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Methyl Affinities of Vinyl Monomers. Part I. Styrene and Phenylated Ethylenes

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RECEIVED MAY 17, 1955

The methyl affinities of the following phenylated ethylenes have been determined: styrene, α-methylstyrene, 1,1-diphenylethylene, stilbene, triphenylethylene and tetraphenylethylene. Discussion of the results demonstrates clearly the importance of the resonance stabilization of the radicals formed in accounting for the increasing reactivity of the olefins in the series styrene, α-methylstyrene and 1,1-diphenylethylene. On the other hand, inspection of the results obtained in the series styrene, stilbene, triphenylethylene and tetraphenylethylene reveals the importance of steric hindrance due to the presence of bulky phenyl groups. There is some indication that the first effect (resonance stabilization of the radical) affects mainly the activation energy of the addition process, while the steric hindrance manifests itself mainly in the entropy of activation. The effects played by steric hindrance in this series parallel the effects observed in the series of substituted quinones discussed in a previous communication. The reactivity of α-methylstyrene is contrasted with its reluctance to polymerize, this problem being discussed in a more detailed fashion.

The addition of radicals to C=C double bonds represents an important class of organic reactions to which belong such processes as the initiation and propagation of vinyl polymerization. The nature of an olefinic compound has a profound effect on the rate of addition, and many factors, such as resonance stabilization of the monomer and of the radical formed, the steric factors, and so forth, contribute to the ultimate reactivity of the monomer.

To assess correctly the contribution of each of these factors to the reactivity of a monomer it is imperative to study, in a systematic way, series of reactions of the type

$$\text{R} + \text{monomer} \longrightarrow \text{R}\cdot\text{monomer}$$

for various classes of monomers, and to vary in an intelligent way the structure of monomers in each class. It is our intention to carry out such a study for reactions involving methyl radicals, and in this communication we are reporting and discussing the first set of results dealing with the class of phenylated ethylenes. The study of other classes of vinyl monomers and related compounds is now in progress. To investigate the reaction

$$\text{CH}_3 + \text{monomer} \longrightarrow \text{CH}_3\cdot\text{monomer}$$

the technique developed by Levy and Szwarc[1] has been applied. The essential features of this technique are as follows. A required amount of the investigated monomer is dissolved in a dilute solution (10^{-2} to 10^{-3} molar) of acetyl peroxide in isooctane. The deaerated mixture is heated for two hours in a sealed ampoule, and then the contents are analyzed for CH_4, C_2H_6 and CO_2. The analytical technique and other experimental details are published elsewhere.[1,2]

The decomposition of acetyl peroxide generates methyl radicals, and it has been shown previously[1,2] that the latter react with the solvent and the monomer according to the equations[3]

$$\text{CH}_3 + \text{iso-C}_8\text{H}_{18} \longrightarrow \text{CH}_4 + \text{iso-C}_8\text{H}_{17} \qquad (1)$$

$$\text{CH}_3 + \text{M} \longrightarrow \text{CH}_3\text{M}\cdot \qquad (2)$$

The initial product of reaction (2) is of course a radical and, hence, it cannot be the final product of the over-all process. It is believed, however, that the radical $CH_3{\cdot}M$ does not react further with methyl radicals, but it disappears in a reaction involving another radical of its own type or a solvent radical S·, *i.e.*

$$2\text{CH}_3\text{M}\cdot \longrightarrow \text{products} \qquad (3)$$

or

$$\text{or CH}_3\text{M}\cdot + \text{S}\cdot \longrightarrow \text{products} \qquad (4)$$

The products yielded by reactions (3) and (4) may result either from a recombination or a disproportionation process. Further evidence in favor of the mechanism proposed is given in references 1 and 2.[4]

The kinetic scheme represented by equations 1, 2, 3 and 4 leads to the following results

$$\text{rate of formation of CH}_4 = k_1(\text{CH}_3)X_\text{S}$$

$$\text{rate of formation of CH}_3\text{M}\cdot = k_2(\text{CH}_3)X_\text{M}$$

where X_S and X_M denote the mole fractions of solvent and monomer, respectively. The formation of $CH_3M\cdot$ results in a decrease of methane formed, the latter can be determined by measuring the amount of methane formed in the absence and in the presence of monomer M. Hence

$$\frac{(\text{the amount of CH}_4 \text{ ``lost''})}{(\text{the amount of CH}_4 \text{ formed})} = \frac{k_2}{k_1} \times \frac{1}{X_\text{S}} \times \frac{1}{t}\int_0^t X_\text{M}\,\mathrm{d}t$$

If X_M remains reasonably constant during the whole course of reaction (*i.e.*, when only a few percentage of a monomer is consumed in the reaction) the above equation is reduced to the expression

$$\frac{k_2}{k_1} = \frac{(\text{the amount of CH}_4 \text{ ``lost''})}{(\text{the amount of CH}_4 \text{ formed})} \times \frac{X_\text{S}}{X_\text{M}}$$

However, if a substantial proportion of a monomer is consumed, which might be the case when the polymerization proceeds rapidly, then the above expression must be modified by introducing a correction factor f. The calculation of the correction factor f has been carried out for two distinct cases: I, when the polymerization is initiated by methyl radicals only, and II, when *all* the radicals formed in the system, *i.e.*, methyl radicals as well as solvent radicals, initiate the polymerization.

In case I we assume that on the average n molecules of monomer are consumed for each methyl radical involved in reaction (2), the following kinetic equations should then be valid

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[1] (a) M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954); (b) THIS JOURNAL, **77**, 1949 (1955); (c) M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

[2] M. Levy and M. Szwarc, THIS JOURNAL, **76**, 5981 (1954).

[3] It was shown in references 1 and 2 that ethane is formed in a cage reaction (see also A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 3486 (1955). Hence, the formation of ethane does not consume "*free*" methyl radicals produced by the decomposition.

[4] In the presence of a reactive monomer M the radical CH_3M may grow to a polymeric radical $CH_3(M)_n\cdot$ which in turn will be terminated by reaction (3) or (4).

$$\mathrm{d}(\mathrm{CH_4}) = k_1(\mathrm{CH_3})X_\mathrm{S}\,\mathrm{d}t$$
$$\mathrm{d}y = k_2(\mathrm{CH_3})(X_\mathrm{M} - n\cdot y)\,\mathrm{d}t$$

where y = (CH_4 "lost") denotes the amount of methyl radicals consumed at time t by reaction (2) in one mole of the mixed solvent. Integration of these equations leads to the expression

$$\frac{k_2}{k_1} = \left\{\frac{(\mathrm{CH_4}\ \text{``lost''})}{(\mathrm{CH_4}\ \text{formed})} \times \frac{X_\mathrm{S}}{X_\mathrm{M}}\right\} \times \left\{\frac{1}{\gamma}\ln(1-\gamma)^{-1}\right\}$$

where γ is the fraction of the monomer which reacted. The quotient in the last bracket represents the correction factor f.

In case II we assumed that n molecules of monomer polymerize for *every* initiating radical. Denoting by u the amount of methyl radicals which react according to equation 1 and by v the amount which initiates polymerization directly, we arrive at the following results. The rate of methane formation $\mathrm{d}u/\mathrm{d}t$ is

$$\mathrm{d}u/\mathrm{d}t = k_1(\mathrm{CH_3})X_\mathrm{S}$$

and the rate of addition of methyl radicals to the monomer $\mathrm{d}v/\mathrm{d}t$ is

$$\mathrm{d}v/\mathrm{d}t = k_2(\mathrm{CH_3})\{(X_\mathrm{M}) - nu - nv\}$$

The solution of these equations leads to the expression

$$\frac{(\mathrm{CH_4}\ \text{formed})}{(\mathrm{CH_4}\ \text{``lost''})} + 1 = \frac{A-1}{\gamma A} \times \{1 - \exp. - [\gamma A(\mathrm{CH_4}\ \text{formed})/(\mathrm{CH_4}\ \text{``lost''})]\}$$

Where γ as previously denotes the fraction of polymerized monomer, while $A = (k_2/k_1)\,(X_\mathrm{S}/X_\mathrm{M})$. As in case I, the evaluation of k_2/k_1 requires the determination of (CH_4 "lost")/(CH_4 formed) $(X_\mathrm{S}/X_\mathrm{M})$ and of γ, *i.e.*, the fraction of polymerized monomer.

From purely experimental considerations it is advantageous to use the ratio $\{(\mathrm{CH_4/CO_2})_\mathrm{S} - (\mathrm{CH_4/CO_2})_\mathrm{M}\}/(\mathrm{CH_4/CO_2})_\mathrm{M}$ instead of the ratio (CH_4 "lost")/(CH_4 formed). In this expression $(\mathrm{CH_4/CO_2})_\mathrm{S}$ denotes the ratio of CH_4/CO_2 formed in an experiment carried out in pure solvent, *i.e.*, in the absence of a monomer, while $(\mathrm{CH_4/CO_2})_\mathrm{M}$ denotes the same ratio obtained from an experiment in which a monomer is present. The benefit results from the fact that the ratio CH_4/CO_2 is less susceptible to small changes in the conditions of experiment than the absolute amount of methane formed.

Results

The following phenylated ethylenes were investigated: styrene, α-methylstyrene, 1,1-diphenylethylene, stilbene, triphenylethylene and tetraphenylethylene. All the monomers but 1,1-diphenylethylene and triphenylethylene were obtained commercially, while the latter two were prepared according to the methods described in "Organic Syntheses."[5] The compounds were purified by standard techniques, and the sharpness of melting point (or boiling point) was considered as a criterion of purity. In the case of styrene, the purification was carried out in two ways: one sample was fractionated under reduced pressure, while another one was distilled, the distillate was washed with dilute alkali, then with diluted sulfuric acid, water and finally dried and redistilled. The results obtained with these samples were identical, proving that the experiments were not vitiated by the presence of some impurities.

Most of the experiments were carried out in isoöctane solution, while some of them were repeated in methyl ethyl ketone solution. The results were calculated on the basis of the simple formula for k_2/k_1, using for these calculations the following values for $(\mathrm{CH_4/CO_2})\mathrm{s}$ (*i.e.*, the ratio of CH_4/CO_2 produced in a pure solvent in absence of a monomer)

in isoöctane at 65°, $(\mathrm{CH_4/CO_2})\mathrm{s} = 0.802$
in isoöctane at 85°, $(\mathrm{CH_4/CO_3})\mathrm{s} = 0.805$
in methyl ethyl ketone at 65°, $(\mathrm{CH_4/CO_2})\mathrm{s} = 0.837$
in methyl ethyl ketone at 85°, $(\mathrm{CH_4/CO_2})\mathrm{s} = 0.857$

The latter values were obtained by averaging the results of a number of "blank" experiments.

The results obtained in isoöctane solution are summarized in Table I, an inspection of which brings out the following observations: (a) the changes in the concentration of monomers, amounting sometimes to as much as a factor of 9, do not affect the value of k_2/k_1. (b) The presence of a monomer does not affect the rate of the unimolecular decomposition of acetyl peroxide (see the k_u values listed in the last column of Table I). The latter observation implies that acetyl peroxide does not react directly with the monomer.

In all experiments listed in Table I the concentration of acetyl peroxide was chosen in such a way that a few per cent. only of monomer were consumed in the course of the reaction.[6] This limitation of the experimental conditions is essential for the application of the simple formula for k_2/k_1 (*i.e.*, for neglecting the correction factors discussed previously). However, a number of experiments were carried out under conditions in which a substantial proportion of monomer was polymerized.[7] In these experiments the weight of the polymeric material formed was determined by weighing the non-volatile residue which remained in the ampoule after the solvent, the unreacted monomer, and the remaining peroxide were removed by vacuum distillation. This weight was used in calculating the extent of polymerization γ (the notation introduced previously). Strangely enough, the correction factors derived on assumption I (*i.e.*, assuming that methyl radicals *only* initiate the polymerization) and based on thus determined γ lead to consistent values for k_2/k_1 which agreed moreover with those obtained under conditions of low extent of polymerization when the corrections are negligible and can therefore be omitted. On the other hand, the corrections computed on assumption II (*all* radicals formed in the system initiate the polymerization)

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[5] H. Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 221; Coll. Vol., II, p. 606.

[6] The experiments carried out at 65° lead to about 5% of decomposition of peroxide in 2 hours (which is the standard time for an experiment). Hence, a 5×10^{-2} M solution of peroxide gives sufficient amount of products and at the same time the consumption of monomer is limited to a few per cent. only. In experiments carried out at 85°, 50–60% of peroxide decomposes during the 2-hour period of heating. Hence, a 5×10^{-3} M solution of peroxide is used to maintain the same conditions of the reaction.

[7] In the case of readily polymerizable monomers, such as styrene, methyl methacrylate, acrylonitrile, or vinyl acetate, the polymerization often consumes a substantial fraction of monomer. For example, at 85° and with 5×10^{-2} M concentration of peroxide, 0.25 mole % solution of styrene seems to polymerize to about 50% in two hours.

TABLE I[a]

Solvent, isoöctane

T, °C.	Mole %	CH_4/CO_2	k_2/k_1	ku × 10^5, sec.$^{-1}$
		Styrene		
65	0.125	0.398	817	0.89
65	.125	.406	785	0.89
65	.25	.270	796	...
65	.25	.275	770	0.89
65	.25	.278	758	0.92
65	.50	.157	824	0.92
85	.125	.441	655	13.3
85	.25	.302	664	13.0
85	.50	.193	634	13.0
		α-Methylstyrene		
65	0.060	0.525	874	0.95
65	.120	.373	958	0.97
65	.127	.358	980	1.00
65	.150	.346	876	0.97
65	.233	.256	950	1.00
65	.513	.145	890	0.97
85	.060	.555	753	17.2
85	.120	.424	750	17.0
85	.127	.390	830	17.0
85	.240	.279	777	17.1
85	.257	.288	695	16.5
85	.513	.170	725	16.2
		1,1-Diphenylethylene		
65	0.0625	0.390	1700	0.95
65	.125	.256	1710	.95
65	.25	.159	1620	.95
65	.25	.174	1460	.95
65	.50	.097	1450	.95
86.5	.125	.385	870	15.5
86.5	.25	.257	850	15.5
86.5	.50	.140	950	15.5
86.5	1.00	.079	905	15.5
		trans-Stilbene		
65	0.50	0.513	113	0.94
65	0.75	.450	104.5	.83
65	1.00	.392	104.5	.94
65	1.00	.390	106	.85
85	0.32	.626	88.5	12.0
85	0.50	.572	80	12.2
85	0.64	.504	92	12.5
85	1.00	.432	84	12.8
85	1.00	.488	64*	...
85	2.00	.318	74	12.2
85	2.50	.309	62*	...
		1,1,2-Triphenylethylene		
65	0.50	0.652	46.9	1.00
65	1.00	.535	50.0	1.03
65	2.00	.437	41.3	1.00
85	0.50	.683	34.8	12.8
85	1.00	.599	33.6	12.8
85	2.00	.476	33.6	12.8

[a] Experimental values denoted by a star have been discarded in calculating the average values.

lead to too high and not self-consistent values for k_2/k_1. These observations were interpreted originally as an indication of the inertness of isoöctyl radicals which, it was believed, should be unable to initiate polymerization[8] because of the steric hindrance due to the presence of the bulky neopentyl group and two methyl groups in such a radical. However, a closer examination of the results showed that the polymeric substance is a mixture of dimers, trimers and tetramers, and if the isoöctyl groups are present as the end groups, then the calculation of γ from the weight is greatly in error. Consequently, all the results obtained under conditions leading to high extent of polymerization were rejected and excluded from Table I.

To substantiate further the experimental findings summarized in Table I the reactivities of some monomers were redetermined in methyl ethyl ketone solution. If the assumed mechanism is valid, then the change of the solvent should lead to a change in the rate constant k_1, leaving essentially unaltered the rate constant of addition k_2 Hence, the values of k_2/k_1' should be proportional to the respective values of k_2/k_1 obtained for the same monomers in isoöctane solution. Here, k_1' denotes the rate constant for the abstraction of a hydrogen atom from methyl ethyl ketone, while k_1 refers to the rate constant of the analogous reaction involving isoöctane. This relationship has been fully substantiated by the data listed in Table II. It is striking that in spite of considerable variations in the values of the individual rate constants k_2/k_1's, which range within a factor of 50, *i.e.*, from 31 to 1590 at 65° and from 27 to 980 at 85°, the ratios $(k_2/k_1)/(k_2/k_1') = k_1'/k_1$ listed in the last column of Table II remain essentially constant, namely, about 9.3 ± 2 at 65° and 8 ± 1 at 85°. The constancy of k_1'/k_1 is considered, therefore, as additional evidence favoring the postulated mechanism. Incidentally, determination of k_1'/k_1's yields a relative value for the chain transfer constants of solvents toward methyl radicals. Thus, the data reported in reference 1b, and in the present paper, lead to the following relative values of chain transfer constants at 85°

isoöctane:toluene:methyl ethyl ketone = 1:3:9

TABLE II

COMPARISON OF k_2/k_1 IN ISOÖCTANE AND k_2/k_1' IN METHYL ETHYL KETONE

Monomer	k_2/k_1 in isoöctane	k_2/k_1' in methyl ethyl ketone	$(k_2/k_1)/(k_2/k_1') = k_1'/k_1$
	$T = 65°$		
1,1-Diphenylethylene	1590	180	8.9
Styrene	792	88	9.0
Diethyl maleate	263	22.4	11.7
Vinyl acetate	31	3.8	8.2
	$T = 85°$		
1,1-Diphenylethylene	980[a]	130	7.5
Styrene	651	94	6.9
Diethyl maleate	162	16.8	9.6
Vinyl acetate	27.5	3.7	7.4

[a] A value intrapolated from $T = 86.5°$.

The average values of the k_2/k_1's listed in Table I are summarized in Table III. The third column of

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(8) These results induced us to investigate the character of polymerization in isoöctane solution. Results, which will be reported later, seem to indicate that the polymerization is somehow inhibited by this solvent.

this table contains the differences of activation energies of the methyl radical addition reactions and the activation energy of the abstraction of a hydrogen atom from isoöctane by a methyl radical. The values quoted for styrene and for stilbene were obtained from Fig. 1. In view of the narrow temperature range within which these reactions were studied, the accuracy of these activation energies is not better than ±1–2 kcal./mole. The last column of Table III contains the values for the methyl affinities of the studied compounds, *i.e.*, the values of the relative rate constants (k_2) of methyl radicals addition reactions referred to the scale in which the rate constant of addition of methyl radicals to benzene has been assumed to be unity. The uniform scale of methyl affinities has been introduced in order to facilitate the comparison of reactivities of various aromatic and olefinic compounds toward methyl radicals.

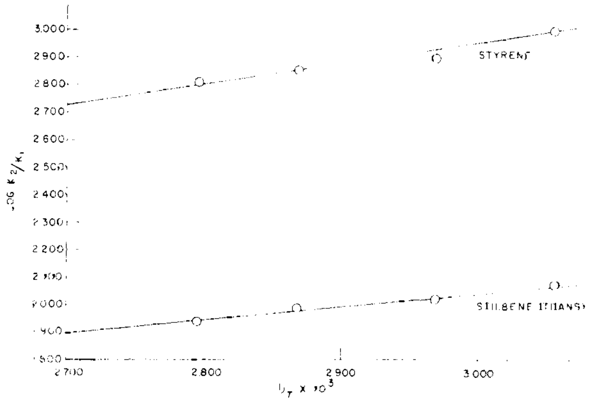


Fig. 1.—Each point represents an average of 3 or 4 experiments carried out at 55, 65, 75, and 85°. The lines drawn correspond to $E_2 - E_1 = 3.0$ kcal./mole for styrene and 2.4 kcal./mole for stilbene.

TABLE III

Monomer	k_2/k_1 at 65°	k_2/k_1 at 85°	ΔE, kcal./mole	Methyl affinity
Styrene	792 ± 26	651 ± 15	−3.0	1630
α-Methylstyrene	926 ± 47	755 ± 46	−2.5	1890
1,1-Diphenylethylene	1590 ± 38	895 ± 42[a]	−6.5	2240
trans-Stilbene	104.5 ± 4	84 ± 9	−2.4	205
1,1,2-Triphenylethylene	46 ± 4.5	34 ± 1	−3.6	85
Tetraphenylethylene	<10	<10	...	<25

[a] This value was obtained at 86.5°.

Discussion

Two procedures may be adopted in discussing the reactivities of the investigated phenylated ethylenes. In the first procedure the experimentally determined values of $E_2 - E_1$ combined with the determined relative values of k_2's are used for calculating the changes in the activation energies and the entropies of activation resulting from the variation of the structure of the olefin. This procedure is undoubtedly the most satisfactory and should be always recommended if the activation energies are determined with sufficient accuracy. However, we doubt whether this is the case in the present studies since the narrow range of temperature within which the reaction was studied,[8a] and perhaps the occurrence of some minor side reactions, might lead to errors in activation energies as great as ±2 kcal./mole.

What can be stated with certainty is this: (1) In all the cases investigated the activation energy of addition is lower than the activation energy of the hydrogen abstraction. In view of the high reactivity of these compounds, this conclusion seems to be plausible. (2) The activation energy for the addition is the lowest in the case of 1,1 diphenylethylene (*i.e.*, ΔE is the most negative). This should be expected in view of the high resonance stabilization of the diphenylmethyl radical.

The difficulties mentioned above force us to base the discussion of reactivities of the investigated phenylated olefins on the relative values of k_2's. Such procedure does not distinguish whether the change in the reactivity is caused by the change in activation energy or in entropy of activation; nevertheless, interesting conclusions can be drawn in spite of this limitation.

It was pointed out by Evans and his colleagues[9] that the reactivity of an olefin should increase with increasing resonance stabilization of the radical formed by the addition of another radical to the olefin. This behavior is illustrated by the series: styrene, α-methylstyrene and 1,1-diphenylethylene. The addition of methyl radicals to each of these olefins probably takes place on the β-carbon atom, and thus the following radicals are formed

$$\underset{\text{I}}{\mathrm{Ph\underset{\cdot}{C}HC_2H_5}} \qquad \underset{\text{II}}{\mathrm{Ph\underset{\cdot}{C}(CH_3)C_2H_5}} \qquad \underset{\text{III}}{\mathrm{Ph_2\underset{\cdot}{C}C_2H_5}}$$

It is obvious that the resonance stabilization of these radicals increases in the above order. The increase in the resonance stabilization of II as compared with I is attributed to the hyperconjugation effect due to the presence of a methyl group, while a much more powerful effect, attributed to the presence of an additional phenyl group, is expected in radical III. (Compare the resonance energy of benzyl radical with that of a diphenylmethyl radical.) These expectations are reflected in the determined methyl affinities which are 1630, 1890 and 2240, respectively.

It is worth stressing that the above explanation attributes the increase of methyl affinities to the decrease in activation energies of the respective reactions, and the experimental findings certainly do not contradict the theory.

Let us now consider the reactivity of stilbene. The methyl affinity of this compound is appreciably lower than that of styrene, the decrease amounting to about one power of ten. The resonance stabilization of the radical derived from stilbene, *i.e.*

$$\underset{\text{IV}}{\mathrm{Ph\cdot\underset{\cdot}{C}H\cdot CH(CH_3)\cdot Ph}}$$

is approximately equal to the resonance stabilization of radical I. On the other hand, the resonance energy of stilbene seems to be slightly higher than that of styrene (see Wheland[10]); and consequently, one would expect stilbene to be slightly less reactive

[8a] The limitation in the temperature range resulted from the too slow rate of the decomposition of acetyl peroxide below 60° and too rapid above 90°.

[9] M. G. Evans, J. Gergely and E. C. Seaman, *J. Polymer Sci.*, **3**, 866 (1948).

[10] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

than styrene. However, the observed decrease in methyl affinity of stilbene seems to be much too great to be accounted for by this effect only.[11] We suggest tentatively that another factor plays an important role in decreasing the reactivity of stilbene, namely, the steric hindrance. The investigation of methyl affinities of quinones[12] demonstrated strikingly the importance of steric hindrance in the addition reactions of methyl radicals to C=C double bonds. These results suggest that the presence of a bulky phenyl group on the carbon atom which is attacked by a methyl radical decreases the probability of a reaction, and if this hypothesis is correct, we would expect a further considerable decrease in the reactivity, if two phenyl groups are substituted on each carbon atom of ethylene. The determination of the methyl affinity of tetraphenylethylene confirms this view entirely. The reactivity of this compound is so low that its methyl affinity could not be determined accurately, the upper limit, however, does not exceed 25. A further check of this hypothesis is provided by the investigation of the reactivity of triphenylethylene. It would appear that the methyl affinity of this compound should be one half of that of stilbene, since only one C atom of triphenylethylene would be available for the reaction (while two C atoms may participate in the reaction involving stilbene). However, one should take into account the increasing resonance stability of radical (V) which would enhance the reactivity of triphenylethylene, and the

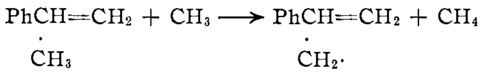
$$\mathrm{Ph_2{\cdot}C{\cdot}C(CH_3){\cdot}Ph}$$

V

steric repulsion effect due to the presence of two phenyl groups in *cis*-configuration[13] which would have an opposite effect on the reactivity. It seems that the two opposing effects cancel each other, since the methyl affinity of triphenylethylene is approximately one-half of that of stilbene.

The shielding effect of bulky groups should manifest itself primarily in the pre-exponential factor, *i.e.*, in the entropy of activation. Indeed inspection of Fig. 1 shows that the activation energies of these reactions are essentially the same for styrene and for stilbene.

The last point which needs further discussion is the apparent inconsistency in the behavior of α-methylstyrene, which seems to be very reactive but at the same time is reluctant to polymerize. One may suspect that the reactive methyl group terminates the polymerization by chain transfer reaction which would lead to an unreactive allyl type radical.[14] If this were the case, then in our system additional methane would be formed by the reaction



$$\mathrm{Ph\underset{CH_3}{C}H{=}CH_2 + CH_3 \longrightarrow Ph\underset{CH_2\cdot}{C}H{=}CH_2 + CH_4}$$

and the occurrence of this process would introduce an error in our calculation of methyl affinity. It is reasonable to assume that the rate constant of the above reaction would be similar to the rate constant of reaction

$$\mathrm{C_6H_5CH_3 + CH_3 \longrightarrow C_6H_5CH_2\cdot + CH_4}$$

and the latter was found to be about six times greater than the rate of addition of methyl radicals to toluene.[16] Assuming further that the methyl affinity of toluene is about unity (*i.e.*, similar to that of benzene), we conclude that the rate of addition of methyl radicals to α-methylstyrene is 600 times faster than the rate of abstraction of hydrogen atoms. Consequently, the occurrence of the latter reaction can be safely neglected.

The reluctance of α-methylstyrene to polymerize should be attributed to the difficulty with which the α-methylstyryl radical attacks α-methylstyrene.[14] However, this monomer seems to be as reactive as styrene if it is attacked by other radicals, *e.g.*, the reactivity ratios r_2 for the pairs methyl methacrylate radical–styrene and methyl methacrylate radical–α-methylstyrene are both 0.5 (see ref. 17), and in the case of methacrylonitrile radicals, the values are 0.25 and 0.35, respectively. On the other hand, the corresponding values for r_1 are much lower for α-methylstyrene, indicating that it is the reaction α-methylstyryl radical + α-methylstyrene which is slow.

Acknowledgment.—The financial support of this investigation by The National Science Foundation and the Monsanto Chemical Company (Plastics Division) is gratefully acknowledged.

SYRACUSE, N. Y.

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[11] To appreciate this point, let us compare the methyl affinities of styrene and 1,1-diphenylethylene on one hand and of styrene and stilbene, keeping in mind that the increase in the resonance energy of diphenyl methyl radical as compared with benzyl radical is undoubtedly much greater than that in stilbene as compared with styrene.

[12] A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 4468 (1955).

[13] The studies of copolymerization indicate that the *cis*-isomers are less reactive than the *trans*-isomers (see *e.g.*, ref. 7). The results obtained in our laboratories confirm this observation. For example, the methyl affinities of diethyl fumarate and diethyl maleate were determined at 1950 and 400, respectively. This work will be discussed in detail in the second paper of this series.

[14] Similar situation arises in the polymerization of allyl acetate (see Bartlett, ref. 15).

[15] P. D. Bartlett and R. Altshul, THIS JOURNAL, **67**, 812, 816 (1945).

[16] Unpublished data from our laboratories.

[17] See *e.g.*, T. Alfrey, J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952.