Addition of Thiophenol to Polycyclic Vinylarenes[1]

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The relative rates of the free-radical addition of thiophenol to several vinylarenes have been determined. The reactions were run in benzene at a temperature of 70 °C. A good correlation was found between reactivity and the total energy difference between the reactant olefin and the carbon-centered radical intermediate. The calculations were carried out utilizing a semiempirical self-consistent field molecular orbital method. A variable bond length technique was incorporated into this approach. A much poorer correlation was found utilizing the free valence, calculated by the same method, for the terminal methylene position of the olefin. These results can be interpreted as showing that the transition state for the addition of thiyl radical to a vinylarene has a considerable contribution from a form that resembles the intermediate carbon-centered radical

The reaction between an alkyl or aryl mercaptan and an olefin (eq 1) to yield a sulfide is a well-known example of a free-radical addition process.[2]

$$RCH{=}CH_2 + R'SH \longrightarrow RCH_2CH_2SR' \qquad (1)$$

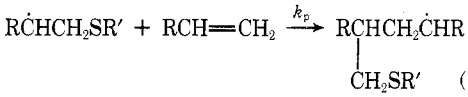
Its radical nature was based on evidence that included the anti-Markownikoff orientation[3] and the rate enhancement both by light[4] and the peroxides.[5] Such evidence led to the formulation of the chain mechanism[6] shown below.

Initiation: $$R'SH \xrightarrow{k(I)} R'S\cdot + H\cdot \qquad (2)$$

Addition: $$R'S\cdot + RCH{=}CH_2 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} R\dot{C}HCH_2SR' \qquad (3)$$

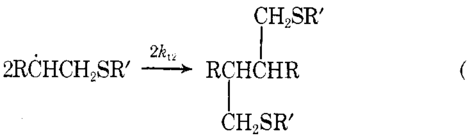
Chain transfer: $$R\dot{C}HCH_2SR' + R'SH \xrightarrow{k_{ct}} RCH_2CH_2SR' + R'S\cdot \qquad (4)$$

Polymerization:

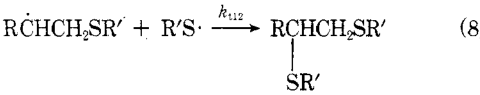


$$R\dot{C}HCH_2SR' + RCH{=}CH_2 \xrightarrow{k_p} RCH(CH_2SR')CH_2\dot{C}HR \qquad (5)$$

Termination: $$2R'S\cdot \xrightarrow{2k_{t1}} R'SSR' \qquad (6)$$



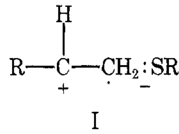
$$2R\dot{C}HCH_2SR' \xrightarrow{2k_{t2}} RCH(CH_2SR')CH(CH_2SR')R \qquad (7)$$



$$R\dot{C}HCH_2SR' + R'S\cdot \xrightarrow{k_{t12}} RCH(SR')CH_2SR' \qquad (8)$$

One of the interesting aspects of this reaction is the reversibility of the addition step (eq 3). It has been shown that *cis*-2-butene is isomerized to the trans compound by methanethiol.[7] This result contrasts, for example, with the observation that during the addition of trichloromethyl radical to 2-butenes no isomerization of the starting materials is observed.[8] Further, it has been suggested that for reactions in which an unstable alkyl thiyl radical adds to an olefin to give a stable carbon-centered radical, the addition is irreversible.[9] However, evidence for this assertion is not conclusive, and the reaction is generally regarded as a facile, reversible addition followed by a rate-determining chain transfer step.[2b,6,10,11]

Several studies have qualitatively[12] and quantitatively[13–15] indicated that substituents in the olefin moiety which donate electrons to the site of the carbon-centered radical (i.e., that would tend to stabilize the intermediate) enhance the rate of the addition reaction, while electron-withdrawing substituents retard it. This effect has been attributed to a contribution by the charge-separated form (I) to the transition state.[12,15] Such a form represents electron transfer to an electronegative attacking radical that precedes atom transfer and bond formation.



$$\overset{+}{R-\underset{}{C}(H)}-CH_2\!:\!\overset{\cdot\;-}{SR'}$$

I

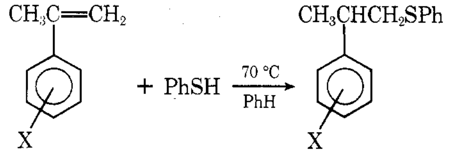
It was felt that an interesting, complementary adjunct to the work dealing with the relationship between the reactivity toward thiyl radical and the electronic characteristics of the olefin moiety would be an examination of the correlation of the rates of reaction for a series of compounds with quantities calculated utilizing a semiempirical self-consistent field approach.[16,17] Unruh and Gleicher[17] have demonstrated that this method gives a good correlation between the relative rates of abstraction from arylmethanes by trichloromethyl radical and the π energy difference between the intermediate carbon-centered radical and the arylmethane reactant. This result was taken as evidence that the transition state of the abstraction process had considerable productlike character.[18] On the other hand, if a better correlation had been observed utilizing some ground-state property of the reactant—free valence, charge density, etc.—then the transition state might be stabilized to a large extent by a contributing form that resembles the reactants.[19] It was felt that a similar study could be made by doing calculations on the olefin reactant and carbon-centered radical intermediate (eq 3).

$$ArCH_3 + \cdot CCl_3 \longrightarrow Ar\dot{C}H_2 + HCCl_3 \qquad (9)$$

Results and Discussion

The technique used for the calculations in this study differed somewhat from that used previously by Unruh and Gleicher.[17] Here, a variable bond length approach has been incorporated into the semiempirical PPPSCF method wherein a new set of bond lengths for the molecule is calculated at the end of each iteration via a linear bond order–bond length relationship.[20,21] These new bond lengths are then used to calculate new values of the repulsion and resonance integrals in the following iteration. Furthermore, the σ energy can be determined using localized-bond models and bond length–bond energy relationships. The total energy is, then, the sum of the carbon–carbon σ and π energies and may more closely reflect the bond length variation observed for "real" molecules than did the earlier method.

The system examined in previous work at this laboratory was the addition of thiophenol to substituted α-methylsty-



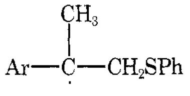
(10)

Table I. Relative Reactivities of Isopropenylarenes toward Thiophenol at 70 °C

Compd (Chart I)	k_x/k_{std}	$\Delta\Delta E_{total}$[a]	F[b]
Phenyl (III)	0.65 ± 0.17[c]	0	0.7816
1-Naph (IV)	0.095 ± 0.01	0.170	0.7859
2-Naph (V)	1.00	0.056	0.7810
9-Anth (VIII)	0.015 ± 0.005	0.507	0.7807
9-Phenanth (IX)	0.033 ± 0.005	0.173	0.7869

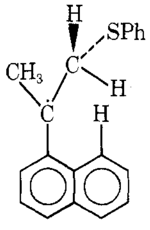
[a] Energy change in eV relative to α-methylstyrene (III). [b] Free valence at the terminal methylene position. [c] Average deviation.

renes at 70 °C in benzene.[15] Originally, it was hoped that a direct extension of this system could be carried out, wherein a series of isopropenylarenes would be allowed to react with thiophenol under the same conditions as before. Two olefins would compete for a limited amount of thiophenol. The relative rates were then to be correlated with either the binding energy differences between the starting olefin and the intermediate free radical (II) or with a ground-state property of the olefin reactant. It is clear from the results in Table I, however, that steric factors are playing a significant role in determining the rate. For any of the compounds with the isopropenyl moiety in a peri position, the rate is lower than expected. This is most likely explained by nonbonded interactions of the type depicted for the structure XII below, where the carbon-centered radical is forced from planarity, thus decreasing the resonance stabilization of the radical.



$$\mathrm{Ar{-}\overset{CH_3}{\underset{\cdot}{C}}{-}CH_2SPh}$$

II



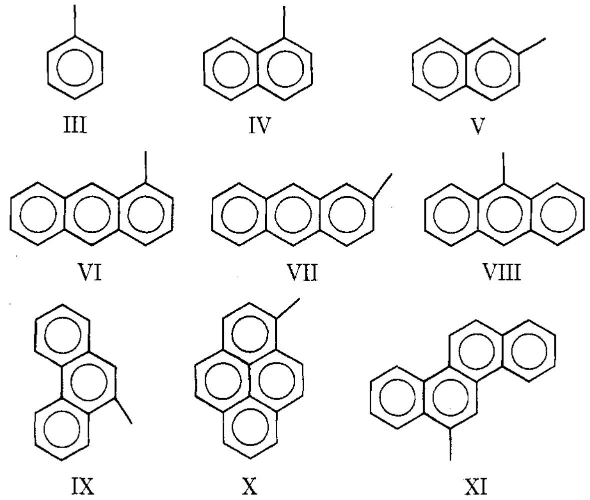
XII

Although interesting, these effects cannot easily be quantitatively incorporated into correlations of reaction rates.

$$\mathrm{ArCH{=}CH_2 + PhSH \xrightarrow[PhH]{70\,°C} ArCH_2CH_2SPh} \qquad (11)$$

Therefore, an alternative system was utilized—thiophenol and vinylarenes. Although these olefins might be thought to have a greater tendency to polymerize than do the corresponding isopropenyl compounds,[22] such reactions were not observed under the experimental conditions. However, it was discovered that the more reactive of these former compounds did seem to polymerize under the conditions encountered during the gas–liquid chromatographic analyses of the reaction mixtures. This problem necessitated a modified method of analyzing the reaction mixtures. The technique finally used involved the measurement of the disappearance of thiophenol and standard olefin (*p*-methoxy-α-methylstyrene). The amount of the vinylarene that disappeared was then calculated by assuming that thiophenol reacted only by addition to the olefins. The amount of the vinylarene that had reacted was then set equal to the difference between the amount of reacted thiophenol and reacted reference olefin. The assumption that thiophenol disappeared only by reaction with the olefins was supported by the apparent lack of any phenyl disulfide or ring-substitution products being formed.

Chart I. Polycyclic Arene Systems



As a test of this modified method of analysis, the original data for the addition of thiophenol to substituted α-methylstyrenes[15] were reexamined. A ρ value of −0.36 ± 0.08 was thus obtained from the correlation of reactivity with the σ^+ substituent parameters. This value is in reasonable agreement with the original value of −0.38 ± 0.02, although the greater uncertainty of the ρ value calculated by the modified method is apparent.

Table II shows the results of the competitive addition of thiophenol to vinylarenes, together with several of the calculated quantities utilized in the attempted correlations with the experimental relative rates. Table III lists the results of these correlations. The correlation of reactivity with the relative total binding energy change is shown in Figure 1. The details of the procedure may be found in the Experimental Section. As can be seen from the results, the uncertainty associated with each relative rate is large. This is probably due

Table II. Relative Reactivities of Vinylarenes toward Thiophenol at 70.0 °C

Registry no.	Compd (Chart I)	Solvent	k_x/k_{std}[a]	$\Delta\Delta E_{total}$	$\Delta\Delta E_\pi$[b]	F[c]
98-83-9	Phenyl (III)	Benzene	0.91 ± 0.14[d]	0	0	0.7697
3710-23-4	2-Naph (V)	Benzene	2.5 ± 0.3	0.061	0.044	0.7691
58873-44-2	9-Phenanth (IX)	Benzene	1.8 ± 0.2	0.125	0.099	0.7748
1855-47-6	1-Naph (IV)	Benzene	3.6 ± 0.5	0.140	0.083	0.7716
58873-45-3	6-Chrys (XI)	Benzene	3.5 ± 0.2	0.142	0.118	0.7827
5668-69-9	2-Anth (VII)	Benzene	5.4 ± 1.2	0.167	0.131	0.7691
58873-46-4	1-Anth (VI)	Benzene	5.9 ± 1.5	0.209	0.143	0.7878
58873-47-5	1-Pyr (X)	Benzene	10.5 ± 3.5	0.234	0.098	0.7747
58873-48-6	9-Anth (VIII)	Benzene	1.6 ± 1.2	0.424	0.375	0.7785

[a] The standard olefin was *p*-methoxy-α-methylstyrene. [b] In electron volts. Changes relative to styrene. [c] Free valence at the terminal methylene position. [d] Average deviation.

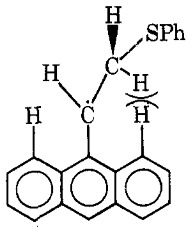
Table III. Correlations between the Reactivities of Vinylarenes and Calculated Quantities[a]

Quantity correlated	Slope	Corr coeff
Total energy change—overall	4.06 ± 0.08[b]	0.932
α-Naphthalene type compds	5.61 ± 0.08	0.944
β-Naphthalene type compds	4.45 ± 0.07	0.972
π-Energy change (SCF)	5.10 ± 0.15	0.730
π-Energy change (HMO)	2.53 ± 0.13	0.858
Total energy change—cation (see discussion)	0.69 ± 0.16	0.802
Free valence	16.7 ± 0.20	0.349

[a] Excluding data for 9-vinylanthracene. [b] Average deviation.

to the indirect method of analysis that was used to determine the rate ratio.

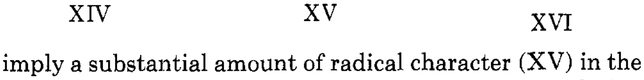
The results seem to indicate that 9-vinylanthracene is much less reactive than would be expected. Apparently, the steric interaction is again more severe in this case. No planar structure is possible which will not show a large peri interaction. Le Fèvre et al. have determined that the angle between the plane of the vinyl group and the plane of the anthracene moiety is 60°.[23] Using this conformation to calculate the energies of the olefin and the radical gave a predicted energy change of −0.110 eV relative to styrene. This corresponds to a predicted reactivity that is much lower than is experimentally observed. Such a discrepancy may reflect either the error in the determination of the conformation of 9-vinylanthracene or that the greater dependence of the radical system upon delocalization may lead to a reduction in the deformation angle at the expense of increased nonbonded interactions which are not explicitly incorporated into the molecular orbital treatment.



XIII

As can be seen in Table III, the total energy change (relative to styrene) calculated by the variable bond length SCF procedure gives a better correlation than either the SCF π binding energy change alone or the HMO π binding energy. Such results seem to indicate the importance of the σ energy component, as well as the previously observed better correlation by the SCF–MO method over the HMO method.[17]

This correlation of reactivity with the energy difference between the intermediate and the olefin reactant seems to



$$\underset{\text{XIV}}{\text{ArCH}{=}\text{CH}_2\cdot\text{SPh}} \longleftrightarrow \underset{\text{XV}}{\text{Ar}\dot{\text{C}}\text{H}{-}\text{CH}_2{-}\text{SPh}} \longleftrightarrow \underset{\text{XVI}}{\text{Ar}\underset{+}{\text{C}}\text{H}{-}\dot{\text{C}}\text{H}_2{:}\underset{-}{\text{SPh}}}$$

imply a substantial amount of radical character (XV) in the transition state of the addition step. The poorer correlation of the reactivity with the energy difference between the olefin and an intermediate carbonium ion (XVII)[24] may reflect a relatively small contribution by the charge-separated form (XVI). The very poor correlation with the free valence certainly is evidence for the lack of any significant stabilization of the transition state by the reactant-like contributing form (XIV). The same was found to be the case when other, appropriate ground-state parameters, such as bond orders or the atom–atom self-polarizability of the terminal carbon, were utilized.

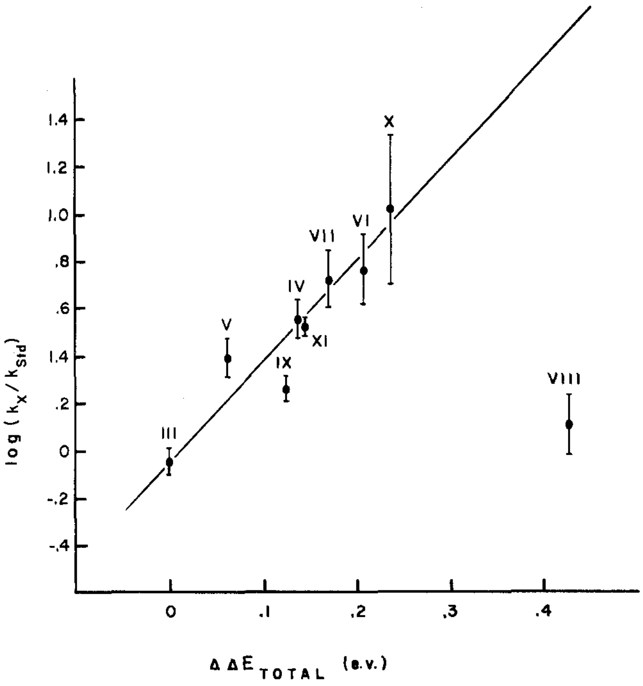
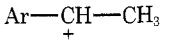


Figure 1. Correlation of log k_x/k_{std} and $\Delta\Delta E_{total}$ for the reaction of vinylarenes with thiophenol.



$$\text{Ar}{-}\underset{+}{\text{CH}}{-}\text{CH}_3$$

XVII

These results indicate a smaller dependence of the rate upon the ability of the arene system to stabilize the transition state of the addition step than was observed earlier for the hydrogen atom abstraction by trichloromethyl radical.[17] This is reasonable in view of the relatively more facile nature of the addition compared to the abstraction process.

Experimental Section

Equipment. NMR spectra were run on either Varian HA-100 or EM-360 spectrometers. Gas–liquid chromatography was done using a Varian Aerograph Model 202B equipped with a thermal conductivity detector and a Sargent recorder with a disc integrator. A 12 ft × 0.25 in. aluminum column packed with 5% SE-30 on Chromosorb W (AW, DMCS) was used for all analyses. Indices of refraction were found using a Bausch and Lombe Abbé refractometer at the indicated temperatures. All melting points were determined on a Mel-Temp apparatus and are uncorrected.

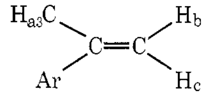
Materials. The purity of all materials, as determined by GLC and/or NMR, was greater than 95%. Reagent grade (Matheson Coleman and Bell) benzene was distilled at 80 °C and dried over sodium wire before use. Reagent grade (Matheson Coleman and Bell) o-dichlorobenzene was stored over Linde molecular sieve. No other

Table IV. Summary of Physical Properties and Overall Yields of the Isopropenylarenes[a]

Compd	Bp (Torr) or mp, °C	n_D^{temp}	Yield, %	Ref
1-Naph	bp 85–100 (1) [114–115 (5)]	1.6053^{25} (1.6137^{20})	78	25
2-Naph	mp 52–53 (56)		83	25
9-Phenan	bp 112–116 (0.05) [163 (20)]	(1.6765^{22})	24	27
9-Anth	mp 81–83 (85–86)		13	28

[a] Literature values in parentheses.

Table V. Summary of NMR Data for the Isopropenylarenes in Carbon Tetrachloride[a]



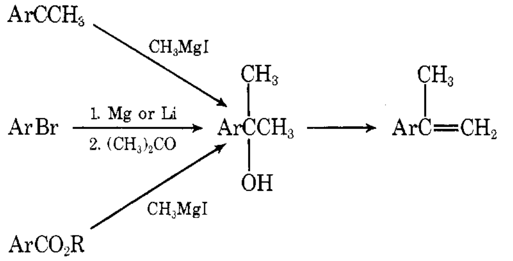
Compd	H_a[b]	H_b[b]	H_c[b]	$H_{aromatic}$
1-Naph	2.16	5.00	5.35	7.10–8.00
2-Naph	2.20	5.10	5.50	7.30–7.80
9-Phenan	2.15	5.10	5.30	7.00–8.50
9-Anth	2.30	5.20	5.70	7.20–8.30

[a] Experimental and calculated proton ratios agree within 5%. [b] Chemical shift from Me_4Si in δ (ppm).

purification was done prior to its use. Commercial α-methylstyrene (Aldrich) was used after distillation at 160–161 °C (760 Torr). Commercial 9-vinylanthracene (Pfaltz and Bauer) was used without further purification. Physical properties and the NMR spectrum can be found in Tables VI and VII, respectively.

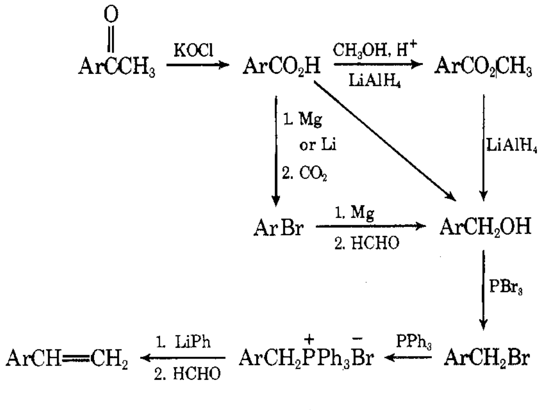
All of the isopropenylarenes were prepared by way of an organometallic addition to a carbonyl compound followed by dehydration of the resulting 2-aryl-2-propanol (Scheme I). The 9-isopropenylphenanthrene derivative was also prepared via a Wittig procedure starting with 9-acetylphenanthrene. Literature procedures were followed. See Table IV for a summary of the physical properties of the isopropenylarenes, as well as references to their syntheses. Table V contains a summary of the NMR data for these compounds.

Scheme I



Several of the vinylarenes (styrene, 1- and 2-vinylnaphthalene) were synthesized by a similar procedure. However, for many of these compounds, the final dehydration was accompanied by extensive polymerization of the product olefin. Thus, Scheme II was followed with reasonable success. Literature procedures[29] were followed for all of the reactions except the final step. The preparation of the olefin was carried out by adding an equimolar amount of phenyllithium in ether to a suspension of the phosphonium bromide in tetrahydrofuran. Formaldehyde was then added. Workup then easily yielded pure olefin. Overall yields starting from the acid were on the order of 10–40%. Tables VI and VII summarize physical properties and NMR data, respectively.

Scheme II



Kinetics. The basic procedure has been described previously.[35] An isopropenylarene, 2-isopropenylnaphthalene, thiophenol, o-dichlorobenzene, and benzene were mixed in the ratio of 1:1:1:1:10, respectively. These solutions were then divided between eight Pyrex ampules, degassed, and sealed under low pressure nitrogen. Seven of these tubes were then heated at 70.0 °C, the eighth being retained as the reference sample. Thermal initiation proved to be adequate in this case, and up to 90% reaction occurred after 30 min. Analysis of the reaction mixtures was identical with the method employed in the earlier study.[15]

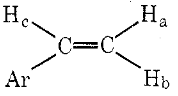
Mixtures containing a vinylarene, p-methoxy-α-methylstyrene, thiophenol, o-dichlorobenzene, and benzene in the approximate ratio

Table VI. Summary of Physical Properties and Overall Yields of Vinylarenes[a]

Compd	Bp (Torr) or mp, °C	$n_D{}^{temp}$	Yield, %	Ref
Styrene	bp 100–110 (50) [145–146 (760)]	1.5430^{25} (1.5463^{20})	48	30
1-Naph	bp 79–80 (0.45) [115–116 (4)]	1.6411^{25} (1.6436^{20})	12	31
2-Naph	mp 64–66 (66)		26	32
1-Anth	mp 53–56 (58–61)		4.2	28
2-Anth	mp 185–189 (187–188)		4.7	28
9-Anth	mp 60–63 (64–67)			28
9-Phenanth	bp 140 (0.1) [194–197 (6)]		10	33
1-Pyr	mp 82–84 (87–89)		20	34
6-Chrys	mp 138–140		2.8	

[a] Literature values in parentheses.

Table VII. Summary of NMR Data for the Vinylarenes in Deuteriochloroform[a]



Registry no.	Compd	H_a[b]	H_b[b]	H_c[b,c]	H_{arom}[b]
100-42-5	Styrene	5.16 (J_{ab} = 1)	5.66 (J_{bc} = 18)	6.65 (J_{ac} = 10)	7.00–7.45
826-74-4	1-Naph	5.36 (J_{ab} = 1)	5.65 (J_{bc} = 18)	(J_{ac} = 10)	7.20–7.45
827-54-3	2-Naph	5.25 (J_{ab} = 1.5)	5.75 (J_{bc} = 18)	6.80 (J_{ac} = 10)	7.20–7.70
22584-39-0	1-Anth	5.41 (J_{ab} = 1.5)	5.74 (J_{bc} = 17)	(J_{ac} = 11)	7.10–8.67
2026-16-6	2-Anth	5.40 (J_{ab} = 0)	5.93 (J_{bc} = 17)	6.97 (J_{ac} = 11)	7.40–8.46
2444-68-0	9-Anth	6.00 (J_{ab} = 2)	5.63 (J_{bc} = 17)	(J_{ac} = 11)	7.33–8.50
14134-06-6	9-Phenanth	5.34 (J_{ab} = 2)	5.69 (J_{bc} = 16)	(J_{ac} = 11)	7.01–8.55
17088-21-0	1-Pyr	5.49 (J_{ab} = 2)	5.87 (J_{bc} = 17)	(J_{ac} = 11)	7.48–8.39
58873-49-7	6-Chrys	5.60 (J_{ab} = 2)	6.00 (J_{bc} = 16)	(J_{ac} = 11)	7.20–9.00

[a] Experimental and calculated proton ratios agree within 5%. [b] Chemical shift from Me_4Si in δ (ppm). Coupling constants in hertz in parentheses. [c] Often partially buried in the "aromatic" signal.

of 1:1:1:1:75 were prepared and divided among eight ampules as before. When the vinylarenes were 1-, 2-, or 9-vinylanthracene or 1-vinylpyrene, about 5 mol % benzoyl peroxide was added to seven of the ampules before sealing. This was done because the vinylanthracenes and 1-vinylpyrene all seemed to undergo photoinduced dimerization reactions. The other compounds were all initiated by light. One ampule was always reserved as a reference solution. Seven ampules were then allowed to react at 70.0 °C in a constant-temperature bath for times ranging from 10 to 40 h. From 15 to 80% of the vinylarenes reacted in this period. When photolytic initiation was used, a 275-W sun lamp was placed 10 cm above the tubes in the bath.

The usual calculations of the relative rates[35] were modified in the following manner. The areas of the olefins and thiophenol relative to the internal standard are calculated by

$$X = A/S \qquad (12)$$

where X is a relative area, A is an actual measured area, and S is the area of the internal standard. Using the normal method of analysis, the rate ratio is given by

$$\frac{R_1}{R_2} = \frac{\ln\left[\dfrac{X_1{}^{\mathrm{i}}}{X_1{}^{\mathrm{f}}}\right]}{\ln\left[\dfrac{X_2{}^{\mathrm{i}}}{X_2{}^{\mathrm{f}}}\right]} \qquad (13)$$

The subscripts refer to olefins 1 and 2 and the superscripts i and f denote unreacted and reacted samples, respectively. If olefin 1 is a vinylarene, the numerator may be calculated as follows

$$\frac{X_1{}^{\mathrm{i}}}{X_1{}^{\mathrm{f}}} = \frac{M_1}{M_1 - M_{\mathrm{s}}\bullet\left[1 - \dfrac{X_{\mathrm{s}}{}^{\mathrm{f}}}{X_{\mathrm{s}}{}^{\mathrm{i}}}\right] + M_2\bullet\left[1 - \dfrac{X_2{}^{\mathrm{f}}}{X_2{}^{\mathrm{i}}}\right]} \qquad (14)$$

where the M's are the number of moles of each of the indicated species that were initially weighed out in the preparation of the reaction mixture. Subscripts refer to olefins 1 and 2 and to thiophenol S. Expression 14 is then substituted into eq 13 and the rate ratio is calculated as before.

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Registry No.—Thiophenol, 108-98-5.

References and Notes

(1) Taken from the Ph.D. Thesis of D. F. Church.
(2) (a) F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940); (b) R. M. Kellog, "Methods in Free Radical Chemistry", Vol. II, E. S. Huyser, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 1.
(3) T. Posner, *Ber. Dtsch. Chem. Ges.*, **38**, 646 (1905).
(4) F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928).
(5) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933).
(6) R. Back, G. Trick, C. McDonald, and C. Sivertz, *Can. J. Chem.*, **32**, 1078 (1954).
(7) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).
(8) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **77**, 4638 (1955).
(9) D. M. Graham, R. L. Mieville, and C. Sivertz, *Can. J. Chem.*, **42**, 2239 (1964).
(10) M. Onyszchuk and C. Sivertz, *Can. J. Chem.*, **33**, 1034 (1955).
(11) R. H. Pallen and C. Sivertz, *Can. J. Chem.*, **35**, 723 (1957).
(12) C. Walling, D. Seymour, and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **70**, 2559 (1948).
(13) J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc. B*, 1191 (1961).
(14) S. Sakai, H. Miyachi, and Y. Ishii, *Bull. Jpn. Pet. Inst.*, **12**, 72 (1970).
(15) D. F. Church and G. J. Gleicher, *J. Org. Chem.*, **40**, 536 (1975).
(16) (a) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969; (b) J. N. Murrell and A. J. Harget, "Semi-Empirical Self-Consistent Field Molecular Orbital Theory of Molecules", Wiley-Interscience, New York, N.Y., 1972.
(17) J. D. Unruh and G. J. Gleicher, *J. Am. Chem. Soc.*, **93**, 2008 (1971).
(18) M. J. S. Dewar and C. C. Thompson, *J. Am. Chem. Soc.*, **87**, 4414 (1965).
(19) H. H. Greenwood and R. McWeeny, *Adv. Phys. Org. Chem.*, **4**, 73 (1966).
(20) M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).
(21) M. J. S. Dewar and T. Morita, *J. . Chem. Soc.*, **91**, 796 (1969).
(22) This latter system was originally chosen because it was felt that the tertiary benzylic-type position would be less prone to undergo reaction with another molecule of olefin, this being due to its greater steric bulk.
(23) R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. B*, 775 (1968).
(24) Form XVII was chosen only as an approximation to the charge-separated form XVI, i.e., a structure having a positive charge at a position α to the arene moiety.
(25) Yu. S. Zal'kind and S. A. Zonis, *J. Gen. Chem. USSR* (*Engl. Transl.*), **6**, 988 (1936).
(26) F. Bergmann and A. Weizmann, *J. Org. Chem.*, **9**, 352 (1936).
(27) E. Bergmann and F. Bergmann, *J. . Chem. Soc.*, **59**, 1443 (1937).
(28) E. G. E. Hawkins, *J. Chem. Soc.*, 3858 (1957).
(29) S. Akiyama, K. Nakasuji, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, **44**, 2231 (1971).
(30) "The Handbook of Chemistry and Physics", 49th ed, R. C. Weast, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p C547.
(31) L. Palfry, S. Sabetay, and D. Sontag, *C. R. Acad. Sci.*, **194**, 2065 (1932).
(32) W. Davies and Q. N. Porter, *J. Chem. Soc.*, 459 (1957).
(33) C. C. Price and B. D. Halpern, *J. Am. Chem. Soc.*, **73**, 818 (1951).
(34) R. G. Flowers and F. S. Nichols, *J. Am. Chem. Soc.*, **71**, 3104 (1949).
(35) G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).

Effect of Acetylene Structure on the Rates and Products of Addition of 4-Chlorobenzenesulfenyl Chloride[†]

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The rates and products of addition of 4-chlorobenzenesulfenyl chloride to acetylene and 12 alkyl-substituted derivatives have been determined in 1,1,2,2-tetrachloroethane at 25 °C. The effect of the alkyl groups on the rate of addition to 10 of the 13 alkynes can be correlated by means of the Taft equation: $\log k_2 = -4.47\Sigma\sigma^* + 1.64$. The three compounds that do not lie on the line contain *tert*-butyl substituents. Polar effects of the substituents on the rates are dominant and steric effects are important only for *tert*-butyl groups. The product regiochemistry, however, is determined by the steric bulk of the substituent. The results are consistent with a mechanism involving bridged thiirenium ion-like rate and product determining transition states.

The electrophilic addition of arenesulfenyl chlorides to alkynes has received much less attention than the analogous addition to alkenes. The majority of work on this subject has been concentrated on the addition to phenyl-substituted alkynes.[2–4] We now wish to present the results of a systematic study of the polar and steric effects of alkyl groups on the rate and products of addition of 4-chlorobenzenesulfenyl chloride to alkynes in 1,1,2,2-tetrachloroethane at 25 °C.

Results and Discussion

Effect of Alkyl Groups on the Rate of Addition. The rates of addition of 4-chlorobenzenesulfenyl chloride to acetylene (**1**) and 12 alkyl-substituted derivatives (**2–13**) were measured by following the disappearance of the 4-chloro-

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[†] Reactions of Sulfenyl Halides and Their Derivatives. 14. For part 13 see ref 1.