experiments it should be independent of the monomer-solvent ratio.

Since rate studies^{9,10} indicate that k_2 , the rate constant for chain growth, is nearly independent of the solvent, the rate constants for the chain transfer reactions between a polymer radical and a series of solvents will have the same relative values as their transfer constants.¹³ It is much easier to determine the transfer constants than the rate constants; it is not necessary to measure any rates, only the number-average molecular weights of the products obtained at low conversions; the actual steady state concentration of free radicals need not be determined or estimated; and the question of the relative importance of disproportionation and of chain transfer with the monomer (reactions 3 and 4) can be evaded. Finally, when the solvent concentration is high enough, then essentially all the chains terminate by transfer with the solvent, and the $1/\bar{P}_0$ term can be neglected. Under such conditions, the value of the transfer constant becomes independent of the mechanisms of chain initiation and termination in the absence of a solvent, and the formula should also be appli-

(13) The slightly lower over-all rates of polymerization reported by Suess, *et al.*, for the chlorinated aliphatic solvents seem at least as likely to be due to a lower activity of chloroalkyl radicals in starting new chains as to a change in the absolute value of k_2 ; cf. discussion following equation (5).

cable to catalyzed polymerizations; the only assumption then needed is that reactions (2) and (5) are of the same kinetic order.

Experimental Data.—Equation (8) will be applied to the data of Suess, Schulz, and their co-workers.^{9,10} They measured the degree of polymerization of styrene at various concentrations in various solvents and at two or three temperatures between 80 and 132°. The data of Suess were taken from experiments in which the extent of polymerization was usually between 1 and 6% but did not exceed 15%. Schulz and co-workers determined the degree of polymerization at about 5% and about 10% reaction, averaging the two nearly identical values. Determination of the degree of polymerization, or average number of styrene units in a polymer molecule, requires determination of the number-average molecular weights of the products. Both groups of workers based their molecular weights on viscosity determinations. The Schulz group determined the factor relating viscosity to molecular weight (as determined by osmotic pressure measurements on fractionated polymers) over the whole experimental range of number-average molecular weights and temperatures; their values should therefore be fairly reliable. The Suess group used a value of the proportionality factor which was later revised by Schulz and co-workers, assumed this factor to be independent of the temperature of polymerization (contrary to the later findings of the other group), and assumed that it remained constant for degrees of polymerization ranging from 62 to 2800, an assumption open to serious question. The results of Suess and co-workers therefore permit accurate comparisons of solvent effects only at 100° and over a moderate range of degree of polymerization; accordingly, only their results at this temperature are cited here.

Calculation of Transfer Constants.—Tables I and II summarize the data of Schulz, Suess and co-workers and give the calculated transfer constant for each experiment.¹⁴ According to equation (8), a plot of [solvent]/[styrene] against $1/\bar{P}$ should give a straight line with slope C for any solvent at one temperature. Figures 1-3 bear out this anticipation.¹⁵ Considering that the \bar{P} values are often averages of only two values which may differ by as much as 5%, and that the values of the transfer constant will be subject to the greatest uncertainty when the differences between \bar{P} and \bar{P}_0 are small, the agreement between theory and experiment seems remarkably good. The ranges of solvent-to-styrene ratios tested often

(14) Suess' data on heptane are omitted because the styrene polymer precipitated as it formed in this solvent.

(15) Suess' data with carbon tetrachloride are not plotted in Fig. 3. They do not fall on a straight line and their inclusion would require a much larger figure; the points would lie close to the $1/\bar{P}$ axis and far above the others. These experiments are not considered a fair test of the chain transfer hypothesis because the validity of Staudinger's relation was not established in the molecular weight range covered by these experiments.

vary by factors of 15 to 30 and the range extends from 1 to 66 in the case of toluene. In view of the discussion of experimental data, the agreement between the two groups of workers is satisfactory; the solvent activities are in the same order and have nearly the same ratio.

TABLE I
TRANSFER CONSTANTS CALCULATED FROM DATA OF
SCHULZ, *et al.*^a

| Styrene (moles/ liter) | [Solvent] ^b [Styrene] | 100° | | 132° | |
|------------------------------|-------------------------------------|-------------------------|-----------------|-----------------------|-----------------|
| | | \bar{P}^c | $C \times 10^4$ | \bar{P}^c | $C \times 10^4$ |
| No Solvent | | | | | |
| 8.72 | 0.0 | 2160 (= \bar{P}_0) | | 1490 (= \bar{P}_0) | |
| Cyclohexane | | | | | |
| 0.485 | 18.0 | | | 482 | 0.779 |
| 0.605 | 14.2 | 1105 | 0.311 | 535 | .843 |
| 0.97 | 8.47 | 1430 | .287 | 758 | .765 |
| 1.51 | 5.06 | 1650 | .282 | 900 | .809 |
| 1.94 | 3.70 | | | 1030 | .809 |
| 3.02 | 2.00 | | | 1220 | .744 |
| 3.88 | 1.32 | 2160 | | | |
| 6.05 | 0.468 | | | 1435 | .556 |
| | | Best value ^d | .31 | | .81 |
| Benzene | | | | | |
| 0.504 | 21.1 | | | 455 | .725 |
| 0.605 | 17.3 | 1000 | .310 | 475 | .828 |
| 1.008 | 9.89 | 1355 | .278 | 685 | .798 |
| 2.52 | 3.17 | 1840 | .255 | 1090 | .776 |
| 6.05 | 0.568 | 2125 | .141 | 1450 | .317 |
| | | Best value | .31 | | .81 |
| Toluene | | | | | |
| 0.605 | 14.46 | 810 | .534 | 435 | 1.12 |
| 0.97 | 8.63 | 1085 | .533 | 615 | 1.10 |
| 1.94 | 3.77 | 1530 | .507 | 900 | 1.16 |
| 3.88 | 1.35 | 1970 | .334 | 1255 | .94 |
| 5.82 | 0.538 | 2140 | .074 | 1420 | .61 |
| | | Best value | .53 | | 1.12 |
| Ethylbenzene | | | | | |
| 0.605 | 12.56 | 455 | 1.38 | 290 | 2.21 |
| 1.008 | 7.16 | 690 | 1.38 | 415 | 2.42 |
| 3.02 | 1.77 | 1315 | 1.68 | 880 | 2.63 |
| 6.05 | 0.413 | 1910 | 1.45 | 1320 | 2.08 |
| | | Best value | 1.38 | | 2.31 |
| Diethylbenzene ^e | | | | | |
| 0.705 | 8.35 | 312 | 3.29 | 202 | 5.13 |
| 1.51 | 3.51 | 600 | 3.43 | 430 | 4.72 |
| 3.02 | 1.39 | 1040 | 3.60 | 710 | 5.32 |
| 6.05 | 0.324 | 1830 | 2.56 | 1240 | 4.17 |
| | | Best value | 3.35 | | 5.13 |

^a C = transfer constant = $(1/\bar{P} - 1/\bar{P}_0)$ [styrene]/[solvent]. ^b The concentrations of solvent were calculated from the stated styrene concentrations, assuming that there is no volume change on mixing styrene and solvent, and using the following values for the concentrations in moles/liter of pure solvents at room temperature (at which the styrene concentration was measured): cyclohexane, 9.25; benzene, 11.26; toluene, 9.41; ethylbenzene, 8.17; diethylbenzene, 6.41; chlorobenzene, 9.84; dichloroethane, 12.7; tetrachloroethane, 9.53; carbon tetrachloride, 10.37. ^c \bar{P} = degree of polymerization = average number of styrene units in polymer molecules. ^d These "best values" correspond to the slopes of the lines in Figs. 1-3, the points at high solvent concentrations being given the most weight in fitting the lines to the points. ^e A fraction of a technical mixture.

Discussion.—Since the concept of chain transfer can account quantitatively for both the rate and degree of polymerization of styrene in a

TABLE II
TRANSFER CONSTANTS AT 100° CALCULATED FROM DATA
OF SUESS, *et al.*^a

| Solvent | [Styrene] (moles/ liter) | [Solvent] ^b [Styrene] | \bar{P}^c | $C \times 10^4$ |
|---------------------------------------|--------------------------------|-------------------------------------|-------------------------|-----------------|
| None | 8.72 | 0.0 | 1900 (= \bar{P}_0) | |
| Benzene | 0.50 | 21.2 | 700 | 0.425 |
| | 1.00 | 10.0 | 1100 | .384 |
| | 3.00 | 2.46 | 1540 | .504 |
| | 5.00 | 0.96 | 1770 | .406 |
| | | | Best value ^d | .42 |
| Chlorobenzene | 1.00 | 8.71 | 1000 | .545 |
| | 3.00 | 2.15 | 1680 | .320 |
| | 6.00 | 0.51 | 1800 | .566 |
| | | | Best value | .54 |
| | Toluene | 0.14 | 66.1 | 190 |
| 0.53 | | 16.7 | 580 | .717 |
| 1.04 | | 7.97 | 530 | .848 |
| 1.86 | | 3.97 | 1200 | .774 |
| 2.32 | | 2.98 | 1350 | .718 |
| 3.07 | | 1.99 | 1500 | .710 |
| 4.52 | | 1.00 | 1700 | .620 |
| | | | Best value | .72 |
| Ethylbenzene | | 0.50 | 15.4 | 380 |
| | 1.50 | 4.51 | 640 | 2.30 |
| | 2.50 | 2.33 | 930 | 2.36 |
| | 4.00 | 1.11 | 1200 | 2.78 |
| | 5.50 | 0.549 | 1460 | 2.89 |
| | | Best value | 2.33 | |
| Diethylbenzene ^e | 2.50 | 1.83 | 600 | 6.24 |
| | 5.00 | 0.546 | 1140 | 6.43 |
| | | | Best value | 6.33 |
| ClCH ₂ -CH ₂ Cl | 3.00 | 2.78 | 630 | 3.82 |
| | 6.00 | 0.660 | 1280 | 3.86 |
| | | | Best value | 3.84 |
| Cl ₂ CH-CHCl ₂ | 3.00 | 2.08 | 380 | 10.1 |
| | 6.00 | 0.495 | 910 | 11.6 |
| | | | Best value | 10.8 |
| CCl ₄ | 3.00 | 2.27 | 62 | 69 |
| | 4.00 | 1.42 | 90 | 75 |
| | 5.50 | 0.696 | 125 | 107 |
| | 7.00 | 0.293 | 230 | 130 |

^{a, b, c, d} Have the same significance as in Table I. * A mixture supposed to be rich in *para* isomer.

number of solvents, we may conclude not only that the concept is a useful working hypothesis, but that the assumptions made in deriving equation (8) are good approximations. Since the effect of solvents can be adequately accounted for by their behavior in chain transfer, it does not yet seem necessary to postulate any effect of dilution *per se* on the degree of polymerization.

Since relative activities of solvents in chain transfer are presumed to be directly proportional to their transfer constants, they will now be discussed on that basis. Benzene and cyclohexane are the least reactive solvents; their transfer constants are identical within experimental error. Among the hydrocarbons, the activities then increase in the order toluene, ethylbenzene, diethyl-

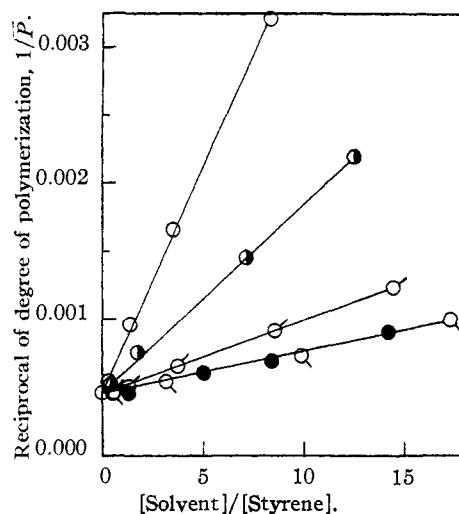


Fig. 1.—Effect of solvents on the degree of polymerization of styrene at 100° (Schulz, *et al.*): benzene, \square ; cyclohexane, \bullet ; toluene, σ ; ethylbenzene, \ominus ; diethylbenzene, \circ .

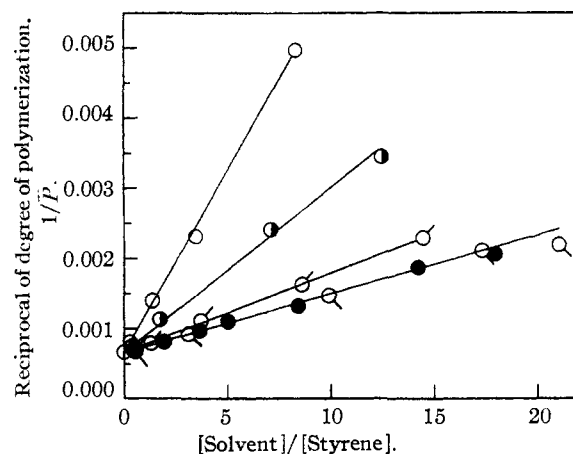


Fig. 2.—Effect of solvents on the degree of polymerization of styrene at 132° (Schulz, *et al.*). The circles have the same significance as in Fig. 1.

benzene. Chlorobenzene has about the same activity as benzene, but the aliphatic chlorides transfer more readily. The higher the proportion of chlorine they contain, the more reactive they are. Carbon tetrachloride is ten to twenty times as reactive as the most reactive hydrocarbon. The hydrocarbons probably lose hydrogen atoms in chain transfer; carbon tetrachloride, and presumably the other aliphatic chlorides, lose chlorine atoms to the growing polymer radicals.

Table III shows the effect of temperature on the transfer constants, using only the "best values" from Table I. At 132°, the constants are 1.5 to 2.5 times as large as at 100°, the temperature coefficient being largest for the least reactive solvents. Since the transfer constant = $C = k_1/k_2$ we can easily calculate the difference

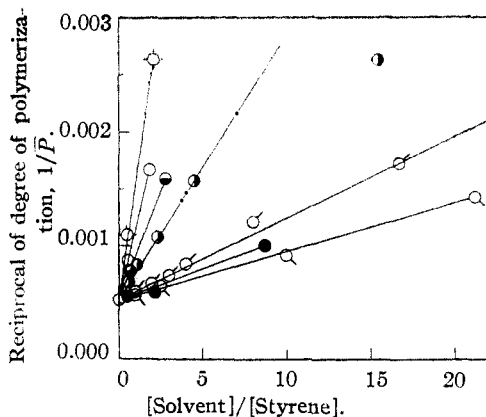


Fig. 3.—Effects of solvents on the degree of polymerization of styrene at 100° (Suess, *et al.*): benzene, \circ ; chlorobenzene, \bullet ; toluene, \odot ; ethylbenzene, \ominus ; *sym*-dichloroethane, \oplus ; diethylbenzene, \circ ; *sym*-tetrachloroethane, \oplus . The line shown for toluene, when extended, passes through the point corresponding to the first toluene experiment in Table II.

between the activation energies, $E_5 - E_2$, by means of the Arrhenius equation.

TABLE III

THE EFFECT OF TEMPERATURE ON TRANSFER CONSTANTS

| Solvent | Transfer constant $\times 10^4$ 100° | Transfer constant $\times 10^4$ 132° | $E_5 - E_2$ (kcal./mole) | E_5 (kcal./mole) |
|--------------|---|---|-----------------------------|-----------------------|
| Cyclohexane | 0.31 | 0.81 | 9.0 | 15.0 |
| Benzene | 0.53 | 1.12 | 7.0 | 13.0 |
| Toluene | 1.38 | 2.31 | 4.8 | 10.8 |
| Ethylbenzene | 3.35 | 5.13 | 4.0 | 10.0 |

These differences are listed in Table III. The activation energy for chain growth alone, E_2 , has been estimated at 5–8 kcal./mole.^{5,16} Taking 6 kcal. as a fair average value, we may add this to the calculated values of $E_5 - E_2$ and obtain values for E_5 alone. These values, as shown in Table III, range from 10–15 kcal. per mole. If the chain transfer reaction is correctly represented by equation (5), these values represent the activation energy required to transfer a hydrogen atom from the solvent to the substituted benzyl radical of a growing styrene polymer. As should be expected, the lowest reactivity goes with the highest activation energy.

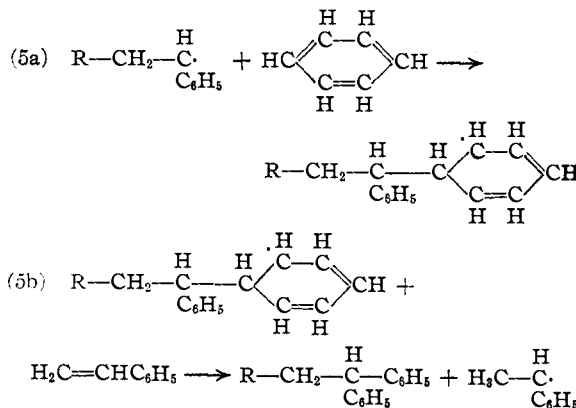
These results on chain transfer with hydrocarbon solvents correlate excellently with what is known about the attack of such molecules by chlorine or bromine atoms in aliphatic substitution. In purely aliphatic hydrocarbons, a halogen atom removes a tertiary hydrogen most easily, a primary hydrogen least easily,¹⁷ but a benzyl hydrogen, such as the α -hydrogen in the side chain of toluene, is removed more easily

(16) Mark and Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, N. Y., 1941, p. 214.

(17) Hass, McBee and Weber, *Ind. Eng. Chem.*, **28**, 333 (1936); Kharasch, Hered and Mayo, *J. Org. Chem.*, **6**, 818 (1941).

than any of these. Since toluene is more active than benzene or cyclohexane in chain transfer, the α -hydrogen of the side chain seems to be responsible for the increased activity of toluene; apparently ethylbenzene is still more reactive because this α -hydrogen atom is secondary instead of primary. This reasoning implies that the substituted secondary benzyl radical of the growing polymer, being relatively unreactive, is very selective, and can remove a secondary α -hydrogen from ethylbenzene more easily than a primary α -hydrogen from toluene. There are twice as many of these α -hydrogen atoms in diethylbenzene as in ethylbenzene; the transfer constants for diethylbenzene are twice as large but the activation energy is about the same.

Because of the activity of benzene and cyclohexane in chain transfer, it is obvious that the activity of the alkylbenzenes cannot be due exclusively to the benzyl hydrogen atoms. The contribution of the benzyl hydrogen atoms is relatively small in toluene, large in diethylbenzene. The listed activation energies for the alkylbenzenes are, therefore, not rigorously calculated but represent effective average values which are useful as a basis for discussion. Further, the possibility that chain transfer with aromatic solvents may involve a sequence of reactions such as the following is consistent with the theoretical development and has not been excluded.¹⁸



Free radicals are known to couple with aromatic nuclei¹⁹ and the alkyl groups may serve to activate the nucleus. It is hoped that experiments with isopropylbenzene and *t*-butylbenzene will determine whether the radical attacks the side chain or the nucleus.

Since all types of hydrocarbons tested show some activity in chain transfer, it follows that

(18) If equations (5a) and (5b) correctly represent chain transfer involving aromatic nuclei, then the activation energies in the last column of Table III probably apply to reaction (5a). Two other equally probable resonating structures can be written for the substituted phenyl radical, the free valence appearing in the *para* or in the other *ortho* position.

(19) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937). This coupling reaction is more probable when the aromatic nucleus contains nitro groups; cf. Price and Durham, *THIS JOURNAL*, **65**, 757 (1943).

during polymerization chain transfer with both monomeric styrene and with polymer must occur. By analogy with benzene, the contribution of the aromatic nucleus to chain transfer with the monomer may be small, but analogies between polystyrene and ethylbenzene suggest that chain transfer with the polymer, leading to chain branching, should be appreciable, particularly at high temperatures and high conversions. Studies of solvents with appropriate structures may therefore assist in attacking the difficult problem of estimating chain branching. Finally, the solvent studies discussed in this paper suggest a simple and accurate procedure for comparing the reactivities of several types of free radicals with a large number of solvents.

Acknowledgment.—The author is indebted to Dr. H. C. Tingey of these Laboratories for helpful suggestions.

Summary

It is postulated that certain solvents reduce the molecular weight of polymerizing styrene

because they transfer hydrogen or chlorine atoms to growing polymer radicals. The activity of the polymer radical is thus transferred to the solvent residue which may then start a new chain. In order to compare solvent reactivities in these chain transfer reactions, a simple theoretical development leads to definition of the "transfer constant" which is characteristic of a solvent. Several transfer constants have been calculated from data in the literature. The results give quantitative support to the theoretical development and permit quantitative comparisons of solvent activities. Activation energies for chain transfer are calculated for some hydrocarbon solvents.

The results suggest that chain transfer between polymer radicals and both monomer and polymer molecules must occur. Chain transfer studies offer a possible attack on the problem of chain branching and a convenient way of studying reactions of free radicals in solution.

PASSAIC, NEW JERSEY

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. VI. The Magnetic Moments of Some Iron(III) Complex Ions¹

BY BURTON WERBEL, V. H. DIBELER AND W. C. VOSBURGH

Complex ion formation by a paramagnetic ion is often accompanied by a decrease in magnetic susceptibility. Pascal² found this to be true in a large number of cases, and believed it to be a general phenomenon. Schaffer and Taylor³ found it true of several complex ions of nickel and copper. More recently it has become clear that complex ions can be divided into two classes on the basis of magnetic measurements.⁴ In the formation of some ions two or more electrons that are unpaired in the free paramagnetic ions become paired, and the magnetic moment decreases. When others are formed the number of unpaired electrons is unchanged, but even so a relatively small decrease in moment may take place.^{3,5} It is probable that this is a decrease in the orbital contribution to the moment and is the result of the change in the electrostatic field when the atoms immediately surrounding the paramagnetic ion are changed.⁶

Van Vleck⁶ (p. 301) has pointed out that manganese(II) and iron(III) ions are in *S* states and

their moments should be pure spin moments with the theoretical value of 5.92 Bohr magnetons. Accordingly, having no orbital contributions the moments of these ions should be unchanged by complex formation, provided that no change in the number of unpaired electrons takes place.

Iron(III) ammonium alum was found by Onnes⁷ to have a susceptibility corresponding to the theoretical moment. Jackson⁸ found that the moments of solid iron(III) acetylacetonate and potassium trioxalatoferrate(III) are practically equal to the theoretical value, as are those of some solid iron salts. Welo⁹ found that many iron(III) solid compounds have moments less than the theoretical, but he found some that approached the theoretical value. Bose¹⁰ measured the susceptibilities of iron(III) chloride, nitrate and sulfate in solution with varying acidity and temperature. The observed moments were lower than the theoretical, but the addition of acid caused the moments to increase, and in the solutions of highest acidity the approach to the theoretical was quite close. Bose suggested that the deviations from the theoretical value might be the result of hydrolysis. He had previously found practically the theoretical moments for manganese salts¹⁰ (p. 605).

(1) Part of a thesis submitted by Burton Werbel in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University. May, 1943.

(2) Pascal, *Ann. chim.*, [8] **16**, 571 (1909).

(3) Schaffer and Taylor, *THIS JOURNAL*, **48**, 843 (1926).

(4) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 104.

(5) Russell, Cooper and Vosburgh, *THIS JOURNAL*, **65**, 1301 (1943).

(6) Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," The Clarendon Press, Oxford, 1932, p. 287.

(7) (a) Onnes and Oosterhuis, *Proc. Acad. Sci. Amsterdam*, **16**, 917 (1914); (b) Cambi and Szegö, *Ber.*, **66**, 657 (1933).

(8) Jackson, *Proc. Roy. Soc. (London)*, **A140**, 705 (1933).

(9) Welo, *Phil. Mag.*, [7] **6**, 481 (1928).

(10) Bose, *Proc. Indian Acad. Sci.*, **A1**, 754 (1935).