[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY]

Methyl Affinities of Substituted Styrenes, their Homologs and Analogs

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Methyl affinities were determined for substituted styrenes and for styrene analogs and homologs, *i.e.*, vinylnaphthalene, 1- and 9-vinylanthracenes, 2- and 4-vinylpyridines and α-vinylthiophene. The relations between the respective structures and methyl affinities were discussed. The effect upon methyl affinity of methyl substituents, located in α- and/or β-position of styrene, was determined and discussed in terms of changes in the coplanarity of the respective molecules and in terms of "blocking" action of methyl substituents present at the reactive center. Methyl affinities of chlorine and methoxy substituted styrenes were investigated. Finally, methyl affinities of dibenzofulvene and some of its derivatives were studied and the respective values were compared with that of 1,1-diphenylethylene.

In this paper we shall report the values of the relative rate constants of methyl radical addition to substituted styrenes, their homologs and analogs, and attempt to correlate them with the structures of the respective substrates. For the sake of brevity we shall refer to these rate constants as methyl affinities.

The experimental method used in determining methyl affinities is described elsewhere.[1-3] Suffice to say that the results are given in the form of a ratio k_2/k_1, the subscripts referring to reactions (1) and (2) as shown

$$\mathrm{CH_3 + isoöctane \longrightarrow CH_4 + isoöctyl\ radical} \quad (1)$$

$$\mathrm{CH_3 + S \longrightarrow S{\cdot}CH_3} \quad (2)$$

In these equations S denotes a styrene derivative or its analog or homolog and SCH_3 the radical formed in the addition reaction. Isoöctane was used as a solvent in all the experiments, and hence k_1 remains constant for the whole series of investigated substrates. Although its absolute value is not known, this is of no importance if only the relative values of k_2 are required.

Experimental

The compounds investigated are listed in Table I. All the experiments were carried out at 65° in isoöctane solution using approximately 10^{-2} *M* concentration of acetyl peroxide, the decomposition of which produced methyl radicals. Some of the investigated compounds interact with radicals in two distinct ways: either the radicals add to the substrates or they abstract from them the labile hydrogen atoms. In such cases the relative rate constants of the addition (k_2/k_1) as well as the relative rate constants of hydrogen abstraction (k_3/k_1) were determined. The method used in these cases was described in reference 3.

TABLE I[a]

Compound	Acquired from	Purified
1-Vinylnaphthalene	Monomer Polymer Co.	Vac. distillation
1-Vinylanthracene	Kindly offered by Dr. Hawkins, Distillers Co., England	Recryst. from ethanol, m.p. 57–60°
9-Vinylanthracene	Kindly offered by Dr. Katz, Hebrew University, Jerusalem	Recrystallized m.p. 64–65°
2-Vinylpyridine	Aldrich Chemicals	Vac. distillation
4-Vinylpyridine	Aldrich Chemicals	Vac. distillation
α-Vinylthiophene	Monomer-Polymer Co.	Twice distilled
2-Chlorostyrene	Monomer-Polymer Co.	Vac. distillation
3-Chlorostyrene	Monomer-Polymer Co.	Vac. distillation
4-Chlorostyrene	Monomer-Polymer Co.	Vac. distillation
2,5-Dichlorostyrene	Monomer-Polymer Co.	Vac. distillation
4-Methoxystyrene	Monomer-Polymer Co.	Vac. distillation
Vinylmesitylene	Monomer-Polymer Co.	Vac. distillation
cis-β-Methylstyrene	Kindly offered by Dr. Overberger	Vac. distillation
trans-β-Methylstyrene	Kindly offered by Dr. Overberger	Vac. distillation
α,β-Dimethylstyrene	Kindly offered by Dr. Overberger	Vac. distillation
α,β,β-Trimethylstyrene	Kindly offered by Dr. Overberger	Vac. distillation
p-Diisopropenylbenzene	Kindly offered by Dow Chem.	Recrystallized
Indene	Commercial	Vac. distilled
Dibenzfulvene	Prepared in our laboratories[4]	Vac. distilled
9-Ethylidene fluorene	Kindly offered by Dr. Kice	Recrystallized
9-iso-Propylidene fluorene	Kindly offered by Dr. Kice	Recrystallized
Fluorene	Commmercial	Recrystallized

[a] Whenever possible the purity of the compounds was checked by gas chromatography.

Results and Discussion

The results are summarized in Table II. All the investigated compounds, with exception of the vinylpyridines, do not react directly with the peroxide. Solutions of acetyl peroxide containing vinylpyridines decomposed, however, slightly faster than the others (the decomposition was enhanced by about 10%). Hence in calculating the k_2/k_1

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(1) M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955).

(2) M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

(3) R. P. Buckley and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A240**, 396 (1957).

(4) Instructions for preparation of this compound have been obtained from Dr. J. L. Kice, University of South Carolina, Columbia, South Carolina.

values for these two compounds, the CH_4/CO_2 ratio was used. No enhancement was observed in the decomposition proceeding in presence of vinylthiophene or methoxystyrene.[5]

TABLE II

METHYL AFFINITIES IN ISOÖCTANE SOLUTION AT 65°

Compound	k_2/k_1	No. of expt.	Range of concn., mole %
Styrene	792 ± 26[a]	..	....
1-Vinylnaphthalene	813 ± 25	4	0.067–0.19
1-Vinylanthracene	1350 ± 30	5	.04–0.135
9-Vinylanthracene	440 ± 10	4	.09–0.31
Vinylmesitylene	104[b]	6	.33–1.43
2-Vinylpyridine	1360 ± 15	6	.5–2.5
4-Vinylpyridine	1360 ± 100	5	.08–0.5
α-Vinylthiophene	2050 ± 50	5	.07–0.41
Styrene	792 ± 26[a]	..	....
α-Methylstyrene	926 ± 47[a]	..	....
p-Di-isopropenylbenzene	2100 ± 50	5	.09–0.24
β-Methylstyrene, *trans*	92.5[b]	3	.47–2.8
β-Methylstyrene, *cis*	40[b]	3	.47–2.8
α,β-Dimethylstyrene	66 (?)	6	.6–3.0
α,β,β-Trimethylstyrene	20[b]	5	.4–3.0
Indene	96[b]	5	.22–2.2
Styrene	792 ± 26	..	....
2-Chlorostyrene	1000 ± 25	6	.1–0.5
3-Chlorostyrene	1040 ± 40	5	.1– .5
4-Chlorostyrene	1020 ± 25	6	.1– .5
2,5-Dichlorostyrene	1210 ± 50	6	.1– .5
4-Methoxystyrene	765 ± 20	4	.1– .4
1,1-Diphenylethylene	1590 ± 38[a]	..	....
Dibenzofulvene	20,000	7	.002–0.02
9-Ethylidenefluorene	2900 ± 170	6	.04–0.22
9-Ethylidenefluorene	3200[b]		Extrapd. to 0 concn.
9-Iso-propylidene fluorene	280 ± 25	4	0.024–0.24
9-Iso-propylidene fluorene	300[b]	4	Extrapd. to 0 concn.

[a] These values are reported by Leavitt, Levy, Szwarc and Stannett, THIS JOURNAL, **77**, 5493 (1955). [b] These values were obtained by the extrapolation to 0 concentration. See for details of the procedure Buckley, Leavitt and Szwarc, *ibid.*, **78**, 5557 (1956), and also reference 3.

The extraordinary high reactivity of dibenzfulvene forced us to work with highly diluted solutions of acetyl peroxide (—10^{-3} *M*) and larger volumes of the reacting liquids. This was necessitated by our desire to keep the concentration of the substrate constant during the experiment.

The results listed in Table II are divided into four groups. The first lists the homologs and analogs of styrene. Methyl affinities were found to increase along the series styrene, 1-vinylnaphthalene and 1-vinylanthracene. Such an increase is explicable in terms of decreasing localization energies on the β-carbon of the vinyl group.[6] On the other hand, methyl affinity of 9-vinylanthracene was found to be much less than that of 1-vinylanthracene and even less that of styrene. Inspection of the models shows that copolanarity of the vinyl group and the aromatic ring is prevented by steric hindrance in 9-vinylanthracene, while molecules of stryene[7] 1-vinylnaphthalene and 1-vinylanthracene are planar. The lack of coplanarity greatly reduces the resonance energy of the resulting radical and thus increases the respective localization energy—this accounts for the observed results. Steric hindrance prevents again the coplanarity in the molecule of vinylmesitylene, and indeed methyl affinity of this compound is exceedingly low.

Presence of a nitrogen atom in a conjugated system tends to decrease the localization energy[6] and thus to increase the respective methyl affinity. This is shown by comparing methyl affinities of pyridine and benzene[1] and in the present work by comparing methyl affinities of styrene and the vinylpyridines. The magnitudes of these effects are

	Increase in methyl affinity by a factor of
Pyridine–benzene	3
Vinylpyridines–styrene	1.7
Isoquinoline–naphthalene	1.6
Quinoline–naphthalene	1.3

Apparently, the effect of a nitrogen atom is less and less pronounced as the size of the conjugated system increases—a result which is intuitively expected.

A similar effect operates probably in vinylthiophene. Its magnitude is much greater (observed factor of about 2.5) than that observed in vinyl pyridines: however, its further discussion should be postponed until more information will be accumulated on methyl affinities of sulfur containing compounds.

The methyl affinities of styrene, α-vinylnaphthalene, the vinylpyridines and α-vinylthiophene parallel the $1/r_1$ (reciprocal of the reactivity ratios in copolymerization) characterizing polystyryl radicals. This point was emphasized previously by Leavitt, *et al.*[8]

The second series of Table II contains styrene derivatives methylated in the α- or β-positions of the vinyl group. A methyl substituent located in the α-position slightly enhances the reactivity of the styrene derivative, and this effect can be accounted quantitatively for in terms of hyperconjugation[9] (the calculated ratio of methyl

TABLE III

THE BLOCKING EFFECT OF METHYL SUBSTITUENT

Compound	k_2/k_1	$(k_2/k_{1\text{unsubst.}})/(k_2/k_{1\text{subst.}})$
Propylene	21.9	..
Butene-2 *trans*	6.9	5.5[a]
Isobutene	35.6	..
Trimethylethylene	5.6	6.4
Styrene	792	..
β-Methylstyrene *trans*	86	9
Butadiene-1,3	2015	..
Hexadiene-2,4	180	11.3
Dibenzfulvene	~20,000	..
10-Methyldibenzfulvene (*i.e.*, 9-ethylidene fluorene)	~3000	7

[a] For calculation of the ratio given in the last column of this table the k_2/k_1 for butene-2 is divided by 2. (Both ends are reactive). Furthermore $^1/_2$ of k_2/k_1 of butene-2 is subtracted from k_2/k_1 of propylene to account for the reactivity of carbon 2.

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[5] These observations pertain to diluted solutions. It is probable that enhancement of the decomposition would be observed in more concentrated solutions.

[6] C. A. Coulson, *J. Chem. Soc.*, 1435 (1955).

[7] *E.g.*, A. J. Petro and C. P. Smyth, THIS JOURNAL, **79**, 6143 (1957).

[8] F. Leavitt, V. Stannett and M. Szwarc, *J. Polymer Sci.*, **31**, 122 (1958).

[9] J. H. Binks and N. Szwarc, *Proc. Chem. Soc.*, 226 (1958); also *J. Chem. Phys.*, in press.

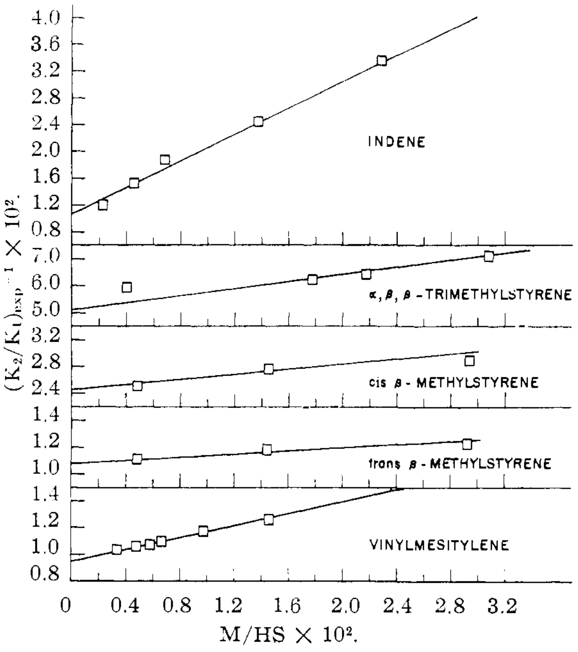

Fig. 1.—Using the equation derived for the calculation of k_2/k_1 in reactions which do not involve H-abstraction from the substrate, one calculates $(k_2/k_1)_{exp}$ in those reactions where H-abstraction from the substrate does take place. It was shown[3] that $(k_2/k_1)_{exp}^{-1}$ varies linearly with the molar ratio of substrate to solvent (M/HS), the intercept giving $(k_2/k_1)^{-1}$ and the slope k_3/k_2.

affinities of α, methylstyrene and styrene is 1.12 while the observed one is 1.17). On the other hand, a methyl substituent placed in the β-position decreases methyl affinity by blocking the reactive center. This is a very general effect and can be utilized for finding the most reactive position of an investigated compound. It seems also that the extent of this inhibition is approximately constant and independent of the reactivity of the substrates as shown by the data listed in Table III. Presence of two methyl substituents on the reactive center increases greatly the steric hindrance as shown by the few examples collected in Table IV. While the average factor determining the steric hindrance of one methyl group is approximately 8 ± 3 (see Table III), the average value for the hindrance caused by two methyl substiuents appears to be about 70. It seems that the contribution of the second methyl substituent of the steric hindrance is only slightly lower than that of the first. However, more data are required to test this hypothesis.

TABLE IV

THE BLOCKING EFFECT OF TWO METHYL SUBSTITUENTS

Compound	k_2/k_1	$(k_2/k_1\text{-unsubst.})/(k_2/k_1\text{subst.})$
α-Methylstyrene	926	. .
α,β,β-Trimethylstyrene	15	62
Butadiene-1,3	2015	. .
2,5-Dimethylhexadiene-2,4	20	100
Dibenzfulvene	~20,000	. .
10,10-Dimethyldibenzfulvene (*i.e.*, 9-isopropylidene fluorene)	300	67

The case of indene deserves some comments. This compound may be considered as a β-methylene substitued styrene which is, of course, coplanar. Its methyl affinity is very close to that of *trans*-β-methylstyrene (96 as compared with 86) and substantially greater than that of *cis*-β-methylstyrene. This shows that the difference in the methyl affinities of *cis*- and *trans*-β-methylstyrenes is due to the lack of coplanarity in the former isomer (compare this case with 9-vinylanthracene and vinyl-mesitylene) and not to the different location of methyl substituent in respect to the C=C double bond. Furthermore, the lower methyl affinity of indene when compared to styrene, attributed to the blocking effect of the CH_2 group, appears to be another argument supporting the hypothesis of non-perpendicular structure of the transition state in methyl radical addition reaction.[10] It is difficult to visualize how this group obstructs the reaction if the methyl radical approaches the molecule in direction perpendicular to the nodal plane. On the other hand, if the radical moves approaching nodal plane, the blocking effect by the CH_2 group might be expected.

The methyl affinity of diisopropenylbenzene is only slightly higher than *twice* the methyl affinity of α-methylstyrene. This slight increase is caused by the greater extent of conjugation in the former compound as compared with the latter one.

The effect of ring substituents on the reactivity of styrene is illustrated by the compounds listed in the third group of Table II. Substitution of chlorine for hydrogen increases the methyl affinities, but the position of the substituent seems to be of no great importance as far as the rate of methyl radical addition is concerned. The enhancing effect of two chlorine substituents seems to demonstrate the additivity of this phenomenon.[11] When presence of one chlorine increases the methyl affinity of the styrene derivative by approximately a factor of 1.25, two chlorines increase it by about a factor of 1.5, *i.e.* $(1.25)^2$.

Presence of a methoxy substituent seems to decrease slightly the respective methyl affinity; the effect is, however, smaller than that observed in other classes of compounds.[12,13]

The last group of Table I lists 1,1-diphenylethylene, dibenzfulvene and its derivatives. The great increase in the reactivity of dibenzfulvene as compared with that of 1,1-diphenylethylene has to be attributed to two factors: the coplanarity of the dibenzfulvene molecule as compared with the skewed shape of 1,1-diphenylethylene and the additional conjugation in the former molecule. Actually, bibenzofulvene is the most reactive hydrocarbon investigated in our laboratory. The blocking effect of methyl substituents, shown by the lower methyl affinities of the last two compounds listed in Table II (*i.e.*, the dibenzfulvenes methylated in the reactive position 10), has been discussed in preceding paragraphs.

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[10] A. Bader, R. P. Buckley, F. Leavitt and M. Szwarc, THIS JOURNAL, **79**, 5621 (1957).

[11] The term "additivity" refers to the log of methyl affinity.

[12] W. J. Heilman, A. Rembaum and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

[13] A. Rajbenbach and M. Szwarc, *Proc. Roy. Soc.* (*London*), in press.

Finally, the effect of structure upon the rate of hydrogen abstraction needs brief discussion. Although a slight trend in $(k_2/k_1)_{\text{exp}}$ (see ref. 3) has been observed for the ten methylated dibenzfulvenes, we doubt whether this trend measures correctly the rate of hydrogen abstraction. The abstraction was definitely observed for vinyl-mesitylene (see Fig. 1) and the value of 2.4 was obtained for $k_{3'}/k_1$, *i.e.*, for the relative rate constant of abstraction per active hydrogen (9 hydrogens are active in vinyl-mesitylene). A considerable abstraction was observed in the reaction involving indene (Fig. 1), and the respective $k_{3'}/k_1$ was found to be 47. The $k_{3'}/k_1$ for toluene[1] seems to be about 1, and thus the value found for vinyl-mesitylene is at least of the expected order of magnitude. The much higher value found for indene arises from two effects: the active hydrogens are secondary and this leads to a ten-fold increase in their reactivity,[3] and the radical formed is conjugated both with a benzene ring and a C=C double bond. This again increases the reactivity, *e.g.*, $k_{3'}/k_1$ for pentadiene-1,4 (secondary hydrogens, radical conjugated to two C=C double bonds) is 20.[13]

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The Photochemical Decomposition of Hydrogen Peroxide in Aqueous Solutions of Allyl Alcohol at 2537 Å.[1]

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The photochemical decomposition of hydrogen peroxide at 2537 Å. has been studied in aqueous solutions with and without added allyl alcohol. At high intensities and low peroxide concentration, the quantum yield for hydrogen peroxide decomposition was independent of intensity and concentration and was found to be 0.94 ± 0.06 in the absence of allyl alcohol and 0.54 ± 0.05 in the presence of allyl alcohol at 27°. These results are consistent with a kinetic interpretation in which the limiting quantum yield in the absence of allyl alcohol should be twice the quantum yield of the primary decomposition of hydrogen peroxide into OH radicals and the limiting yield in the presence of allyl alcohol should be just equal to the quantum yield of the primary decomposition. Evidence for the formation of tetrahydroxyhexane was obtained. This is expected if the mechanism is the addition of hydroxyl radical to allyl alcohol and then association of the diol free-radicals.

Introduction

Independent studies of the vapor phase[2] and aqueous solution[3] photodecomposition of hydrogen peroxide at 2537 Å. have shown that at relatively high intensities and low peroxide concentrations the chain reaction may be suppressed. Under these conditions, the decomposition may be explained by the consecutive reactions

$$H_2O_2 + h\nu \longrightarrow 2OH \qquad k_1I_a \quad (1)$$

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \qquad k_2 \quad (2)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad k_3 \quad (3)$$

The limiting quantum yield at 25° has been variously reported as 1.7 ± 0.4 in the gas phase[2] and 1.4 ± 0.1,[3] 0.98 ± 0.05,[4] 1.9 ± 0.1[5] and 1.00 ± 0.02[6] in solution. The values reported by Lea[3] and by Dainton and Rowbottom[5] were both obtained with unfiltered light from quartz low pressure mercury resonance lamps. Since no precautions were used to eliminate the 1849 Å. resonance radiation generally emitted from such lamps, the values reported are open to serious question. The results of Hunt and Taube[4] and of Baxendale and Wilson[6] are in remarkably good agreement with each other and may be taken as reliable within the stated limits of error.

The complete mechanism for the chain decomposition of H_2O_2 is generally considered to include also the reaction

$$HO_2 + H_2O_2 \longrightarrow H_2O + OH + O_2 \qquad k_4 \quad (4)$$

The quantum yield for peroxide decomposition is then

$$\Phi = 2k_1 + 2k_4(k_1/k_3I_a)^{1/2}(H_2O_2) \qquad (5)$$

Under the limiting conditions referred to, the quantum yield of peroxide decomposition is $2k_1$. Thus one-half the limiting quantum yield is k_1 or the primary quantum yield for peroxide decomposition into OH radicals. This quantity is susceptible to direct experimental determination, and specific methods for the determination of hydroxyl radicals have been used to evaluate k_1.[6,7]

Free-radical trapping by the use of olefinic compounds is a more general method applicable to a wide variety of free-radicals. The nature of the problems involved in water solutions at wave lengths as low as 2537 Å. have been discussed earlier.[8] We wish to report here the use of allyl alcohol, water soluble and transparent at 2537 Å., as a scavenger for free-radicals formed in the photolysis of hydrogen peroxide. Allyl alcohol

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[1] Sponsored by the Office of Ordnance Research, U. S. Army, and by the Research Corporation.

[2] D. H. Volman, *J. Chem. Phys.*, **17**, 947 (1949).

[3] D. E. Lea, *Trans. Faraday Soc.*, **45**, 81 (1949).

[4] J. P. Hunt and H. Taube, THIS JOURNAL, **74**, 5999 (1952).

[5] F. S. Dainton and J. Rowbottom, *Trans. Faraday Soc.*, **49**, 1160 (1953).

[6] J. H. Baxendale and J. A. Wilson, *ibid.*, **53**, 344 (1957).

[7] J. L. Weeks and M. S. Matheson, THIS JOURNAL, **78**, 1276 (1956).

[8] D. H. Volman, J. C. Chen and L. W. Swanson, *ibid.*, **81**, 756 (1959).