Photopolymerization Mechanisms. II. Rates of Ionic Dark Addition of Benzenesulfinate Ions to Acrylic Monomers

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The reaction rates for sulfone formation by the ionic dark addition of benzenesulfinate ions to acrylic monomers are compared with the quantum efficiency of monomer free-radical polymerization initiated by dye-triplet redox reaction with benzenesulfinate ions. In aqueous solutions both ionic addition rates and photopolymerization yields are decreased by electron-withdrawing para substituents on benzenesulfinate. A Hammett equation correlation for the rate constants of ionic addition to acrylamide shows a ρ value of -1.23. Steric effects of using ortho in place of para groups decrease the dark reaction rates three to four times as much as they do the photopolymerization yields for a particular substituent. The temperature dependence for the rate constant (M^{-1} sec^{-1}) of benzenesulfinate ion addition to acrylamide is $k \cong 2.2 \times 10^7 \exp(-17.5 \text{ kcal}/RT)$. The rate constants for the ionic addition of *p*-toluenesulfinate ions to different acrylic monomers vary over five orders of magnitude, while the photopolymer quantum yields change by only one order of magnitude. Steric and electronic effects in the monomer structure decrease the ionic dark reaction rates with methacrylic structures and with diacetoneacrylamide. Fast addition rates are obtained with acrylic acid and hydroxyethyl acrylate. *N*-Methylolacrylamide, acrylic acid, and diacetoneacrylamide are polymerized more efficiently than acrylamide. Aqueous solutions of diacetoneacrylamide containing *o*-toluenesulfinate ions and Methylene Blue have long-term dark stability as well as good sensitivity for high photopolymer yield.

Introduction

We are studying the reaction mechanisms in photopolymerizable solutions, particularly those in which dye-sensitized reactions with benzenesulfinate ions initiate the free-radical polymerization of acrylic monomers.[1] These reactions are of interest in rapid-access imaging processes,[2] including high-resolution holographic recordings.[3,4] In the first paper of this series[1] we investigated the reactions of photoexcited Methylene Blue with para-substituted benzenesulfinate ions and the resulting free-radical polymerization of acrylamide solutions. Sulfinic acids are also known to add to unsaturated compounds to form sulfones.[5,6] Benzenesulfinate ions react similarly[7] with acrylic monomers in an ionic dark reaction (eq 1) which

$$\text{X-C}_6\text{H}_4\text{SO}_2^- + \text{CH}_2{=}\text{CHY} + \text{H}_2\text{O} \xrightarrow{k} \text{X-C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}_2\text{Y} + \text{OH}^- \quad (1)$$

(where $Y = \text{CONH}_2$, COO^-, COOH, CN, etc.)

can be considered as a Michael-type addition.[8] The sulfones are unreactive with photoexcited dyes as compared to sulfinates. Thus the dark reaction limits the shelf life of the photopolymerizable solutions because high monomer concentrations gradually use up sulfinate ions and decrease the photosensitivity. In this paper ortho and para substituents on benzenesulfinate ions as well as differences in monomer structure are studied to determine electronic and steric effects on the dark reaction (eq 1) as compared to the photopolymerization efficiency. In brief, our goal was to find structures which would decrease the rate of the dark ionic addition of benzenesulfinates to acrylic monomers without decreasing the free-radical polymerization efficiency initiated by dye-triplet redox reactions with these benzenesulfinate ions. Our studies are in aqueous solutions, mainly in the pH range of 6 to 8 where efficient photopolymerization can occur by Methylene Blue sensitization. Acrylamide is used as the monomer with which to compare the effects of ortho and para substituents on benzenesulfinate ions; and *p*-toluenesulfinate ions are used to compare the effects of different acrylic monomer structures.

Schjånberg[5] measured the rate constant for the addition of benzenesulfinic acid to acrylic acid in the low pH range (about 1.1 to 1.7) where the sulfinic acid would be partly ionized and the acrylic acid would be essentially all in the acid form. Ogata, *et al.*,[7] studied the addition of para-substituted benzenesulfinate ions to acrylonitrile; in buffered aqueous solutions at 50° they found a Hammett ρ value of -1.15. Kinetic studies also have been made of sulfone formation by benzenesulfinate ions reaction with other substrates; substituent effect correlations were reported by Ogata, *et al.*,[9] on the addition to *p*-benzoquinone, by Ritchie, *et al.*,[10] on the addition to diazonium salts, and by Lindberg[11] on the displacement reaction with bromoacetamide and bromoacetate. In general, the rates of these reactions were accelerated by electron-releasing substituents; the reported ρ values ranged between -1.55 and -0.712. Lindberg[11] also studied the bromide displacement reaction with ortho-substituted benzenesulfinates and found that they reacted more slowly than the corresponding para-substituted ions.

Experimental Section

Kinetics of Ionic Addition Reactions. The dark reaction rate was followed by measuring the OH^- liberated as sulfone is formed (eq 1), using aqueous solutions in which no dye was added. The monomer solution (45 ml) was adjusted to the desired pH, mixed with the sodium salt of the

TABLE I: Ultraviolet Peaks of Sulfones

Sulfone	λ_{max}, nm	$10^{-2}\epsilon_{max}$
$C_6H_5SO_2CH_2CH_2CONH_2$	272	9.1
	265	10.6
	258	7.6
p-$CH_2C_6H_4SO_2CH_2CH_2CONH_2$	273	6.5
	264	7.7
	262	7.9
p-$CH_3CONHC_6H_4SO_2CH_2CH_2CONH_2$	261	184
p-$CH_3C_6H_4SO_2CH_2CH_2COOCH_3$	273	6.3
	262	7.7
p-$CH_3C_6H_4SO_2CH_2CH_2COOH$	273	6.2
	263	7.5

benzenesulfinate solution (5 ml of 0.1 N), and placed in a constant temperature bath. In most runs the pH was maintained constant within ±0.05 units by the addition of 0.25 N HCl added from an automatic titration instrument connected to the electrodes of an expanded scale pH meter. The pH was recorded continuously, showing each addition of acid. Usually the reactions were followed to about 70% completion, and at the end of each run the total volume of acid added was used to calibrate the average volume of each droplet. The rate of acid addition was assumed equal to the rate of sulfone formation. Generally the initial reaction mixture was 1 to 5 N in acrylic monomer and 0.01 N in sulfinate ions, so that the monomer concentration was essentially constant and the reaction rate followed *pseudo*-first-order kinetics. Corrections were made when lower concentrations of monomer were used.

Manual titrations with a microburet were used to follow the addition reactions with the barium, strontium, and potassium acrylate monomers, and for the slow reactions with methacrylic monomers. The electrodes were placed in the reaction mixture only during the titrations, and the pH did not vary more than ±0.2 units.

The addition rate of p-toluenesulfinate to acrylic acid was followed spectrophotometrically using a Cary 14R. Equal volumes of 0.2 N solutions were mixed, adjusted to the desired pH with a small volume of acid, and held in a thermostated bath. Aliquots were transferred to a fused silica cell at regular intervals and the absorbance at 270 nm was measured to follow the sulfone formation. The reaction followed second-order kinetics.

Photopolymerization. The quantum yields of bleaching and polymerization were measured as previously described.[1] N_2-bubbled 1 N acrylic monomer solutions were used at pH 7. They contained 20% by volume of phosphate buffer (Beckman) and had concentrations of either 4×10^{-3} N or 1×10^{-2} N sodium p-toluenesulfinate, and 8×10^{-6} M Methylene Blue. They were exposed with a narrow band of light passed by a 667-nm interference filter in front of a 100-W Zr arc lamp. The incident light intensity was about 5×10^{14} photons cm^{-2} sec^{-1}. The method of analyzing the polymerization yield varied with the monomer being studied. The photopolymers from acrylamide and barium acrylate were isolated by precipitation in methanol, filtering, drying, and weighing. Poly(diacetoneacrylamide) was precipitated in water, filtered, dried, and weighed. The polymer yields from solutions of acrylic acid, potassium acrylate, N-methylolacrylamide, and methacrylamide were determined by monomer analysis before and after exposure, using a bromine addition method.[12]

Materials. Sodium benzenesulfinate and sodium o-aminobenzenesulfinate (Eastman), sodium p-toluenesulfinate (Aldrich), and p-acetamidobenzenesulfinic acid (Aldrich) were used as received. The sodium salts of p-chloro-, p-bromo-, p-nitro-, o-methyl-, and 2,4,6-trimethylbenzenesulfinic acid were synthesized from the corresponding sulfonyl chlorides by reduction with sodium sulfite.[13] They were purified by precipitation as the ferric sulfinates[14] and converted to aqueous sodium sulfinate solution. p-Aminobenzenesulfinic acid was prepared by the hydrolysis of p-acetamidobenzenesulfinic acid with sodium hydroxide by the method of Lindberg[15] (neutralization equivalent: calcd 157, found 156). Sulfinate purity was checked by uv spectra,[16] and when possible by potentiometric titration.[17]

Acrylamide (J. T. Baker), methacrylamide (Rohm and Haas), and diacetoneacrylamide (Lubrizol) were purifed by recrystallization. Acrylic acid and ethyl acrylate (J. T. Baker) and acrylonitrile (Eastman) were purified by vacuum distillation. 2-Hydroxyethyl acrylate and 2-methoxyethyl acrylate (Polyscience) and 2-hydroxyethyl methacrylate (Rohm and Haas) were vacuum distilled after treatment with barium hydroxide and drying. N-Methylolacrylamide (American Cyanamid) and hydroxymethyldiacetoneacrylamide (Lubrizol) were used as received. Metal acrylate solutions (K, Ba, Sr) were made by neutralization of acrylic acid with the metal hydroxides.

Sulfones. The addition of benzenesulfinic acid to acrylic monomers (as in eq 1) has been used to produce the corresponding sulfones with yields in the 70–90% range.[6,18,19] We prepared several sulfones in this manner and recorded their ultraviolet spectra, which are summarized in Table I. Three sulfones were made from acrylamide. Aqueous solutions of the sulfinate (25 ml, 0.5 M) and acrylamide (5 ml, 5 M) were mixed and allowed to stand 1 week at room temperature, then neutralized with HCl. 3-(p-Tolylsulfonyl)propionamide (recrystallized from aqueous ethanol, mp 176–177°; lit.[6] 175–177°) crystallized out readily, whereas 3-phenolsulfonylpropionamide (flakes, recrystallized from aqueous ethanol, mp 125–126°; lit.[6] 126–127°) and 3-(p-acetamidophenylsulfonyl)propionamide (needles, recrystallized from anhydrous ethanol, mp 189–190°; lit.[6] 190–191°) crystallized only after removal of some of the solvent and refrigeration for 3 weeks. Methyl 3-(p-tolylsulfonyl)propionate was prepared by treating 10 g of sodium p-toluenesulfinate with 35 g of methyl acrylate in 500 ml of a water–methanol solution (1:2) at 50° for 8 hr. Water was added and on cooling an oil separated out, which was crystallized from water: mp 72–73° (lit.[6] 73.5–75°). Hydrolysis of this methyl ester with 6 N HCl was used to obtain the 3-(p-tolylsulfonyl)propionic acid, which was recrystallized from water: mp 112–113° (lit.[6] 112–113°).

Nonradical Nature of Sulfinate Addition Reaction. The following experiments were conducted to show that the dark reaction was not a free-radical process, which has been suggested as an alternative mechanism.[20] (a) The reaction products from addition reaction of benzenesulfinates with acrylamide were dumped into excess methanol. No precipitate of polyacrylamide was observed. (b) The dark reaction rate of p-toluenesulfinate addition to acrylamide was observed to be the same in the presence or absence of 0.1% p-methoxyphenol, a free-radical reaction inhibitor, when studied by the automatic titration method outlined above. (c) The rate of pH change from the addition reaction was observed to be the same in the presence or absence of oxygen. Reactants mixed after vacuum evacuation (freeze-thaw technique with solutions in side arms) showed the same rate of color change from a pH indicator as solutions exposed to air. In each case 0.5 ml of 0.1 *N* sodium *p*-toluenesulfinate was mixed with 4.5 ml of 40% acrylamide containing 0.1% *p*-methoxyphenol and a few drops of *m*-Cresol Purple. (d) A quantitative comparison of the *p*-toluenesulfinate ion concentration remaining in evacuated *vs.* open solutions of acrylamide was made 19 hr after mixing solutions as in c (but without an indicator). In each case a 0.25-ml aliquot of the reaction solution was added to 2.25 ml of 4.0 *N* barium acrylate and 0.25 ml of 6 × 10^{-3} *M* Methylene Blue. The induction periods and rates of barium acrylate photopolymerization[21] were identical within experimental error. This showed that after 19 hr the sulfinate ion concentration in the acrylamide was the same whether oxygen had been present or absent.

Stability of Sulfinate Solutions. Potentiometric titrations[17] of 0.1 *N* sodium benzenesulfinate and sodium *p*-toluenesulfinate solutions stored at room temperature showed no change in sulfinate concentration over periods of several years. Air oxidation of these sulfinate solutions is negligible[22] compared to the ionic addition reactions, even at 80°.

Results

Sulfinate Ion Addition to Acrylamide. The rate of the thermal addition of various benzenesulfinates to acrylamide was measured by following the rate of OH^- liberation as in eq 1. (No dye was present and no polymerization occurred.) A typical rate constant plot is shown in Figure 1, where the *p*-toluenesulfinate ion concentration at each point was calculated from the initial value minus the acid added to maintain the pH at 7. *Pseudo*-first-order kinetics were followed, as expected due to the large excess of monomer. Table II shows a summary of various rate constants calculated from the slope of the line in plots similar to Figure 1. A given set of standardized reactant solutions showed good reproducibility for the calculated rate constant (better than ±10%). However, considerably wider variations (10-30%) were observed between some individual rate constant values measured at different times with different standardized reactant solutions. Such variations are shown in the *p*-toluenesulfinate data in the first row of Table II. We do not know the source of these variations. However, they may have been partly due to differences in the pick-up of carbon dioxide by the monomer solutions during the kinetic runs. Nitrogen-bubbled solutions consistently gave slightly higher rate constants, *e.g.*, 7.4 × 10^{-6} M^{-1} sec^{-1} for the *p*-toluenesulfinate addition. The second row shows that the average rate constants were not significantly different over the pH range 6-9. The third row in Table II shows that somewhat higher rate constants were obtained using 1.0 and 2.5 *M* monomer as compared to the highly concentrated 5.1 *M* acrylamide solutions. The next two rows show the effect of temperature on a series of kinetic runs made with *p*-toluenesulfinate and with benzenesulfinate. Each series was run with the same sulfinate and acrylamide solutions. Arrhenius equation plots of these rate constants (in M^{-1} sec^{-1}) gave $\log k_{CH_3} = (-17.1 \pm 0.7)/2.3RT + 7.3 \pm 0.5$ and $\log k_H = (-17.5 \pm 0.4)/2.3RT + 7.3 \pm 0.3$, respectively. The last two rows in Table II show the average reaction rate constants for other para- and ortho-substituted benzenesulfinate ionic addition reactions.

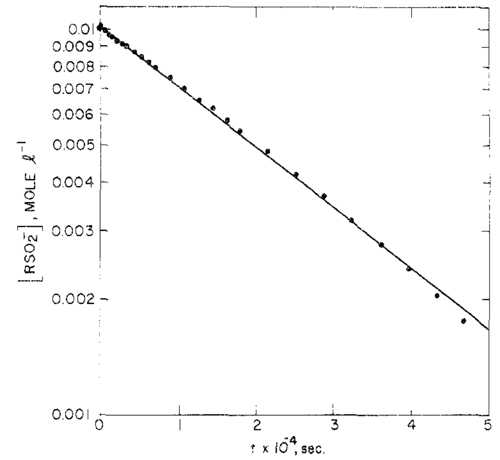


Figure 1. Kinetic plot for addition of *p*-toluenesulfinate ions to 5.06 *N* acrylamide, pH 7, 25° ($k = 7.4 \times 10^{-6}$ M^{-1} sec^{-1}).

TABLE II: Rate Constants for Ionic Addition to Acrylamide

$X\text{-}C_6H_4SO_2^-$	Variable condition[a]	Obsd rate constants,[b] 10^6k
X = *p*-CH_3		(6.8, 6.6, 6.4, 8.0, 7.4) = 7.0 av
p-CH_3	pH	7.9 (pH 6), 7.0 (pH 7), 6.5 (pH 8), 7.4 (pH 9)
p-CH_3	[Acrylamide]	7.0 (5.1 *M*), 9.1 (2.5 *M*), 8.8 (1.0 *M*)
p-CH_3	Temp	3.3 (20°), 6.4 (25°), 8.8 (30°), 15.2 (35°), 22.2 (40°)
H	Temp	2.1 (20°), 3.5 (25°), 5.3 (30°), 9.6 (35°), 13.9 (40°)
p-X		16.4 (NH_2), 3.5 (CH_3CONH), 1.8 (Br), 1.7 (Cl), 0.3 (NO_2)
o-X		5.3 (NH_2), 1.6 (CH_3), 0.03 (NO_2), 0.3 (2,4,6-CH_3)

[a] When not varied; 5.07 *M* acrylamide, 0.01 *M* sulfinate, 25°, pH 7. [b] Average values from different reactant solutions, except for temperature runs where the same solutions were compared.

Photopolymerization of Acrylamide. When a dye such as Methylene Blue was added to acrylamide solutions containing benzenesulfinate ions, exposure to light caused photopolymerization to occur much more rapidly than the ionic dark reaction. We have shown[1] that this polymerization is initiated by free radicals generated from the sulfinate ion redox reaction with the triplet state of the dye (eq 2). The efficiency of photopolymerization is related to

$$X\text{-}C_6H_4SO_2^- + {}^3D^+ \xrightarrow{k^*} X\text{-}C_6H_4SO_2\cdot + D\cdot \qquad (2)$$

the rate of this dye-triplet reaction with the sulfinate ions. We compared the effects of ortho- and para-substituted benzenesulfinate ions by measuring the quantum yields of dye bleaching (Φ_B) and acrylamide polymerization (Φ_M) under the same conditions. These results are summarized in Table III.

p-Toluenesulfinate and Acrylic Monomers. The effect of the monomer structure on the rate of the sulfinate ionic dark addition reaction was studied by using *p*-toluenesulfinate with various acrylic monomers in the absence of dye. The results are shown in Table IV. Whenever possible, 1 *N* aqueous monomer solutions were used at pH 7. Methylene Blue was added and dye-sensitized polymerization quantum yields were measured for many of these monomer solutions.

TABLE III: Photopolymerization of Acrylamide[a]

	Φ_B		Φ_M	
$X-C_6H_4SO_2^-$	*o*-X	*p*-X	*o*-X	*p*-X
X = NH_2	0.13	0.12	1250	1180
CH_3	0.13	0.15	1740	1740
CH_3CONH		0.09		1260
H		0.14		1730
Cl		0.07		930
Br		0.05		730
NO_2	0.004	0.02	85	280
Mesitylene	0.09		1100	

[a] Quantum yields from 4×10^{-3} *M* sulfinate and 8×10^{-6} *M* Methylene Blue in 1 *M* acrylamide, pH 7, 25°, 4×10^{14} photons cm^{-2} sec^{-1} incident intensity.

TABLE IV: Dark Reaction Rates of *p*-Toluenesulfinate Ion Addition to Monomers Compared with Dye-Sensitized Photopolymerization Yields

	Ionic addition rate[b]	Dye-sensitized photopolymerization[c]	
Monomer[a]	10^6k	$10^{-3}\Phi_M$	Φ_B
2-Hydroxyethyl acrylate[d]	1.1×10^3		
Acrylic acid[e]	9.1×10^2	2.2	0.07
Ethyl acrylate[d]	1.9×10^2		
Hydroxymethyldiacetoneacrylamide	6.2×10		
Acrylonitrile	5.2×10		
Barium acrylate	2.6×10	1.5	
Strontium acrylate	2.6×10		
Potassium acrylate	2.0×10	0.64	0.13
Methoxyethyl acrylate[d]	1.9×10		
N-Methylolacrylamide	1.5×10	5.4	0.12
Acrylamide	8.8	1.3	0.13
Diacetoneacrylamide	0.80	2.0	
2-Hydroxyethyl methacrylate[d]	0.08		
Methacrylamide	0.02	0.31	0.15

[a] 1.0 *N* monomer, 10^{-2} *M* *p*-toluenesulfinate, and pH 7 except where specified. [b] At 25°, *k* in M^{-1} sec^{-1}. [c] 8×10^{-6} *M* Methylene blue and 5.2×10^{14} photons cm^{-2} sec^{-1} intensity. [d] 0.25 *M* monomer. [e] Monomer 0.1 *M* for addition reaction and 1 *M* for photopolymerization, pH 2.5.

Discussion

Effect of Conditions. The rate of the *p*-toluenesulfinate ion dark addition to acrylamide was independent of pH (in the 6-9 range) and the presence or absence of oxygen. The kinetics of the dark reaction are consistent with the nucleophilic addition of the sulfinate ion to the double bond being the rate-determining step, as has been assumed by others[7] for similar reactions. However, eq 1 should be considered a reversible reaction in which the equilibrium is far to the right under the experimental conditions. The reversibility of Michael-type additions is well known,[8,23] and the elimination of arylsulfinic acids from aryl ethyl sulfones under strongly basic conditions has been clearly established.[24-28] For example, benzenesulfinate ions are produced from 3-phenylsulfonylpropionic acid in water in the pH 11-13 range.[29] However, at lower pH's the reactants in eq 1 give an almost quantitative yield of the sulfone addition product.[6,18,19] Arrhenius equation plots of temperature effects on the rate constants (for benzenesulfinate and *p*-toluenesulfinate addition to acrylamide) showed that the reactions had an activation energy of about 17 kcal/mol and a frequency factor with log $A \cong 7.3$. This low-frequency factor may be related to the ambident nucleophilicity[9] of the benzenesulfinate ion, but the frequency factors of other Michael-type addition reactions vary over a wide range and both higher and lower *A* values have been reported.[7,30-33]

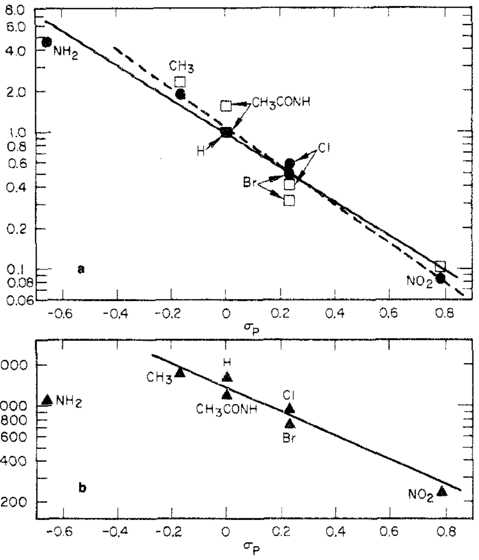


Figure 2. Hammett equation correlations for para-substituted benzenesulfinate ion reactions in pH 7 aqueous acrylamide solutions: (a) ratio of rate constants, (●) ionic dark addition reaction in 5 *M* monomer, (□) dye-triplet redox reaction in 1 *M* monomer; (b) (▲) quantum yield of monomer polymerized in 1 *M* monomer, using 4×10^{-3} *M* sulfinate and 8×10^{-6} *M* dye.

Effect of Para Substituents. The rates of ionic addition of para-substituted benzenesulfinate ions to acrylamide increased with the electron-releasing character of the substituent. Figure 2a shows a Hammett equation plot of the rate constant ratios (solid points) at 25°. This gives a ρ value of -1.23 when the amino substituent is included, as shown by the solid line. This is very close to the ρ value of -1.15 found by Ogata, *et al.*,[7] for similar reactions with aqueous acrylonitrile at 50°, and it falls in the general range of ρ values reported for other reactions of para-substituted benzenesulfinate ions.[9-11]

We previously used plots of quenching-corrected quantum yields of Methylene Blue bleaching in acrylamide to determine the relative rate constants for eq 2, which is the reaction of the dye-triplet state with para-substituted benzenesulfinate ions.[1] These calculated triplet redox rate constant ratios (k_X^*/k_H^*) are shown by the open squares in Figure 2a. We did not previously study the *p*-NH_2 substituent. If the *p*-NH_2 data point is excluded from our present studies, then the broken line in Figure 2a shows the least-squares plot for the ionic dark addition reaction (eq 1) by the other six substituents (solid points). The dye-triplet state redox reaction (eq 2) substituents (open squares) also fit the broken line correlation in Figure 2a, with a ρ value of -1.44. Thus, while the photopolymerizable solutions are made more thermally stable by using benzenesulfinate ions with electron-withdrawing para substituents, these groups cause a corresponding decrease in the rate constants for the generation of free radicals from the dye-triplet redox reaction.

The photopolymer yields from monomer solutions at a particular light intensity and sulfinate concentration (Table III) also varied with the para substituents, but not as sharply as the rate constants in reactions 1 and 2. Excluding the p-NH_2 substituent, the slope of a Hammett equation plot had a ρ value of -0.88 as shown in Figure 2b for the quantum yields of acrylamide polymerization. Many factors affect these quantum yields, including sulfinate ion quenching of the photoexcited dye, and the relative rates of free-radical initiation and termination. Quenching of the excited dye decreased the free-radical yield from all of the substituted sulfinates as compared to benzenesulfinate.[1] Also, the polymerization quantum yield is inversely proportional to the square root of the light intensity when benzenesulfinate is used with Methylene Blue. This is typical of photopolymerizations in which the propagation reaction is proportional to the radical concentration while the termination reaction is proportional to the square of the radical concentration. Similarly, the electron-withdrawing para-substituted benzenesulfinates give a lower concentration of free-radical initiators so that the photopolymer quantum yield is decreased, but not as much as the relative rate of free-radical formation. If this was the only factor involved, then the photopolymer quantum yields would be proportional to the square root of the initiator concentration,[34] so that (Φ_X/Φ_H) would equal $(k_X{}^*/k_H{}^*)^{1/2}$ and the Hammett equation constant for polymerization would be $\rho = -1.44/2 = -0.72$. This is not far from the observed value of -0.88 shown in Figure 2b.

In the para-substituted series, the unsubstituted benzenesulfinate is the most useful dye-sensitized initiator for acrylamide polymerization. At high concentrations it causes less quenching of the dye and provides the highest polymer yield.[1] It has an intermediate rate of thermal deactivation (ionic addition) with the monomer. Electron-donating groups cause a faster dark reaction and due to quenching effects do not give higher photopolymer yields, while electron-withdrawing groups slow down both the dark reaction and the photopolymerization.

Effect of Ortho Substituents. We expected ortho-substituted benzenesulfinate ions to undergo sulfone formation more slowly[11] than the corresponding para compounds due to steric hindrance. This was indeed the case for all the ortho derivatives we studied. The dark reactions of the o-nitro-, o-methyl-, and o-aminobenzenesulfinates were between one-tenth and one-third as fast as their para isomers. As shown in Table V, the dye-sensitized photopolymerization and bleaching reactions were much less affected by the use of ortho in place of para substituents. We found less excited state dye quenching by the o-amino- than the p-aminobenzenesulfinate, and this is partly responsible for the improved polymer yield from this ortho derivative. The o-toluenesulfinate gave as high a polymer yield ($\Phi_M = 1740$) as was obtained with p-toluenesulfinate and benzenesulfinate, and its rate constant for ionic addition ($1.6 \times 10^{-5}\ M^{-1}$ sec) was slower than either of these other two sulfinates. The additional steric hindrance in sodium 2,4,6-trimethylbenzenesulfinate further decreased the rate of ionic addition ($k = 3 \times 10^{-7}$ M^{-1} sec), but also decreased the photopolymer yield ($\Phi_M = 1100$).

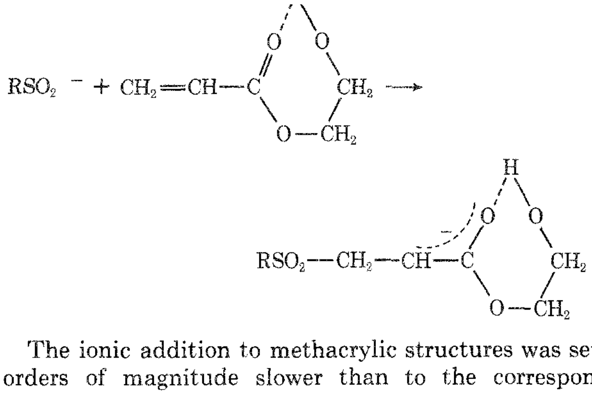
Both electronic and steric effects control the reactivity of ortho-substituted benzenesulfinates. Compared to the same para group, the steric hindrance of an ortho group slows down appreciably the rate of ionic addition to the monomer. There is a much smaller steric effect on the dye-sensitized formation of free radicals (eq 2) and subsequent polymerization. The net result of electron-releasing and steric hindrance effects in the o-toluenesulfinate ion is that a high photopolymerization efficiency is obtained while the rate of thermal deactivation (ionic addition) is decreased as compared to the benzenesulfinate or p-toluenesulfinate ions. Thus, o-toluenesulfinate is the most effective of these structures for dye-sensitized polymerization.

TABLE V: Effect of Ortho and Para Substituents on Benzenesulfinate Ion Reaction Rates with Acrylamide

	Thermal addition[a] sulfone formation	Photopolymerization[b]	
		Dye bleaching	Polymerization
$X\text{-}C_6H_4SO_2{}^-$	k_o/k_p	$(\Phi_B)_o/(\Phi_B)_p$	$(\Phi_M)_o/(\Phi_M)_p$
X = NH_2	0.32	1.1	1.1
CH_3	0.23	0.88	1.0
NO_2	0.10	0.20	0.31

[a] Rate constants in 5 M acrylamide. [b] Polymerizations in 1 M acrylamide.

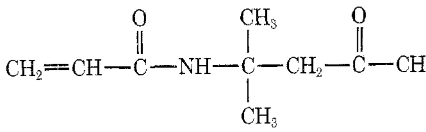
Effect of Monomer Structure. The results summarized in Table IV show that differences in monomer structure caused the ionic addition reaction rates to vary by five orders of magnitude, while the polymerization quantum yield changed by only one order of magnitude. In the acrylic series $CH_2{=}CH\text{-}Y$, the rate constant of the ionic addition reaction varied with Y in the following order: $COOH > COOEt > CN > COO^- > CONH_2$. Although electron-withdrawing substituents on the olefin generally tend to accelerate the rate of Michael-type addition reactions, it is difficult to separate inductive, resonance, and steric effects. The effect of the acrylic Y substituents on the relative rates of other Michael-type addition reactions do not always fall in the same order. Our results are in good agreement with the results of Friedman, *et al.*,[35,36] who found that the rate constants for Y groups were in the order $COOMe > CN > CONH_2$ for the addition of glycine and for the addition of mercaptopropionic acid to the acrylic structures. However, studies on the addition of alcohols[37,38] have shown a different sequence of relative rates where $CN > COOMe > CONH_2$. The resonance interaction in the transition state is probably affected by the reactant being added to the double bond. The hydroxyl groups in 2-hydroxyethyl acrylate, hydroxymethyldiacetoneacrylamide, and N-methylolacrylamide increased the relative rate of sulfinate addition. This may be due to intramolecular hydrogen bonding between hydroxyl groups and the carbonyl group, which would favor the formation of the anion intermediate as illustrated in eq 3.



(3)

The ionic addition to methacrylic structures was several orders of magnitude slower than to the corresponding acrylic monomers. The α-methyl acrylic substituent makes the β carbon relatively more negative and thus decreases the rate of nucleophilic attack by the sulfinate ion. α-Methyl substituents generally retard Michael-type addition reactions,[36-38] and while both electronic and steric effects are involved, Friedman and Wall[36] concluded that the effect is primarily electronic.

The ionic addition rate to diacetoneacrylamide appeared to be unusually slow as compared to acrylamide. However, molecular models indicate that its *tert*-butyl type of substituent has a steric effect that may reduce the coplanarity of the acrylic carbonyl with the double bond or that may hinder the approach of the sulfinate ion to the β carbon when these groups are coplanar. This would decrease the carbonyl resonance interaction and could be responsible for the slower rate of sulfinate ion addition. Similar effects have been reported[38] for the addition of alcohols to N-alkylacrylamides, where the reaction with N-*tert*-butylacrylamide was too slow to be determined.



$$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

In the photopolymerizations, the initial free radical yield from the dye-triplet reaction with p-toluenesulfinate should be approximately the same for all the runs at pH 7. The differences in the quantum yield of bleaching (Table IV) were small, so that main differences in the polymer yields are due to the efficiency of radical capture, propagation, and termination. The photopolymer yields did not vary with monomer structure at all like the rates of the ionic dark reaction. For example, the ratio of the photopolymer quantum yield divided by the dark reaction rate constant is 2.4×10^6 for acrylic acid, 1.5×10^8 for acrylamide, 3.6×10^8 for N-methylolacrylamide, 2.5×10^9 for diacetoneacrylamide, and 1.6×10^{10} for methacrylamide. These last three monomers are of interest for photopolymerization imaging. The methacrylamide dark reaction is 400 times slower than acrylamide, while its photopolymer yield is only four times lower. Methacrylamide has a slower free-radical propagation rate and a faster termination rate than acrylamide,[39] which accounts for the lower photopolymer yield. N-Methylolacrylamide gave four times better photopolymer yield than acrylamide, while its dark reaction rate constant was only twice as fast. It gives a gel-type polymer and it is of interest as a monomer component to increase the sensitivity of photopolymerization imaging systems. The p-toluenesulfinate ionic addition rate to diacetoneacrylamide is ten times slower than to acrylamide, and it gave a higher photopolymer yield. This is a very favorable combination of monomer properties, although poly(diacetoneacrylamide) is insoluble and gives a light scattering image which is suitable for direct readout but not for holography. We found that added steric retardation of the ionic addition dark reaction with diacetoneacrylamide was obtained with o-toluenesulfinate ions, without any significant decrease in the photopolymer yields; pH 7 buffered samples of this monomer and the sulfinate remained highly photosensitive for a month at room temperature.

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