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Studies of Sulfonyl Radicals. II.[1] Relative Reactivities of Addition Reactions of Sulfonyl Free Radicals to Vinyl Monomers

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Addition reactions of various vinyl monomers towards the free methanesulfonyl and arenesulfonyl radicals have been investigated. Relative reactivities of *p*-methylstyrene (M_2) to styrene (M_1) towards methane- and *para*-substituted benzenesulfonyl radicals are hardly affected by the kind of sulfonyl radical, suggesting that an unpaired electron of methanesulfonyl and arenesulfonyl radicals is localized mainly on sulfonyl groups. Relative reactivities obtained with vinyl monomers were correlated to Hammett's σ_p values with $\rho_p=-3.6$ and also to Alfrey-Price's *e* values, indicating that sulfonyl radicals are strongly electrophilic. The highest selectivity of the benzenesulfonyl radical, obtained in the comparison of the selectivity of a number of radicals in addition reactions towards three representative monomers (Table 5), also supports the above conclusion.

In previous papers concerning radical copolymerization of sulfur dioxide and styrene emphasis has been laid on two aspects of the growing sulfonyl radicals ($\sim SO_2\text{-}CH_2CH(C_6H_5)\text{-}\dot{S}O_2$ and $\sim CH_2CH(C_6H_5)\text{-}CH_2CH(C_6H_5)\text{-}\dot{S}O_2$), *viz.*, their reactivity and their relationship to the compositions of poly(styrene sulfone).[2]

In this paper we report the reactivities relative to styrene of addition reactions of various vinyl monomers towards benzenesulfonyl and other sulfonyl radicals, giving a discussion on the nature of sulfonyl radicals. The formations of sulfonyl radicals from sulfonyl iodides have been studied by many investigators.[3-5] Corrêa and Waters[3] showed that addition of sulfonyl iodide to styrene occurs with very little polymerization. They have investigated on the addition reaction of *p*-toluenesulfonyl radical to *para*- or *meta*-substituted styrenes, showing that sulfonyl radical has an electrophilic character from the values of $\rho(\rho=-0.55$ or $\rho^+=-0.50)$ in the Hammett plot.[6] Truce and his co-workers have studied addition reaction to allenes and acetylene.[4,7]

We have investigated the same type of addition reaction of various vinyl monomers such as styrene, methyl methacrylate, acrylonitrile, and 1-hexene, by using sulfonyl iodides.

Experimental

Materials. Benzene, toluene, chlorobenzene, decane, and vinyl monomers were purified in the usual way. *p*-Methylstyrene was prepared from 1-(*p*-tolyl)ethanol by $KHSO_4$ dehydration and distilled twice under reduced pressure. Vinyl monomers were stored at temperature below −20 °C after purification.

Benzene-, *p*-toluene-, *p*-chlorobenzene-, and methane-sulfonyl iodide were synthesized from the corresponding sulfonyl chlorides.[21,22] *p*-Methoxybenzenesulfonyl iodide was synthesized from anisole and chlorosulfuric acid by means of the corresponding chloride.[23] All the sulfonyl iodides except methanesulfonyl iodide were recrystallized at least twice from carbon tetrachloride and dried under reduced pressure at temperatures below −20 °C in order to prevent decomposition.

Found: C, 26.57; H, 2.05%. Calcd for $C_6H_5IO_2S$ (benzenesulfonyl iodide): C, 26.87; H, 1.87%.

Found; C, 29.88; H, 2.33%. Calcd for $C_7H_7IO_2S$ (*p*-toluenesulfonyl iodide): C, 29.79; H, 2.48%.

Found: C, 28.03; H, 2.68%. Calcd for $C_7H_7IO_3S$ (*p*-methoxybenzenesulfonyl iodide): C, 28.29; H, 2.35%.

Found: C, 23.84; H, 1.48%. Calcd for $C_6H_4ClIO_2S$ (*p*-chlorobenzenesulfonyl iodide): C, 23.82; H, 1.32%.

Competitive Addition of Styrene and p-Methylstyrene towards Benzenesulfonyl Iodide. Toluene solution containing a definite amount of styrene (0.84 to 3.22 mmol), *p*-methylstyrene (0.94 to 3.15 mmol), and benzenesulfonyl iodide (0.55 to 2.14 mmol) was placed in a Pyrex glass reaction tube covered with an aluminum foil to intercept the light. The reaction tube thus prepared was connected to a vacuum system, the solution was frozen, and then the system was degassed in the usual way at least three times. After the last freeze-pump-thaw cycle, the system was closed and disconnected from the vacuum system. The reaction tube was placed in an ice-water mixture and the reaction was initiated with daylight by removing the aluminum foil. In the dark, the reaction did not occur even after 24 h. Under our experimental conditions, benzenesulfonyl iodide charged was almost completely consumed within 30 min and the yellow reaction solution became colorless at the end of the reaction. The reaction mixture was then washed with 10% aqueous $Na_2S_2O_3$ to remove any trace of sulfonyl iodide and iodine, and the products were isolated from *ca.* 75 ml petroleum ether (bp, 40—60 °C) at −60—−70 °C. After a few mg of 4-*t*-butylcatechol had been added to the petroleum ether solution to prevent polymerization, the quantities of unreacted styrene and *p*-methylstyrene were determined by GLC analysis (diethylene glycol adipate polyester column) using chlorobenzene as an internal standard. We also determined the quantities of products by NMR analysis in $CDCl_3$ using tetramethylsilane as an internal standard; relative reactivities determined by both methods were almost the same (Table 3). In the competitive addition of styrene and *p*-methylstyrene towards benzenesulfonyl iodide the ratio of the reacting monomers to initial sulfonyl iodide was nearly unity, indicating the formation of 1 : 1 adducts.

Results and Discussion

Reliability of Our Relative Rate Constants. Our first intention in this study was to confirm the fact that no reverse reaction of addition of sulfonyl radicals to vinyl monomers takes place. The free radical addition of sulfonyl iodides to olefinic double bonds has been studied extensively and the following chain mechanism is generally accepted.

$$RSO_2I \longrightarrow RSO_2\cdot + I\cdot \tag{1}$$

$$RSO_2\cdot + CH_2{=}C(R')R'' \xrightarrow{k_1} RSO_2CH_2\dot{C}(R')R'' \tag{2}$$

$$RSO_2CH_2\dot{C}(R')R'' + RSO_2I \xrightarrow{k_a} RSO_2CH_2C(R')R''I + R\dot{S}O_2 \qquad (3)$$

If we use two monomers (M_1 and M_2), then we obtain

$$\frac{\log (M_{2,0}/M_2)}{\log (M_{1,0}/M_1)} = \frac{k_2}{k_1}$$

where k_1 and k_2 are the rate constants for competitive addition reaction (Eq. 2) of M_1 (styrene) and M_2 monomer towards sulfonyl radicals, respectively, and $M_{1,0}$ (and $M_{2,0}$) and M_1 (and M_2) the initial and final concentrations, respectively, of styrene (and those of monomers which are able to compete in addition reaction with styrene).

The relative reactivities of vinyl monomers to styrene (k_2/k_1) have been determined by means of Eq. 4. If a reverse reaction of Eq. 2 occurs to a great extent, our k_2/k_1 values obtained from Eq. 4 should vary with the concentration of RSO_2I. In the competitive addition reaction of styrene and *p*-methylstyrene (M_2) towards benzenesulfonyl iodide, we have confirmed the reverse reaction does not take place, namely in Table 1 the k_2/k_1 values show no significant variation with the concentration change of benzenesulfonyl iodide. For other monomer pairs we have also checked the constancy of k_2/k_1 with varying concentrations of RSO_2I (Table 2). Skell and McNamara[8] observed in the addition of benzenesulfonyl iodide to *cis*- and *trans*-2-butene at 0°C that from either olefin, neither was isomerized during the course of reaction, indicating also the absence of the reverse reaction of Eq. 2.

TABLE 1. RELATIVE REACTIVITIES (k_2/k_1) OF ADDITION REACTIONS OF *p*-METHYLSTYRENE (M_2) TO STYRENE (M_1) TOWARDS BENZENESULFONYL RADICAL IN TOLUENE AT 0 °C UNDER VARIOUS CONDITIONS[a)]

$[M_1]_0$ (mol/l)	$[M_2]_0$ (mol/l)	$\frac{[M_2]_0}{[M_1]_0}$	$[PhSO_2I]_0$ (mol/l)	$\frac{k_2}{k_1}$
0.084	0.265	3.15	0.214	1.60
0.127	0.128	1.01	0.214	1.70
0.322	0.094	0.29	0.214	1.73
0.143	0.106	0.74	0.171	1.78
0.153	0.135	0.88	0.144	1.81[b)]
0.127	0.128	1.01	0.105	1.63
0.124	0.121	0.98	0.104	1.66
0.124	0.121	0.98	0.104	1.69[c)]
0.137	0.113	0.82	0.078	1.89
0.122	0.104	0.85	0.056	1.63
0.181	0.113	0.62	0.055	1.86

a) Reactions were initiated in daylight, unless otherwise stated. b) In the dark, reaction time; 92 h, conversion based on iodide; 67%. c) With 300 W mercury lamp, reaction time; 0.5 h.

TABLE 2. RELATIVE REACTIVITIES OF VARIOUS PAIRS OF M_1 AND M_2 TOWARDS BENZENESULFONYL RADICAL IN TOLUENE AT 0 °C

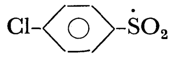
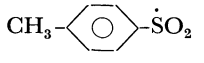
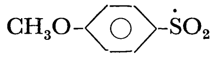
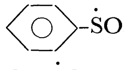
M_1	M_2	Runs[a)]	k_2/k_1
Styrene	α-Methylstyrene	3	3.21±0.29[b)]
	p-Methylstyrene	9	1.72±0.10
	t-Butyl methacrylate	3	0.14±0.02
	Isopropyl methacrylate	4	0.10±0.01
Methyl methacrylate	*t*-Butyl methacrylate	2	2.01±0.05
	Isopropyl methacrylate	3	1.20±0.10
Vinyl acetate	Methyl methacrylate	3	9.83±0.37
	Methyl acrylate	3	1.57±0.08
	Acrylonitrile	2	0.73±0.08
	1-Hexene	3	2.49±0.17

a) $[PhSO_2I]_0$ was varied from 0.046 to 0.302 mol/l. b) Standard deviation.

GLC analyses of the resulting solutions indicate that within experimental error, quantitative amounts of $RSO_2CH_2C(R')R''I$ were obtained in each experiment; it is strongly suggested that the polymerization process of the vinyl monomers, $RSO_2CH_2\dot{C}(R')R''+CH_2=C(R')R'' \rightarrow RSO_2CH_2C(R')R''-CH_2\dot{C}(R')R''$, hardly occurs in accordance with the results of Corrêa and Waters.[3)] Table 1 also indicates that the k_2/k_1 values are neither affected by the ratios of the concentration of styrene and *p*-methylstyrene, nor by the kind of light initiating the reactions, nor by converstion of the reaction, suggesting that our relative reactivities are reliable.

Effects of the Structure of Sulfonyl Iodides on the Relative Reactivities of p-*Methylstyrene to Styrene.* The relative rates for the addition reactions of *p*-methylstyrene to styrene towards methane- and *para*-substituted arenesulfonyl radicals are summarized in Table 3; the k_2/k_1 values of arenesulfonyl radicals are hardly affected by the kind of *para*-substituent and are almost the same as in the case of methanesulfonyl radical, suggesting that an unpaired electron of arenesulfonyl radicals is localized mainly on sulfonyl groups and that the conjugation of an unpaired electron with π-electron of phenyl rings is small since the relative rates would be affected by the stability and polarity of a radical. The results are in line with the conclusions obtained from ESR studies carried out by McMillan and Waters[9)] and Davies and Roberts;[10)] in spectra for the benzenesulfonyl radical, the *ortho*-hydrogen hyperfine constant [*a*(*o*-H)] was larger than *a*(*p*-H) and a relatively large value was obtained from *a*(*m*-H). This may be also supported by the fact that $CH_3SO_2N=NC_6H_5$ can

TABLE 3. RELATIVE REACTIVITIES OF *p*-METHYLSTYRENE TO STYRENE TOWARDS ARENESULFONYL AND METHANESULFONYL RADICALS IN TOLUENE AT 0 °C

Sulfonyl radical	Runs	k_2/k_1
	4	1.80±0.06[a)]
	6	1.63±0.08 (1.53)[b)]
	4	1.73±0.08 (1.78)[b)]
	9	1.72±0.10
$CH_3\dot{S}O_2$	3	1.79±0.06

a) Standard deviation. b) Values obtained from product analyses with 60 MHz NMR.

decompose thermally into $CH_3\dot{S}O_2$ and $\dot{C}_6H_5$ at the similar rate as $C_6H_5SO_2N{=}NC_6H_5$.[11-13]

Relative Reactivities among Vinyl Monomers. Styrene, α-methylstyrene, *p*-methylstyrene, *t*-butyl methacrylate, isopropyl methacrylate, methyl methacrylate, methyl acrylate, acrylonitrile, 1-hexene, and vinyl acetate were used for competitive addition reactions. Three kinds of relative reactivities for addition of various vinyl monomers towards benzenesulfonyl radical have been determined (Table 4). Since the relative reactivities of these vinyl monomers are spread over a wide range of *ca.* 500 fold, we have used three monomers having different reactivity, styrene, methyl methacrylate, and vinyl acetate, as a reference monomer. This was found to be reasonable from the experimental results: we obtained $k_{t\text{-BuMA}}/k_{\text{Sty}}=0.138$, $k_{i\text{-PrMA}}/k_{\text{Sty}}=0.097$, $k_{t\text{-BuMA}}/k_{\text{MMA}}=2.01$, and $k_{i\text{-PrMA}}/k_{\text{MMA}}=1.20$, thus we can calculate the two $k_{\text{MMA}}/k_{\text{Sty}}$ values from different combinations, *i.e.*, one based on *t*-BuMA and the other on *i*-PrMA. The former gave 0.069 and the latter 0.081, which agree with the value obtained from direct competitive addition reaction, $k_{\text{MMA}}/k_{\text{Sty}}=0.077$. The relative reactivity between MMA and vinyl acetate has been calculated by the analysis of NMR data.

Table 4. Relative reactivities on vinyl monomers towards benzenesulfonyl radical in toluene at 0 °C

Vinyl monomer	Q[a]	e[a]	σ_p[b]	k_2/k_1
α-Methylstyrene	0.98	−1.27	−0.18	3.21
p-Methylstyrene	1.27	−0.98		1.72
Styrene	1.00	−0.80	−0.01	(1.00)
t-Butyl methacrylate	1.18	−0.35		0.14
Isopropyl methacrylate	1.20	−0.15		0.10
Methyl methacrylate	0.74	0.40	0.28	0.08
Methyl acrylate	0.42	0.60	0.45	0.012
Acrylonitrile	0.60	1.20	0.66	0.006
1-Hexene	0.019	−0.28		0.02
Vinyl acetate	0.026	−0.22		0.008

a) Alfrey-Price's Q and e values, see Ref. 14. b) Hammett's *para*-substituent constants.

The relative rates based on the styrene monomer, calculated from the results in Table 2, are shown in Table 4 together with Alfrey-Price Q and e values.[14] These relative rates can be correlated with both e values and Hammett σ_p values (Fig. 1); they are divided into two groups, one (the upper line in Fig. 1) containing conjugated monomers ($Q \geq 0.42$) and the other unconjugated monomers ($Q \leq 0.026$). The fact that the linear relationship with a steep slope ($\rho_p=-3.6$) exists between e values (or σ_p values) and the relative rates suggests that the benzenesulfonyl radical and also other sulfonyl radicals are highly polar and electrophilic in accordance with the result of Corrêa and Waters[6] that the *p*-toluenesulfonyl radical is electrophilic.

Selectivities for addition reaction of a number of free radicals towards three representative vinyl monomers are given in Table 5. The sulfonyl radical shows the highest selectivity. This is attributable to a strong electrophilic character[20] of the benzenesulfonyl radical since the e value of monomers is an important factor for addition reactions among conjugated vinyl monomers (Fig. 1).

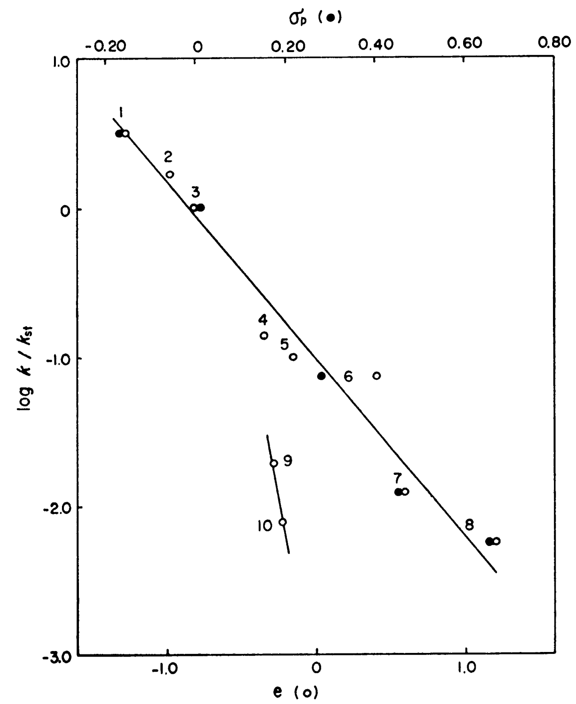


Fig. 1. Relationship between logarithmic relative reactivities and the Alfrey-Price's e (○) or the Hammett's σ_p (●) values.
1, α-Methylstyrene; 2, *p*-methylstyrene; 3, styrene (reference monomer); 4, *t*-butyl methacrylate; 5, isopropyl methacrylate; 6, methyl methacrylate; 7, methyl acrylate; 8, acrylonitrile; 9, 1-Hexene; 10, vinyl acetate.

Table 5. Relative reactivies of radicals towards three monomers

Radical	Temp (°C)	Styrene	MMA[b]	VAc[c]	Ref.
Phenyl	60	1.00	1.8	0.23	(15)
Phenyl	60	1.00	1.7	0.08	(16)
Benzoyloxy	60	1.00	0.1	0.4	(17)
Methyl	65	1.00	1.8	0.05	(18)
Polystyryl	60	1.00	1.9	0.02	(19)
Poly(AN[a])	60	1.00	0.3	0.01	(19)
Poly(MMA[b])	60	1.00	0.55	0.03	(19)
Poly(VAc[c])	60	1.00	0.33	0.01	(19)
Benzenesulfonyl	0	1.00	0.08	0.008	this work

a) Acrylonitrile. b) Methyl methacrylate. c) Vinyl acetate.

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