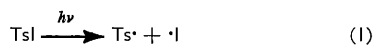


Evidence for the Electrophilic Character of the Toluene-*p*-Sulphonyl Free Radical: Relative Rates of its Addition to Some Substituted Styrenes

By C. M. M. da Silva Corrêa and William A. Waters,* The Dyson Perrins Laboratory, Oxford University, Oxford OX1 3QY

Relative rates of photochemically promoted additions of toluene-*p*-sulphonyl iodide to styrene and four of its derivatives have been measured in benzene solutions containing picric acid to inhibit concurrent polymerisation. Electron-attracting substituents in the Ar group of Ar·CH₂·CH₂ retard the rate of addition of Tol·SO₂· to the double bond. With reference to σ⁺ (Brown) ρ is estimated as -0.50 and with reference to σ (Hammett) as -0.55.

WE have shown¹ that the addition of toluene-*p*-sulphonyl iodide to styrene is a photochemically promoted homolytic reaction (1)—(3) which occurs with very little polymerisation (4) of the styrene, and from a



study of the reaction between toluene-*p*-sulphonyl iodide and polycyclic aromatic hydrocarbons² have inferred that the toluene-*p*-sulphonyl radical MeC₆H₄·SO₂· has electrophilic character. We have now substantiated the latter conclusion by measuring the relative rates of addition of toluene-*p*-sulphonyl iodide to styrene and several substituted styrenes (see Table 2) in benzene solution by g.l.c. measurement of consumption of styrene monomers when two of these are allowed to react competitively with less than an equivalent of toluene-*p*-sulphonyl iodide.

¹ C. M. M. da S. Corrêa and W. A. Waters, *J. Chem. Soc. (C)*, 1968, 1874.

² C. M. M. da S. Corrêa and W. A. Waters, *J. Chem. Soc. (C)*, 1968, 1880.

Reaction (2) is of the first order with respect to monomeric styrene (M) and if this is rate-determining then we obtain equation (5) where $[M_0]$, $[M_0']$, and $[M_t], [M_t']$

$$k'/k = (\log [M_t'] - \log [M_0']) / (\log [M_t] - \log [M_0]) \quad (5)$$

are the initial and final concentrations of the styrene monomers and k and k' the rate constants for addition of toluene-*p*-sulphonyl radicals. However with $[M_0]$ and $[M_0']$ both greater than $[Ts \cdot I]_0$ reaction (3) becomes slow when the addition is nearly complete and, as we have found, some loss of monomeric styrene by polymerisation (4) can then occur. Consistent measurements of relative rate constants, k'/k , have however been obtained by adding picric acid to the reacting mixtures to inhibit polymerisation of the styrenes; it failed however with the most reactive of these which we examined, *viz.*, *p*-methoxystyrene. Since g.l.c. measurements of relative peak areas are most accurate when these areas are approximately equal, *p*-bromostyrene was chosen as the reference monomer.

Table 2 and the Figures show that, as expected, the presence of electron-attracting substituents in the styrene nucleus decreases the rate of addition of toluene-*p*-sulphonyl radicals. The relationship $\log k/k_0 = \rho^+ \sigma^+$, apposite for the addition of a polar reagent (Figure 2), accords with our findings slightly better than the Hammett $\rho \sigma$ relationship and the small values of ρ^+ (-0.50) or ρ (-0.55) are consistent with a homolytic but not a heterolytic process.

EXPERIMENTAL

Materials.—The styrenes were twice distilled under reduced pressure and stored at 0 °C in the absence of light. *p*-Chloro- and *m*-nitro-styrenes were made by thermal decarboxylation of the corresponding cinnamic acids and *p*-methylstyrene by dehydration of 2-*p*-tolylethanol; styrene and *p*-bromostyrene were purchased reagent-quality materials. Toluene-*p*-sulphonyl iodide was prepared as described in ref. 1 and analytical quality benzene was dried and then distilled before use.

Procedure.—Weighed quantities (100–300 mg) of two styrene derivatives (one of which was *p*-bromostyrene) were placed in Pyrex glass tubes surrounded by black paper, dissolved in benzene (10 ml), and mixed with a smaller amount (*cf.* Table 1) of toluene-*p*-sulphonyl iodide. The tubes were then stoppered, placed in a thermostat at 43 °C, and irradiated with a mercury lamp for 30 min, by which time nearly all the toluene-*p*-sulphonyl iodide had been consumed. The tubes were then cooled, 2,4,6-tri-*t*-butylphenol (6 mg) was added to each to inhibit styrene polymerisation during all subsequent operations, and then a weighed amount of either durene or *p*-nitrotoluene to serve as an internal standard for g.l.c. analysis by means of a Pye chromatograph, model I4 (serial 104) equipped with a hydrogen flame ionisation detector and coupled to a KENT electronic integrator (Chromalog 2). Nitrogen was used as carrier gas and the column packings were either Carbowax 20M containing terephthalic acid or Chromosorb W, or polyethylene glycol succinate on Embacel (60–100 mesh).

The ratios $F = M \cdot A_s : S_0 \cdot A_m$ between the peak areas given by standard substance (A_s) and by each monomeric

styrene (A_m) and their concentrations (S, M) were separately determined for a wide range of mixtures which had not been illuminated. The average analytical errors in M_{found} were

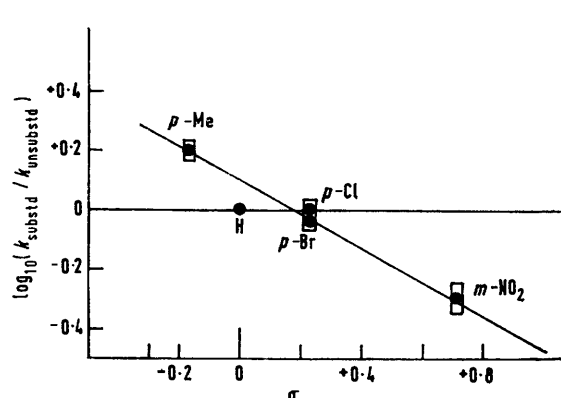


FIGURE 1 Plot of $\log(k'/k)$ against Hammett's σ constant

TABLE 1

Competition between styrene and *p*-bromostyrene

Reactants (mmol)			$\frac{k_{\text{styrene}}}{k_{\text{bromostyrene}}}$
Styrene	<i>p</i> -Bromostyrene	TsI	
A No inhibitor			
1.34	0.79	0.31	1.58
0.82	0.99	0.34	0.81
1.26	1.61	0.33	0.97
1.28	1.16	0.26	1.03
1.64	1.34	0.31	0.75
B Picric acid added			
1.17	1.26	0.48	1.04
0.82	1.56	0.44	1.09
1.69	1.07	0.45	0.98
0.84	0.85	0.45	1.16
1.25	0.75	0.45	1.16

TABLE 2

Relative rate ratios in presence of picric acid

Styrene	k'/k	No. of comparisons
<i>p</i> -Methylstyrene	1.57 ± 0.15	4
Styrene	1.00	—
<i>p</i> -Bromostyrene	0.92 ± 0.08	5
<i>p</i> -Chlorostyrene	1.00 ± 0.07	5
<i>m</i> -Nitrostyrene	0.51 ± 0.07	6

These figures have been calculated by use of the rate data given in Table 1B since styrene was not the primary standard; see text.

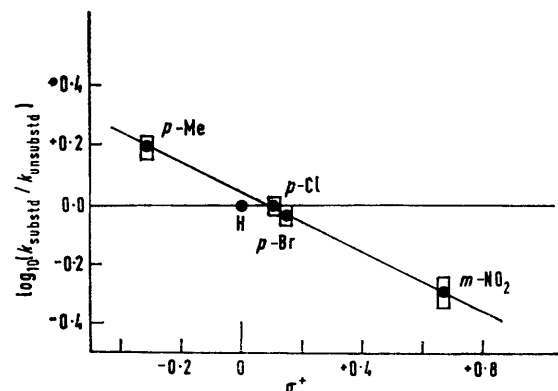


FIGURE 2 Plot of $\log(k'/k)$ against Brown's σ^+ constant

$\pm 4\%$ but variations of up to 30% were found in k'/k . This error was however reduced to $\pm 10\%$ by the use of a 0.5% solution of picric acid in benzene instead of pure benzene as the solvent.

RESULTS

Table 1 illustrates the improvement in the consistency of k'/k resulting from the addition of picric acid: Table 2

summarises the results which are plotted logarithmically in Figures 1 and 2.³

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³ σ and σ^+ Values are taken from C. K. Ingold, 'Structure and Mechanisms in Organic Chemistry,' Bell, London, 1969, 2nd edn., p. 1207.
