The Sulfinic Acid-Initiated Polymerization of Methyl Methacrylate*†

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INTRODUCTION

Sulfinic acids (I) are organic acids of tetravalent sulfur which are known for their tendency to decompose. Aliphatic sulfinic acids are less stable than aromatic sulfinic acids, and the short-chain aliphatic acids are less stable than the longer-chain acids.¹ The least stable sulfinic acids appear to be the disulfinic acids where the two groups are in close proximity to each other as in o-benzenedisulfinic acid² and 2,2'-biphenyldisulfinic acid.³

The currently accepted mechanism for the deomposition of sulfinic acids first proposed by Hinsberg⁴ postulates as the initial step a disproportionation to the corresponding sulfonic acids (II) and sulfenic acids (III); the sulfenic acids are then proposed to react with another molecule of the sulfinic acid, forming the thiolsulfonate (IV) with removal of water (cf. references 1 and 7 for a more detailed discussion of this theory).

$$2\text{RSO}_{2}\text{H} \xrightarrow{} \text{RSO}_{3}\text{H} + \text{RSOH}$$
(I) (II) (III)
$$\xrightarrow{| \text{RSO}_{2}\text{H} } \text{RSO}_{2}\text{SR} + \text{H}_{2}\text{O}$$
(IV)

Reactive sulfenic acid intermediates are made plausible by their resistance to isolation except in the singularly interesting case of 1-anthraquinonesulfenic acid.^{5,6} The instability of sulfenic acids has been attributed to a propensity to disproportionate to the corresponding thiols and sulfinic acids in much the same manner as do sulfinic acids.⁷

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[†] This is the 18th in a series of papers concerned with the preparation and polymerization of monomers. For the previous paper in this series, see C. G. Overberger and P. V. Bonsignore, J. Am. Chem. Soc., 80, 5431 (1958).

Hagger⁸ brought attention to the sulfinic acids as efficient room-temperature polymerization initiators for vinyl monomers such as methyl methacrylate and styrene. The sulfinic acids are of interest as polymerization initiators because of (1) the light stability of polymers formed by initiation with sulfinic acids either alone or in conjunction with benzoyl peroxide, and (2) the absence of the usual induction period prior to polymerization. Sulfinic acid derivatives with good storage stability but which are nevertheless effective accelerators of monomer-polymer mixtures at room temperture have been reported recently.⁹⁻¹³ Compounds such as α -hydroxysulfones, α -aminosulfones, and amine salts of sulfinic acids have been of greatest interest.

Bredereck et al.¹⁴ have suggested that a redox system(s) capable of initiating vinyl polymerization may arise via disproportionation of the sulfinic acids to the corresponding sulfonic acids and sulfenic acids; however, the nature of the primary radical or the process by which it is formed has not been determined. The rate of polymerization of methyl methacrylate initiated by *p*-toluenesulfinic acid has been determined to be firstorder in monomer and proportional to the square root of the sulfinic acid concentration, and to have an activation energy of 12.6 kcal./mole.⁸

A wide variety of compounds have been reported to affect the rate of sulfinic acid-initiated polymerization. Marvel¹⁵ has demonstrated that there is an optimum amount of oxygen which can be present in a sulfinic acid initiated emulsion polymerization of styrene-butadiene. The presence of hydroquinone has been shown to accelerate the rate of polymerization, the optimum amount being equimolar with the sulfinic acid.^{8,16} The presence of quinhydrone likewise caused an acceleration in the rate of polymerization, while quinone caused complete inhibition. Peroxide and hydroperoxides¹⁶⁻¹⁸ greatly increased the rate of polymerization as did inorganic and organic halide salts.¹⁴ Marvel¹ also showed with the styrene-butadiene emulsion system that dodecanethiol and ferric sulfate increase the rate of polymerization, and that there is an optimum acid concentration at pH 1.9. Bredereck,¹⁴ on the other hand, found in his experiments with methyl methacrylate the opposite effect of inhibition by strong acids such as *p*-toluenesulfonic acid.

The sensitivity to oxygen of the rate of sulfinic acid-initiated polymerization caused Bredereck,^{14,19} Wagner,²⁰ and Horner²¹ to suggest that the sulfinic acid-oxygen system may be separate and independent of the redox system(s) which can operate with or without the presence of oxygen. Bredereck has in addition suggested that halide ion is necessary for the operation of the sulfinic acid-oxygen initiator system. The present study of the decomposition of sulfinic acids in methyl methacrylate was carried out with a highly purified system in a dilatometer under high vacuum. It is the opinion of the authors that the data presented represent a close approximation to that which would be obtained for the sulfinic acids in monomer in the absence of any traces of rate-affecting impurities.

EXPERIMENTAL

Dilatometer

A twin-capillary dilatometer similar in design to that previously described by Bartlett and Kwart²² was used. It was found necessary to modify the construction to make possible the application of suction to one of the capillaries so that at the end of a kinetic run the polymer solution could be rapidly removed from the reaction bulb; this was accomplished by attaching a small ground-glass joint to the top of one of the capillaries.

High Vacuum System

A high-vacuum system was employed for purifying and loading monomer into the dilatometer. This apparatus incorporated with some modification the main features of the system used by Bartlett.²³ The dilatometers were sealed to the vacuum system, flushed with nitrogen, loaded with the sulfinic acid contained in a glass weighing boat, and sealed off except to the vacuum The dilatometers were degassed, and 50.00 ± 0.01 ml. of methyl system. methacrylate was distilled into them from a volumetric vessel (volumes were measured at the temperature at which the run was to be made). The monomer had been purified by distillation from a reservoir onto powdered barium oxide, distillation into a vessel where prepolymerization was carried out under a General Electric H85-A3 lamp with benzil as a photosensitizer, and distillation of the unreacted monomer into the volumetric vessel. After the dilatometers had been loaded with monomer, they were sealed off from the vacuum system. To follow the course of the polymerization, the monomer was thawed and the solids dissolved; details of the manipulation of this type of dilatometer in preparation for taking readings have been adequately described elsewhere.²³

At the end of a run, the dilatometers were broken open so as to expose the ground-glass joint on the capillary, and the polymer solution was withdrawn from the reaction bulb with gentle vacuum into a cooled flask. The polymer was precipitated with 500 ml. of cold methanol and dried by the frozen benzene technique.²⁴

Purification of the Sulfinic Acids

The sulfinic acids were purified as described by the following procedure for benzenesulfinic acid.

Sodium Benzenesulfinate

A solution of 100 g. of sodium benzenesulfinate (Eastman White Label) in 300 ml. of distilled water was filtered and diluted to 1 liter. A concentrated solution of ferric chloride in distilled water was added until no more precipitate formed.²⁵ The ferric salt was removed by filtration and washed with a dilute, acidic ferric chloride solution. Cold 5% sodium hydroxide was added to a mixture of the ferric salt and 300 ml. of water; the ferric hydroxide was removed by filtration. The filtrate was placed in a refrigerator overnight and then refiltered.

The sodium benzenesulfinate solution was acidified with cold, concentrated hydrochloric acid until the solution clouded permanently. After crystallization had started, acid was again added slowly with stirring until no more precipitate formed. The acid was removed by filtration and washed with 20 ml. of ice-cold water.

The benzenesulfinic acid was added to 500 ml. of water, then sodium hydroxide solution was added until pH 8 was obtained, and the solution was brought to a volume of 600 ml. The solution was passed through a cation exchange column, containing the sodium form of Amberlite IRC-50 prepared by treating the resin with a saturated solution of sodium bicarbonate. The effluent was collected when a drop of it in acidic ferric chloride solution gave an orange precipitate of ferric benzenesulfinate. The sulfinate solution was washed from the column with water, the end being indicated by the absence of an orange precipitate in acidic ferric chloride solution.

Benzenesulfinic Acid

The sodium benzenesulfinate solution was cooled in ice and acidified with cold, concentrated hydrochloric acid so that the sulfinic acid crystallized slowly. The acid was removed by filtration and washed with 20 ml. of ice-cold water.

The benzenesulfinic acid was dissolved in 200 ml. of diethyl ether. The solution was dried by stirring with anhydrous magnesium sulfate for 10 minutes, filtered, and then redistilled petroleum ether (b.p. 35–37°) was added slowly with stirring until the acid started to crystallize. The mixture was filtered to remove the first fraction of acid, and more petroleum ether was added to give a middle fraction which was removed by filtration and washed with petroleum ether. The middle fraction was recrystallized from dimethyl ether (Matheson Co. b.p. -23.7°) and *n*-butane (Matheson Co., b.p. -0.6°) under nitrogen, placed in a 150-ml. Erlenmeyer flask with a standard-taper 24/40 joint, and the remaining solvent removed with a high-vacuum pump at 10^{-4} - 10^{-5} mm. for a half hour at room temperature. The evacuated flask was filled with nitrogen, stoppered, and stored at Dry Ice temperatures. This sample of benzenesulfinic acid melted at 85–86° (theor. m.p. 85°).²⁵

p-Methoxybenzenesulfinic Acid

p-Methoxybenzenesulfonyl chloride was prepared according to the procedure of Morgan and Cretcher²⁶ for the chlorosulfonation of anisole.

The crude material from 100 g. (0.93 mole) of anisole after removal of the chloroform solvent was reduced with alkaline sulfite in the conventional manner. To 233 g. (1.86 moles) of sodium sulfite in 2 l. of distilled water was added the crude sulforyl chloride. The mixture was heated to $60-70^{\circ}$ (performing this reduction at ice temperatures is time consuming and unnecessary) with stirring and continuous addition of cold, concentrated sodium hydroxide to keep the solution alkaline to litmus. After complete solution of the sulfonyl chloride, the solution was cooled to room temperature, filtered, acidified, and concentrated ferric chloride solution was added until no more ferric *p*-methoxybenzenesulfinate precipitated. The ferric salt was collected by filtration, washed with dilute, acidic ferric chloride solution until free from the odor of sulfur dioxide, and decomposed by a cold solution of sodium hydroxide. The ferric hydroxide was removed by filtration, and the filtrate was slowly neutralized by concentrated hydrochloric acid with stirring. The crystalline *p*-methoxybenzenesulfinic acid was removed by filtration, washed with a small amount of ice-cold distilled water, and dissolved in dilute sodium hydroxide. Conversion of the sodium salt to p-methoxybenzenesulfinic acid was carried out according to the procedure described above for benzenesulfinic acid. The acid crystallized from dimethyl ether and *n*-butane melted at $98-99^{\circ}$ (theor. m.p. $97-98^{\circ}$ ²⁵).

p-Trifluoromethylbenzenesulfinic Acid

p-Bromobenzotrifluoride was prepared according to the procedure described by Markarian.²⁷

From 171 g. (1.0 moles) of *p*-bromotoluene (Eastman White Label) and 480 g. (3.0 moles) of bromine was obtained after one crystallization from hot hexane 340 g. (84%) of *p*-bromobenzotribromide, m.p. 76–79° (theor. m.p. $81-82^{\circ 27}$).

From 175 g. (0.43 mole) of the above *p*-bromobenzotribromide and 89.4 g. (0.50 mole) of antimony trifluoride was obtained after distillation through a 1 ft. glass-helices-packed column 61 g. (76%) of *p*-bromobenzotrifluoride boiling at 155–157° (uncorr.), $n_{\rm D}^{25} = 1.4716$ (theor. b.p. 153–5°, $n_{\rm D}^{25} = 1.4705^{27}$).

The above 61 g. (0.33 mole) of *p*-bromobenzotrifluoride was added under nitrogen to 8.0 g. (0.33 mole) of magnesium turnings and 100 ml. of anhydrous ether. Approximately 10 g. of the bromide was added to start the reaction and the remainder was added in 200 ml. of anhydrous ether as rapidly as possible. Refluxing was maintained for a half hour after addition was complete. The flask contents were diluted with 300 ml. ether and cooled to -40° with an acetone-Dry Ice bath. Anhydrous sulfur dioxide was bubbled in rapidly with stirring at -40° for a half hour; the flask contents were then allowed to warm to room temperature with continued addition of sulfur dioxide. Water was added dropwise to the rapidly stirred reaction mixture; when approximately 30 ml. of water had been added, a voluminous hydrolysis product precipitated and vigorous refluxing of the ether required cooling of the flask with ice-water. The mixture was poured into a 3-l. beaker, 500 ml. water and 10 g. of sodium hydroxide were added, and the ether was removed by heating on the steam bath with stirring. Filtration, acidification, and addition of a concentrated ferric chloride solution gave the usual orange precipitate of ferric p-trifluoromethylbenzenesulfinate. Treatment of the solid hydrolysis product with acid, base, and filtration gave additional sodium sulfinate which upon acidification and addition of ferric chloride gave a precipitate of the ferric sulfinate which was added to the main portion. The ferric sulfinate was decomposed by a cold solution of sodium hydroxide, ferric hydroxide was removed by filtration, and the filtrate was slowly neutralized by cold, concentrated hydrochloric acid with stirring. The crystalline *p*-trifluoromethylbenzenesulfinic acid was removed by filtration, washed with a small amount of ice-cold distilled water, and dissolved in dilute sodium hydroxide. Conversion of the sodium salt to the acid was carried out according to the procedure described above for benzenesulfinic acid. The acid crystallized from dimethyl ether-*n*-butane melted at 84-85°.

ANAL. Caled. for C7H502SF3: S15.25%; F27.13%. Found: S15.23%; F26.97%.

Methyl Methacrylate

A constant-boiling middle fraction of methyl methacrylate was collected by fractional vacuum distillation of an inhibitor-free sample through a 1-ft. Vigreaux column, $n_{\rm D}^{20} = 1.4155$ (theor. $n_{\rm D}^{20} = 1.4152$ ²⁸). This monomer was placed in its reservoir on the high vacuum system, degassed, and stored at Dry Ice temperatures.

Copolymerization. Free Radical Nature of the Propagating Chain

In order to confirm the free radical nature of the sulfinic acid initiated polymerization of vinyl monomers, p-chlorostyrene and methyl methacrylate were copolymerized with approximately 0.1M p-toluenesulfinic acid

p-Chlorostyrene–Methyl Methacrylate.	Monomer-Polymer Composition
Mole fraction <i>p</i> -chlorostyrene in monomer	Mole fraction <i>p</i> -chlorostyrene in polymer
0.110	0.204
0.192	0.311
0.319	0.390
0.524	0.560
0.774	0.663

TABLE I

as the initiator at 20° in degassed, sealed tubes. The composition of five copolymers prepared at five different mole fractions of comonomers was determined by chlorine analysis; the results are given in Table I. A copolymer composition curve with r_1 and r_2 equal to 0.4 adequately fits the data. This curve resembles that for benzoyl peroxide-initiated copolymerization at 60°, ²⁹ and indicates that the propagating chain in sulfinic acid-initiated vinyl polymerization is a free radical.

Calculation of Rates from Dilatometer Data

For a free radical polymerization, the rate of polymerization is proportional to the concentration of propagating chains. The usual steady-state assumption that the rate of formation of propagating chains is equal to the rate of their termination results in the familiar kinetic expression:

$$(-d[M]/dt = K[I]^{n/2}[M])$$

or

$$(d \ln [M_0]/[M])/dt = K[I]^{n/2}$$

where [M] is the monomer concentration, [I] is the initiator concentration, and n is the order of the rate of formation of primary radicals. The quantity $[M_0]/[M]$ was calculated from $-\Delta h$, the average of the cathetometer readings (in centimeters) on the two capillaries subtracted from the average of the initial readings, as follows:

$$[M_0]/[M] = (m_0/V_0)/(m/V) = (m_0/m)(V/V_0) = (1/1 - x)(V/V_0)$$

where x is the fractional conversion of monomer to polymer,

$$\frac{1}{1 - x} = \frac{1}{[1 - C(A/V_0)(-\Delta h)]}$$

and

$$V/V_0 = 1 - [A(-\Delta h)/V_0]$$

where A is the sum of the areas of the two capillaries and C is the conversion factor for methyl methacrylate relating the fractional contraction in volume to the fractional conversion of monomer to polymer. The conversion factor C has been determined by MacKay and Melville³⁰ to be 3.60 at 20.9° and 3.48 at 30.15°, and is a constant up to at least 10% conversion. A/V_0 is determined during calibration of the dilatometer as being equal to the weight of mercury corresponding to $-\Delta h = 1$ cm. divided by the weight of mercury held by the dilatometer bulb and capillaries filled to approximately V_0 .

The rate data reported here were obtained with dilatometers in which $A/V_0 = 2 \times 10^{-4}$ and 4×10^{-4} cm.⁻¹.

EXPERIMENTAL RESULTS AND DISCUSSION

Benzenesulfinic Acid

The rate of polymerization of methyl methacrylate as a function of benzenesulfinic acid concentration was determined with three different samples of the acid. Samples 1 and 2 were prepared from sodium benzene-sulfinate by the procedure outline above, except that the sodium salt was not passed through a cation exchange column, and the sulfinic acid after fractional crystallization from diethyl ether-petroleum ether (b.p. 35-37°) was dried at 20° at approximately 10^{-3} mm. for a half hour. Sample 3 was prepared as described in the general procedure above.



Fig. 1. Benzenesulfinic acid in methyl methacrylate. Conversion vs. time: (1) 0.02, (2) 0.04, (3), 0.06, and (4) 0.08M sulfinic acid. The data in A (sample 3) were determined at 30°C., those in B and C (samples 1 and 2) at 20°C.

In Figure 1 is plotted conversion versus time for benzenesulfinic acid in 0.02, 0.04, 0.06, and 0.08M concentrations at 20° for samples 1 and 2 and 30° for sample 3. The rate curves are characterized by a short induction period followed by a fast initial rate which rapidly slows down and approaches near linearity. The rate of polymerization was arbitrarily chosen as the slope of the last portion of the curve, i.e., for a 400-min. run, the last 200 min. were approximated by a straight line, the slope of which was taken as the rate. The rates of polymerization are compiled in Table II.

·····	Temp.,	Acid	$d\ln \frac{[M_0]}{[M]}/dt$
Acid	°C.	concentration, M	$ imes 10^7$
Benzenesulfinic			
Sample 1	20.0	0.02	1.17
	20.0	0.04	2.30
	20.0	0.06	4.53
	20.0	0.08	5.68
Sample 2	20.0	0.02	0.78
	20.0	0.04	1.40
	20.0	0.06	2.34
	20.0	0.08	3.26
Sample 3	30.0	0.02	1.06
	30.0	0.04	2 , 42
	30.0	0.06	4.82
	30.0	0.08	7.68
	20.0	0.06	2.88
	10.0	0.06	1.22
p-Methoxybenzenesulfinic			
	30.0	0.01	1.00
	30.0	0.02	2.63
	30.0	0.04	8.00
	30.0	0.06	14.67
	30.0	0.08	23.50
p-Trifluoromethylbenzenesulfinic			
	30.0	0.02	0.87
	30.0	0.04	1.54
	30.0	0.08	3.00

TABLE II Sulfinic Acid-Initiated Polymerization of Methyl Methacrylate

In Figure 2 is plotted the logarithm of the rate of polymerization versus the logarithm of the concentration of benzenesulfinic acid. There is a tendency for the curves to be concave upward, indicating an increase in the apparent order with increasing concentration of the sulfinic acid. It can be seen from the slope of this plot that the rate of polymerization is at least first order with respect to the benzenesulfinic acid concentration.



Fig. 2. Plot the logarithm rate of polymerization vs. the logarithm concentration of sulfinic acid. A: p-CF₃ ϕ SO₂H; B: sample 1 (Δ , ϕ SO₂H, 20°; sample 2 (O), ϕ SO₂H, 20°; (\Box) ϕ SO₂H, 30°; C: p-CH₃O ϕ SO₂H.



Fig. 3. Benzenesulfinic acid in methyl methacrylate diluted with benzene. Conversion vs. time at 30° : (1) undiluted methyl methacrylate; (2) 80:20 methyl methacrylate-benzene (by volume).

In an effort to determine the order of benzenesulfinic acid-initiated polymerization of methyl methacrylate with respect to monomer, benzene was added as an inert diluent. Sample 3 of the benzensulfinic acid was used in 0.05M concentration at 20°. From the vacuum distillation of an inhibitor-free sample of methyl methacrylate was obtained a constantboiling middle fraction; 40 ml. of this freshly distilled monomer was pipetted into the reservoir of a dilatometer which was sealed to the high-vacuum system while being flushed with nitrogen, and which contained the benzenesulfinic acid. At the same time, 50 ml. of monomer was added to another dilatometer similarly attached to the high-vacuum system. To the first dilatometer containing the 40 ml. of monomer was added 10 ml. of benzene which was a middle fraction obtained from the distillation of constant-boiling material at atmospheric pressure under nitrogen. While a nitrogen atmosphere was maintained, the contents of both dilatometers were sealed off except to the vacuum system. After five cycles of degassing by freezing, evacuation, and thawing, the dilatometers were sealed off from the vacuum system.

Conversion versus time for monomer and for 80:20 monomer-benzene is shown in Figure 3. A conversion factor C of 3.61/0.8 was used to calculate the rate for the experiment with 80:20 monomer-benzene. The rate of polymerization for undiluted monomer was 2.90×10^{-7} sec.⁻¹ and for 80:20 monomer-benzene the rate was 4.04×10^{-7} sec.⁻¹. The unexpected failure of the rate of polymerization of diluted monomer to be less than the corresponding rate for undiluted monomer precludes the use of benzene as a diluent for obtaining the order of the rate of polymerization with respect to methyl methacrylate.

The energy of activation for the overall process of benzenesulfinic acidinitiated polymerization of methyl methacrylate was determined from the rates at 10°, 20°, and 30°. Sample 3 of the benzenesulfinic acid was used in 0.06 molar concentration. The rate data are plotted in Figure 4 and the rates of polymerization are tabulated in Table II. The energy of activation, as calculated by the method of least squares, is 11.7 kcal./mole.

p-Methoxybenzenesulfinic Acid

The rate of polymerization of methyl methacrylate as a function of pmethoxybenzenesulfinic acid concentration was determined. This sulfinic acid was purified in the manner described above for benzenesulfinic acid. It was in addition found necessary to "homogenize" this sample of sulfinic acid by thoroughly breaking up clusters of crystals and mixing with a spatula; preliminary experiments prior to "homogenization" showed that varying rates were obtained as different portions of the acid were weighed into the dilatometers.

Conversion versus time at 30° at 0.01, 0.02, 0.04, 0.06, and 0.08*M* concentrations is plotted in Figure 5. The rates of polymerization are tabulated in Table II. It is readily apparent by comparison of the curves in Figure 5 for *p*-methoxybenzenesulfinic acid with the corresponding curves for benzenesulfinic acid in Figure 1 that the presence of an electron-donating substituent on the phenyl ring enhances the initiation ability of the sulfinic acid. If it is assumed that the instability of sulfinic acids parallels their initiation ability, then benzenesulfinic acids with electron-donating substituents on the rings are less stable than the unsubstituted compound.

A log-log plot of the rate of polymerization versus *p*-methoxybenzenesulfinic acid concentration is given in Figure 2C. The straight line with slope of 3/2 drawn through the five points fits the data quite well, indicating that within the concentration range studied the order of the rate of polymerization with respect to *p*-methoxybenzenesulfinic acid is 3/2. There is



Fig. 4. Benzenesulfinic acid (sample 3) in methyl methacrylate. Conversion vs. time: (3) 10°, (2) 20°, and (1) 30°; 0.06*M* sulfinic acid.



Fig. 5. p-Methoxybenzenesulfinic acid in methyl methacrylate. Conversion vs. time at 30°: (5) 0.01, (4) 0.02, (3) 0.04, (2) 0.06, and (1) 0.08M sulfinic acid.

apparently no tendency for the plot to be concave upward as is the case with the corresponding plot for benzenesulfinic acid in Figure 2B.

p-Trifluoromethylbenzenesulfinic Acid

The rate of polymerization of methyl methacrylate as a function of p-trifluoromethylbenzenesulfinic acid concentration was determined. This sulfinic acid was purified in the manner described above for benzenesulfinic acid. The p-trifluoromethyl group was chosen as an electron-withdrawing



Time, min.

Fig. 6. p-Trifluoromethylbenzenesulfinic acid in methyl methacrylate. Conversion vs. time at 30°: (3) 0.02, (2) 0.04, and (1) 0.08M sulfinic acid.



Fig. 7. Mixed sulfinic acids in methyl methacrylate. Conversion vs. time at 30° : (1) 0.02*M* benzenesulfinic acid and 0.02*M p*-methoxy benzenesulfinic acid; (2) 0.02*M p*-methoxy benzenesulfinic acid.

substituent after it was found that *p*-nitrobenzenesulfinic acid is insoluble in nonpolar solvents such as ether and methyl methacrylate.

Conversion versus time at 30° at 0.02, 0.04, and 0.08*M* concentration is plotted in Figure 6. The rates are tabulated in Table II. It is seen that the initiation ability of substituted benzenesulfinic acids is decreased when the substituent is electron-withdrawing in nature.

A log-log plot of the rate of polymerization versus p-trifluoromethylbenzenesulfinic acid concentration is given in Figure 2A. The three points of the plot fall reasonably close to the straight line with a slope of 1, and there appears to be a slight curvature concave upward as in the similar plot for benzenesulfinic acid in Figure 2B.

Mixed Sulfinic Acids

p-Methoxybenzenesulfinic acid in 0.02M concentration was dissolved in monomer with 0.02M benzenesulfinic acid in one experiment, and with 0.02M p-trifluoromethylbenzenesulfinic acid in another. Conversion versus time at 30° is given in Figure 7. The rates together with appropriate comparison rates are given in Table III. In both experiments essentially the same rates were obtained, and the expected acceleration in rate was not observed. It can be seen by comparison of the rates in Table III that p-methoxybenzenesulfinic acid prefers to react with itself rather than with either benzenesulfinic acid or p-trifluoromethylbenzenesulfinic acid. In more general terms, the data indicate that an electropositively substituted

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Exp. no.	Sulfinic acid	Acid concentration, M	$d \ln rac{\mathrm{M_0}}{\mathrm{[M]}}/dt \ imes 10^7$
- 1	p -CH ₃ O ϕ SO ₂ H	0.02	5.63
	$\phi SO_2 H$	0.02	
2	p -CH ₃ O ϕ SO ₂ H	0.02	5.45
	$p ext{-} ext{CF}_{3}\phi ext{SO}_{2} ext{H}$	0.02	
3	p -CH ₃ O ϕ SO ₂ H	0.02	2.63
4	p -CH ₃ O ϕ SO ₃ H	0.04	8.00
5	$\phi SO_2 H$	0.02	1.06
6	p -CF ₃ ϕ SO ₂ H	0.02	0.87

TABLE III Mixed Benzenesulfinic Acids in Methyl Methacrylate at 30°

benzenesulfinic acid reacts with itself at a faster rate than with an electronegatively substituted benzenesulfinic acid, and at a faster rate than the latter with itself. These results can be interpreted as ruling out a redox system in the form of a disproportionation as the rate-determining step.

Effect on Rate of Polymerization by a Sulfonic Acid

p-Toluenesulfonic acid was added to the dilatometers with the sulfinic acid and the usual procedure was followed for charging the dilatometer.



Fig. 8. (A) Benzenesulfinic acid with toluenesulfinic acid in methyl methacrylate. Conversion vs. time at 30°: (1) 0.06 M benzenesulfinic acid with 0.003M p-toluenesulfonic acid; (2) same as (1) but with a different sample of p-toluenesulfonic acid; (3) 0.06M benzenesulfinic acid with 0.006M p-toluenesulfonic acid [same sample as in (2)]; (4) 0.06M benzenesulfinic acid. (B) p-Methoxybenzenesulfinic acid with p-toluenesulfonic acid in methyl methacrylate. Conversion vs. time at 30°: (1) 0.02M p-methoxybenzenesulfinic acid with 0.010M p-toluenesulfonic acid; (3) 0.040M p-methoxybenzenesulfinic acid with 0.005M p-toluenesulfonic acid; (4) 0.020M p-methoxybenzenesulfinic acid.

Conversion versus time for experiments with benzenesulfinic acid (sample 3) with added *p*-toluenesulfonic acid at 30° is plotted in Figure 8A. The rates of polymerization are tabulated in Table IV. In experiments 2 and 3, two samples of *p*-toluenesulfonic acid were added to 0.06M benzenesulfinic acid in 5 mole-% concentration (0.003M). The rate in both cases was

		acrylate		
Exp. no.	Sulfinic acid	Concentration of sulfinic acid, M	Concentration of p -toluene sulfonic acid, M	$d \ln rac{\mathrm{M_0}}{\mathrm{[M]}}/dt imes 10^7$
1	$\phi SO_2 H$	0.06	0.000	4.82
2	"	0.06	0.003	9.41
3	"	0.06	0.003	9.83
4	"	0.06	0.006	9.58
5	p -CH ₃ O ϕ SO ₂ H	0.02	0.005	3.64
6		0.02	0.010	4.00
7	"	0.04	0.005	11.46
8	**	0.02		2.63
9	"	0.04		8.00

TABLE IV *p*-Toluenesulfonic Acid in the Sulfinic Acid-Initiated Polymerization of Methyl Meth-

approximately double the rate for benzenesulfinic acid in the absence of added p-toluenesulfonic acid. Doubling the sulfonic acid concentration in experiment 4 to 10 mole-% gave the same amount of acceleration in rate of polymerization as did the 5 mole-% concentration.

p-Toluenesulfonic acid was added with *p*-methoxybenzenesulfinic acid to methyl methacrylate. Conversion versus time is plotted in Figure 8B. The rates of polymerization together with appropriate comparison rates in the absence of added sulfonic acid are tabulated in Table IV. The rate of polymerization was accelerated by the addition of the sulfonic acid, although to a lesser extent than in the case of the benzenesulfinic acid.

There appears to be little variation in the amount of acceleration in the rate of polymerization as the sulfonic acid was varied from 5 to 50 mole-% of the sulfinic acid concentration. With the experimental technique employed it was not possible to determine the nature of the acid catalysis in the concentration range 0 to 5 mole-% of the sulfinic acid, but it is apparent from the data presented that a plateau in the rate of polymerization exists which drops off sharply as the sulfonic acid concentration approaches zero. This large effect at low sulfonic acid concentrations was very likely a major cause for the variation in rate of polymerization from sample to sample of a sulfinic acid. The samples of sulfinic acid used to obtain the rate data reported here are certain to have undergone some autoxidation during the various manipulations in storage, transfer, and weighing; with the experimental technique used, however, there is no convenient way of determining the rate of sulfinic acid.

Effect of Some Additives on the Rate of Polymerization

Di-*n*-butylamine hydrochloride (0.0005 mole) was added to benzenesulfinic acid in 0.06M concentration in a dilatometer experiment carried out in the usual manner at 30°. The amine hydrochloride was not noticeably soluble, and some of the solid was carried by the liquid through the capillaries into the bulb of the dilatometer. A plot of conversion versus time is given in Figure 9 together with a comparison plot for the benzenesulfinic acid alone. It is seen that the rate was accelerated and that it continuously increased with time, possibly due to slow solution of the hydrochloride in the bulb of the dilatometer during the course of the run.

Bredereck's¹⁴ experiments showed that the monomer-polymer dough polymerization of methyl methacrylate was accelerated by p-toluenesulfinic acid with or without added benzoyl peroxide when the sulfinic acid was precipitated from water by neutralization of the sodium salt with hydrochloric acid. Recrystallization from ether caused the sulfinic acid to lose most of its activity, while washing with an aqueous solution of sodium chloride resulted in full reactivation. It is Bredereck's contention that it is halogen ion whose presence is necessary for the sulfinic acid to be active, and that the advantage of di-*n*-butylamine hydrochloride is in its greater



Fig. 9. Benzenesulfinic acid with di-*n*-butylamine hydrochloride in methyl methacrylate. Conversion vs. time at 30° : (1) 0.06*M* benzenesulfinic acid with 0.01*M* di-*n*-butylaminehydrochloride; (2) 0.06*M* benzenesulfinic acid.

solubility in nonpolar media. A dilatometer experiment was made in the usual manner with a sample of benzenesulfinic acid prepared as described by Bredereck by precipitation of the acid from an aqueous solution of the sodium salt, and the rate of polymerization was not appreciably different from corresponding rates where the benzenesulfinic acid had been further purified by crystallization from organic solvents. The monomer was turbid, apparently due to insoluble inorganic material present in the sulfinic acid, but a plot of conversion versus time in no way resembled that for the polymerization in which di-n-butylamine hydrochloride was added to the highly purified benenzesulfinic acid. The rate of polymerization's being increased by amine hydrochloride as compared to its indifference to the presence of sodium chloride may well be due to a solubility difference as suggested by Bredereck, but the "deactivation-reactivation cycle" found by Bredereck with the monomer-polymer dough polymerization was not observed in the present dilatometer experiments where oxygen was excluded.

The use of ferric chloride to precipitate ferric sulfinates as a part of the purification sequence for sodium sulfinates prior to their neutralization to the acid made it desirable to determine the effect on the rate of polymerization of the presence of small amounts of ferric ion in the sulfinic acid initiator. In preparing a sample of benzenesulfinic acid, no attempt was made to remove ferric ion after decomposition of the ferric benzenesulfinate with sodium hydroxide; neutralization of the sodium salt then precipitated the benzenesulfinic acid together with ferric salts which gave a slightly orange color to the solid. The orange color was carried through the recrystallization from ether-petroleum ether. A dilatometer run was made in the usual manner with this sample of benzenesulfinic acid, and another dilatometer run was made in which ferric benzenesulfinate was added to sample 3 of the benzenesulfinic acid described above; no significant change in the rate of polymerization was noted with the ferric salts present.

Peroxide-Sulfinic Acid Initiation

Several dilatometer runs were made with benzoyl peroxide and benzenesulfinic acid (sample 3) in methyl methacrylate at 20°. The peroxide was placed in the dilatometer together with the sulfinic acid and the dilatometers were loaded in the usual manner. Conversion versus time is plotted



Fig. 10. Benzenesulfinic acid (sample 3) with benzoyl peroxide and dicumyl peroxide in methyl methacrylate. Conversion vs. time at 50° : (1) 0.001*M* benzenesulfinic acid, 0.01*M* benzoyl peroxide; (2) 0.002*M* benzenesulfinic acid, 0.01*M* benzoyl peroxide; (3) 0.004*M* benzenesulfinic acid, 0.01*M* benzoyl peroxide; (4) 0.01*M* benzenesulfinic acid, 0.01*M* benzoyl peroxide; (5) 0.01*M* benzenesulfinic acid, 0.002*M* benzoyl peroxide; (6) 0.01*M p*-tolucnesulfinic acid, 0.010*M* dicumyl peroxide; (7) 0.01*M* benzenesulfinic acid (predicted by extrapolation of data presented above).

in Figure 10 for five ratios of benzenesulfinic acid to benzoyl peroxide (curves 1-5); curve 6 was obtained with 0.01M *p*-toluenesulfinic acid and 0.01M dicumyl peroxide, and curve 7 is a comparison curve for 0.01M benzensulfinic acid predicted by extrapolation of the data presented above.

The rate curves for benzoyl peroxide-benzenesulfinic acid are characterized by a rather sharp break occurring somewhere between 0 and 100 minutes. The shape of these curves should serve as a warning against the inadequacy of methods of measurement of these rates where only one point for conversion versus time is determined.

The rate of polymerization for dicumyl peroxide with p-toluenesulfinic acid was constant over the whole of the reaction, a most unusual occurrence in sulfinic acid-initiated polymerization.

GENERAL DISCUSSION

The highly unstable nature of the 2,2'-biphenyldisulfinic acids (V) is of considerable interest in connection with the mechanism of sulfinic acid decomposition. The unique characteristic of this type of disulfinic acid which must be responsible for its unusually high instability is the high frequency of intramolecular collision of sulfinic acid groups. According to the disproportionation theory for the decomposition of sulfinic acids, (V) must be disproportionating in a rate-determining step to an intramolecular sulfenic acid-sulfonic acid (II), since an intermolecular disproportionation would be expected to proceed at a rate of the same order as that of the comparatively stable and isolatable 4,4'-biphenyldisulfinic acid.³ This theory, however, also demands an intramolecular sulfenic acid-sulfinic acid (VIII) for formation of the observed thiolsulfonate (VII), a requirement which is clearly incompatible with an initial disproportionation forming (VI).



The yields of (VII) obtained further rule out (VIII) as an intermediate. Armarego³¹ reduced 4,4',6,6'-tetramethyl-2,2'-biphenyldisulfonyl chloride with alkaline sulfite and upon acidification the disulfinic acid formed the corresponding thiolsulfonate in 72% overall yield. A similar reduction performed to check the yield reported by Armarego gave an 87% overall yield of pure (III) from 2,2'-biphenyldisulfonyl chloride. However, by the disproportionation mechanism, the maximum obtainable theoretical yield based on the disulfonyl chloride and with assumption of a 100% yield in reduction to disulfinate is only 50% [half of (V) is wasted with respect to the formation of (VII) by formation of (IX)]. Thus, both the rate and yield of thiolsulfonate formation preclude a sulfenic acid as an intermediate in the decomposition of the 2,2'-biphenyldisulfinic acids.

While ruling out a sulfenic acid intermediate, the 2,2'-biphenyldisulfinic acids also show that the rate-determining process in sulfinic acid decomposition involves the attack of one sulfinic acid group upon another, and that this process results in thiolsulfonate formation from these two groups. \mathbf{It} is apparent, however, that in going from two sulfinic acid groups to the thiolsulfonate, the sulfur undergoes a net decrease in oxidation level of two while the elements of hydrogen peroxide are eliminated. This reduction can account for the oxidation of sulfinic acid to sulfonic acid observed during the decomposition of sulfinic acids in the absence of other reducing agents (e.g., sulfurous acid present from the acidification of excess sulfite in the alkaline sulfite reduction of a sulforyl chloride). In the presence of monomer, the sulfonic acid formed by sulfinic acid oxidation should cause a continuous increase in the rate of polymerization, but the rates obtained from the dilatometer curves for conversion versus time slowly decreased during the course of a kinetic run. Possible explanations are that simultaneously with sulfonic acid formation a retarder is formed the presence of which more than offsets any acceleration the sulfonic acid would effect, or possibly the sulfonic acid is not formed at all in monomer as opposed to an inert solvent, and concurrently with thiolsulfonate formation, monomer is being oxidized instead of sulfinic acid.

Although thiolsulfonate is the isolated product of decomposition, there is the possibility that it is formed by rearrangement of an initially-formed disulfoxide. Evidence that disulfoxides readily rearrange to the thiolsulfonate can be found in the hydrolysis of the tetrabromide or tetraiodide of a disulfide³² and in the coupling of sulfinyl chlorides with zinc,³³ in each of these cases only a thiosulfonate has been isolated, whereas one could reasonably expect a disulfoxide. In the case of (VII), a thiolsulfonate structure is confirmed by the infrared spectrum which corresponds with that of phenyl benzenethiolsulfonate.³⁴

The data on the rate of polymerization versus concentration of sulfinic acid show the rate to be proportional to a power of the concentration varying from 1 to 3/2. The kinetics indicates an initiation step which is at least second-order in sulfinic acid, and is consistent with a reaction between sulfinic acid molecules which is at least bimolecular in nature. It is thus believed that the rates determined are a measure of the rate of decomposition of the sulfinic acids in methyl methacrylate rather than a measure of their oxidation or reduction by some other compound. If this is actually the case, then the only explanation offered for the reports in the literature of the rate of polymerization being of a lower order of 1/2 with respect to the sulfinic acid is that there were present sufficient amounts of other compounds which are oxidizing or reducing agents and which formed a redox system(s) capable of initiating polymerization at a rate sufficient to mask the rate of polymerization induced by the sulfinic acid alone. This implies that the rates reported here must be slower than the rates observed by other workers who found the rates to be 1/2 order in sulfinic acid. Although direct comparison of rates is impossible, the rates reported here are extremely slow, and it was shown that the addition of small amounts of some compounds accelerated these rates.

It is suggested that the nonlinearity of the log-log plot of the rate of polymerization versus benzenesulfinic acid concentration in Figure 2 may be due to hydrogen bonding between sulfinic acid molecules. Benzenesulfinic acid has been shown to be highly associated in nonpolar solvents by infrared analysis in carbon tetrachloride³⁵ and by the measurement of freezing-point depressions of benzene solutions.³⁶ Failure to observe an expected decrease in rate upon dilution of methyl methacrylate with benzene is also probably due to an increase in hydrogen bonding. This effect suggests the possibility that the rate of initiation of polymerization may vary from monomer to monomer as changes occur in the degree of association of sulfinic acid molecules. Additional support for this suggestion can be found in the reported stability of a methanol solution of *p*toluenesulfinic acid under nitrogen as compared to the instability of a solution in a nonhydroxylic solvent.^{14,19-21}

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References

- 1. C. S. Marvel and R. S. Johnson, J. Org. Chem., 13, 822 (1948).
- 2. W. R. H. Hurtley and S. Smiles, J. Chem. Soc., 1926, 1821.
- 3. H. J. Barber and S. Smiles, J. Chem. Soc., 1928, 1141.
- 4. O. Hinsberg, Ber., 36, 107 (1903).
- 5. K. Fries, Ber., 45, 2965 (1912).
- 6. T. C. Bruice and R. T. Markiw, J. Am. Chem. Soc., 79, 3150 (1957).
- 7. N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, Chem. Revs., 39, 269 (1946).
- 8. O. Hagger, Helv. Chim. Acta, 31, 1624 (1948).
- 9. H. Bredereck and E. Bader, Ber., 87, 129 (1954).
- 10. H. Bredereck, E. Bader, and A. Wohnhas, Makromol. Chem., 12, 100 (1954).
- 11. H. Bredereck, E. Bader, and G. Hoschele, Ber., 87, 784 (1954).
- 12. E. Bader and H. D. Hermann, Ber., 88, 41 (1955).
- 13. G. M. Brauer and F. R. Burns, J. Polymer Sci., 19, 311 (1956).
- 14. H. Bredereck, E. Bader, G. Brod, G. Hoschele, and G. Pfleiderer, *Ber.*, 89, 731 (1956).

15. C. S. Marvel and N. A. Meinhardt, J. Polymer Sci., 6, 733 (1951).

16. J. L. Ynfiesta, J. F. Yanes and F. R. Sanchez, Anales real soc. espan. fis. y quim. (Madrid), 47B, 53 (1951).

17. O. Hagger, Helv. Chim. Acta, 34, 1872 (1951).

18. Y. Hashihama, H. Sumitomo, and J. Okabe, J. Chem. Soc. (Japan), Ind. Chem. Soc., 56, 25 (1953).

19. H. Bredereck, G. Hoschele, A. Wagner, A. Fohmann, and K. Ludwig, Angew. Chem., 68, 306 (1956).

20. A. Wagner, Angew. Chem., 69, 694 (1957).

21. L. Horner and O. H. Basedow, Ann., 612, 108 (1958).

22. P. D. Bartlett and H. Kwart, J. Am. Chem. Soc., 72, 1051 (1950).

23. H. Kwart, H. S. Broadbent, and P. D. Bartlett, J. Am. Chem. Soc., 72, 1062 (1950).

24. F. M. Lewis and F. R. Mayo, Ind. Eng. Chem., Anal. Ed., 17, 134 (1945).

25. S. Krishna and H. Singh, J. Am. Chem. Soc., 50, 792 (1928).

26. M. S. Morgan and L. H. Cretcher, Preparation of Organic Intermediates, Wiley, New York, 1951, 191.

27. M. Markarian, J. Am. Chem. Soc., 74, 1858 (1952).

28. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, J. Am. Chem. Soc., 71, 497 (1949).

29. C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, J. Am. Chem. Soc., 70, 1537 (1948).

30. M. H. McKay and H. W. Melville, Trans. Faraday Soc., 45, 323 (1949).

31. W. L. F. Armarego and E. E. Turner, J. Chem. Soc., 1956, 3668.

32. Fromm, Z. angew. Chem., 24, 1125 (1911).

33. D. Barnard, J. Chem. Soc., 1957, 4673.

34. J. Cymerman and J. B. Willis, J. Chem. Soc., 1951, 1332.

35. S. Detoni and D. Hadzi, J. Chem. Soc., 1955, 3163.

36. W. G. Wright, J. Chem. Soc., 1949, 683.

Synopsis

The rate of polymerization of methyl methacrylate initiated by p-methoxybenzenesulfinic acid, benzenesulfinic acid, and p-trifluoromethylbenzenesulfinic acid in the absence of oxygen was studied. The p-methoxy substituent accelerated the rate while the p-trifluoromethyl substituent acted as a retarder. The order of the rate with respect to sulfinic acid concentration varied between 1 and 3/2; this is consistent with an initiation process of kinetic order between 2 and 3. Dilution of the monomer with benzene in an attempt to determine the order of the rate of polymerization with respect to monomer unexpectedly resulted in an increase in rate. Mixtures of p-methoxybenzenesulfinic acid and p-trifluoromethylbenzenesulfinic acid did not give an acceleration in rate. The rate of polymerization was accelerated by sulfonic acid, benzoyl peroxide, dicumyl peroxide, and di-n-butylamine hydrochloride. Decomposition of the very unstable 2,2'-biphenyldisulfinic acid by disproportionation to the intramolecular sulfonic acidsulfenic acid was shown to be incompatible with the yield and rate of formation of the thiolsulfonate. The gross features of a mechanism consistent with the polymerization data is proposed.

Résumé

On a étudié la vitesse de polymérisation du méthacrylate de méthyle initié par l'acide *p*-méthoxybenzènesulfinique, l'acide benzènesulfinique et l'acide *p*-trifluorométhylbenzènesulfinique en absence d'oxygène. Le groupe *p*-méthoxylè accélère la vitesse tandis que le groupe *p*-trifluorométhyle agit come retardateur. L'ordre de la vitesse par rapport à la concentration én acide sulfinique varie entre 1 et 3/2 en accord avec un processus d'initiation d'ordre 2 à 3. La dilution du monomère avec du benzène dans le but de déterminer l'ordre de la vitesse de polymérisation par rapport au monomère montre une augmentation inattendue de la vitesse. Des mélanges d'acide *p*-méthoxybenzènesulfinique et d'acide *p*-trifluorométhylbenzènesulfinique ne produisent pas une accélération de la vitesse. La vitesse de polymérisation est accélérée par l'acide sulfonique, le peroxyde de benzoyle, le peroxyde de dicumyle et le chlorohydrate de di-*n*-butylamine. La décomposition de l'acide 2,2'-biphényldisulfinique, très instable, par l'intermédiaire d'un disporportionnement intramoléculaire (acide sulfonique-acide sulfénique) est incompatible avec le rendement et la vitesse de formation due thiolsulfonate. A partir des résultats de polymérisation, on propose un méchnisme dans ses grandes lignes.

Zusammenfassung

Die Polymerisationsgeschwindigkeit von Methylmethacrylat wurde bei Verwendung von p-Methoxybenzolsulfinsäure, Benzolsulfinsäure und p-Trifluormethylbenzolsulfinsäure als Starter in Abwesenheit von Sauerstoff untersucht. Die p-Methoxygruppe erhöhte die Geschwindigkeit, während die p-Trifluormethylgruppe verzögernd wirkte. Die Ordnung der Geschwindigkeit in bezug auf die Sulfinsäurekonzentration variierte zwischen 1 und 3/2; das entspricht einer Startreaktion mit einer kinetischen Ordnung zwischen 2 und 3. Die Verdünnung des Monomeren mit Benzol, die zur Bestimmung der Ordnung der Polymerisationsgeschwindigkeit in bezug auf das Monomere vorgenommen wurde, ergab unerwarteter Weise eine Ehröhung der Geschwindigkeit. Mischungen von p-Methoxybenzolsulfinsäure und p-Trifluoromethylbenzolsulfinsäure lieferten keine Geschwindigkeitszunahme. Die Polymeriationsgeschwindigkeit wurde durch Sulfonsäure, Benzoylperoxyd, Dicumylperoxyd und Di-n-Butylaminhydrochlorid beschleunigt. Es wurde gezeigt, dass eine Zersetzung der sehr instabilen 2,2'-Biphenyldisulfinsäure durch Disproportionierung zur intramolekularen Sulfon-Sulfensäure mit der Ausbeute und der Bildungsgeschwindigkeit des Thiolsulfonates nicht vereinbar ist. In grossen Zügen wire ein Mechanismus, der mit den Polymerisationsdaten vereinbar ist, vorgeschlagen.

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