**Registry No.**—**2**, 27069-39-2; **3**, 53596-99-9; **4**, 53597-00-5; **5**, 53597-01-6; **6**, 24795-49-1; **7**, 53597-02-7; **8**, 53597-03-8; **9**, 53597-04-9; **10**, 53597-05-0; **11**, 53597-06-1; **12**, 42391-78-6; propane-1,3-dithiol di-*p*-toluenesulfonate, 3866-79-3; methyl fluorosulfonate, 421-20-5.

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(10) We thank Professor C. H. Heathcock for kindly supplying us with the spectra of this compound.

(11) The apparatus described by W. S. Johnson and W. P. Schneider ["Organic Syntheses," Collect. Vol. IV, New York, N.Y., 1963, p 132] was used to maintain an argon atmosphere. The isolation procedure consisted of thorough extractions with the specified solvent, washing the combined extracts with saturated brine solution, and drying the extracts over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts under reduced pressure on a rotary evaporator. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. Infrared spectra were obtained with a Perkin-Elmer 137 spectrophotometer. Infrared absorption are reported in wavelengths (μm) and are standardized with reference to the 6.24-μm peak of polystyrene. Nuclear magnetic resonance spectra were recorded with a Varian T-60 spectrometer. Signals are reported as the chemical shift downfield from tetramethylsilane (TMS) in parts per million (ppm) of the applied field. The multiplicity of the peak is abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; multiplet, m. Coupling constants are reported in hertz (Hz). Melting points were determined on a calibrated Thomas capillary melting point apparatus. Melting points are not corrected.

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# The Effect of Substituents on the Addition of Thiophenol to α-Methylstyrene[1]

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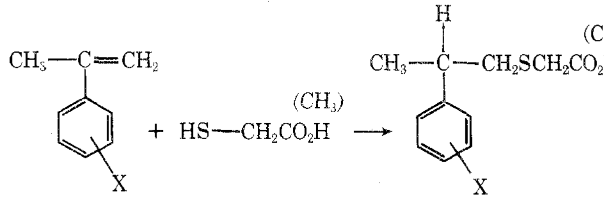
The additions of free radicals in general,[2] and of thiyl radicals in particular,[3] to carbon–carbon double bonds have been studied extensively over the years. Examples of the application of Hammett-type linear free-energy treatments to such a reaction, however, are rather rare.[4] In the case of thiyl radical addition, previous work[4b,c] tended to indicate that electron-donating substituents enhanced the rate of addition, while electron-withdrawing substituents retarded it. However, these studies, which dealt with the reaction (eq 1) between thioglycolic acid (or its methyl ester) and substituted α-methylstyrenes, suffer due to the small number of different substituted compounds examined and the possibility of competing ionic addition in certain cases. It was felt that a more extensive Hammett study of this reaction might be of interest.



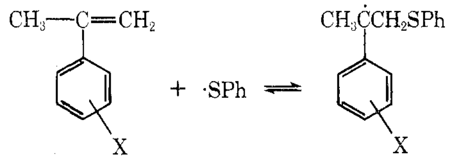
(1)

**Table I**
**Relative Reactivities of Substituted α-Methylstyrenes toward Thiyl Radicals at 70°**

| Substituent | Registry no. | $\sigma^a$ | $\sigma^{+a}$ | $k_X/k_H$ |
|---|---|---|---|---|
| $p$-$CH_3O$ | 1712-69-2 | −0.27 | −0.778 | 1.85 ± 0.13 |
| $p$-$CH_3$ | 1195-32-0 | −0.17 | −0.311 | 1.36 ± 0.18 |
| $m$-$CH_3$ | 1124-20-5 | −0.07 | −0.066 | 1.15 ± 0.09 |
| H | 98-83-9 | 0.00 | 0.00 | 1.00 |
| $m$-$CH_3O$ | 25108-57-0 | 0.12 | 0.047 | 1.02 ± 0.07 |
| $p$-Cl | 1712-70-5 | 0.23 | 0.114 | 0.98 ± 0.04 |
| $m$-Cl | 1712-71-6 | 0.37 | 0.399 | 0.69 ± 0.10 |
| $m$-$CF_3$ | 368-79-6 | 0.47 | 0.52 | 0.58 ± 0.07 |
| $p$-$NO_2$ | 1830-68-8 | 0.78 | 0.790 | 0.99 ± 0.10 |

[a] Reference 5.

The system chosen for study involved photoinduced competitive reactions of pairs of substituted α-methylstyrenes with thiophenol under nitrogen at reduced pressure. It was felt that the possible reversibility of addition step[2,3] (eq 2) should not affect the validity of the result from the linear free-energy treatment under these conditions. In support of this assumption was an experiment of Cadogan and Sadler[4c] in which they found that the relative reactivity ratio for a pair of substituted α-methylstyrenes toward the thiyl radical derived from methyl thioglycolate remained constant as the relative initial concentration of methyl thioglycolate was varied.



(2)

Our results for the relative reactivities of substituted α-methylstyrenes toward the thiyl radical from thiophenol in benzene at 70° are listed in Table I. Nearly identical reactivity ratios were obtained when thiyl radicals were thermally, rather than photolytically, generated. In the former case, however, a lessened total reactivity was observed. When a linear free-energy treatment is applied using the Hammett $\sigma$ constants, a $\rho$ value of $-0.57 \pm 0.03$ (correlation coefficient, $r = -0.962$) is obtained, while using the Okamoto–Brown $\sigma^+$ parameters gives $\rho$ equal to $-0.38 \pm 0.02$ ($r = -0.984$).[5] Both of these $\rho$ values were obtained using all of the data points except that corresponding to the para nitro compound. A graphic presentation of the linear free-energy treatment using the $\sigma^+$ parameters is shown in Figure 1.

The anomalously high reactivity of *p*-nitro-α-methylstyrene observed in this study has also been noted in previous work[4c,d] for strongly electron-withdrawing substituents in the para position. It has been attributed to enhanced resonance stabilization of the benzylic free radical by such groups. An alternative explanation is suggested by the work of Walling, *et al.*[6] In a copolymerization study, the relative reactivities of a series of substituted styrenes toward styrene radical were determined. These results show rate enhancement by electron-withdrawing substituents and tend to correlate with the $\sigma^-$ parameters. Thus, the high reactivity of the para nitro compound in the present study could be due to copolymerization taking place preferentially to,

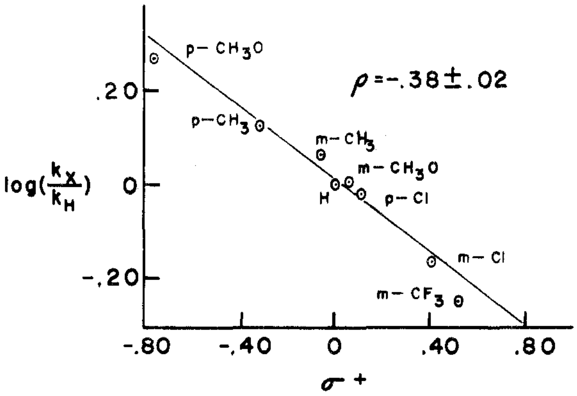
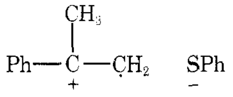


**Figure 1.** Correlation of log $k_X/k_H$ and $\sigma^+$ for the addition of thiophenol to substituted $\alpha$-methylstyrenes.

or together with, the desired addition process. This possibility was supported by an experiment in which a small amount of thiophenol caused more than twice the expected amount of *p*-nitro-$\alpha$-methylstyrene to react.

The reaction shows a modest dependence upon the substituent in the $\alpha$-methylstyrene system. The $\rho$ value appears to be consistent with the exothermic addition step.[7] In terms of the Hammond postulate,[8] the transition state should tend to resemble the olefin plus thiyl radical more than the intermediate benzylic radical, giving rise to less sensitivity of the reaction to the substituent. Furthermore, the better correlation was obtained with the $\sigma^+$ parameters. In the formalism of Russell,[9] this result can be taken as evidence for significant contribution by structure I to the transition state of the addition step. Another explanation of such substituent effects, suggested by a number of groups,[4c–e] is that they arise out of initial complex formation between the olefin and radical. However, at the present time, no definitive choice between these two interpretations can be made.



$$\mathrm{Ph{-}\overset{CH_3}{\underset{+}{C}}{-}\underset{\cdot}{C}H_2\quad \underset{-}{SPh}}$$

I

## Experimental Section

**Materials.** Reagent benzene and *o*-dichlorobenzene were used without further purification. Commercial $\alpha$-methylstyrene was distilled before use. In general, the substituted $\alpha$-methylstyrenes were prepared from the appropriate aryl Grignard and acetone, followed by dehydration, according to literature methods.[10] *p*-Nitro-$\alpha$-methylstyrene was prepared from cumene by nitration, followed by bromination with *N*-bromosuccinimide, and dehydrobromination.[11] Glc analysis showed the purity of all compounds to be greater than 98%. Physical properties of all compounds agreed with literature values.

**Equipment.** All glc analyses were performed on a Varian Aerograph Model 202B and a Sargent recorder with a disc integrator. A 0.25 in. × 12 ft aluminum column packed with 5% SE-30 on Chromosorb W or a 0.25 in. × 12 ft aluminum column packed with 8% FFAP on Chromosorb W were used.

**Product Studies.** An approximate 1:1:5 mixture of thiophenol, $\alpha$-methylstyrene, and benzene was irradiated with a 275-w sunlamp for 1 hr at 70°. Glc analysis showed only the reactants (>94% reacted) and one other peak of considerably longer retention time. Isolation and analysis of this component showed that it was 2-phenyl-1-thiophenoxypropane.

A similar study was carried out for *p*-methoxy-$\alpha$-methylstyrene. From this study it was determined that less than 4% of the olefin disappeared *via* polymerization. Total reaction was again greater than 90%.

A final study was carried out to determine whether the overall reaction was reversible. Equimolar amounts of 2-phenyl-1-thiophenoxypropane and *p*-methoxy-$\alpha$-methylstyrene were allowed to react for 45 min in benzene at 70°. No $\alpha$-methylstyrene was observed to be formed and the para methoxy compound decreased by no more than 2%.

**Kinetics.** The basic kinetic procedure has been described previously.[12] Mixtures of approximately 1:1:1:1:5 $\alpha$-methylstyrene I, $\alpha$-methylstyrene II, thiophenol, *o*-dichlorobenzene, and benzene were used. Reaction times varied from 35 to 90 min with per cent reaction 31–62%. The substituted $\alpha$-methylstyrenes were run against *p*-chloro-$\alpha$-methylstyrene in order to facilitate glc analysis. The rates of reaction relative to *p*-chloro-$\alpha$-methylstyrene were then adjusted so that the parent hydrocarbon had a relative reactivity of 1.00.

**Registry No.**—Thiophenol, 108-98-5.

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