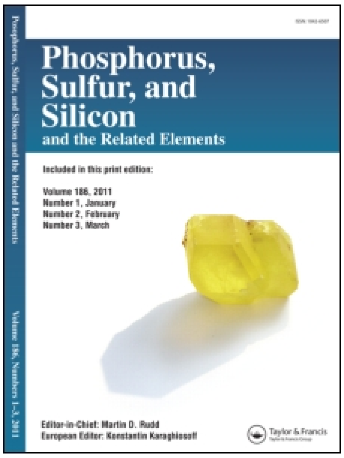

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THE THIOSULFINATE INHIBITION OF METHACRYLATE POLYMERIZATION

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Substituent influence on the efficiencies of a series of aryl thiosulfinates in inhibiting the polymerization of methyl methacrylate, representative of vinyl monomers, has been examined. Attention is drawn to the role of the sulfinyl group in reactions of organosulfur compounds.

Key words: Thiosulfinate, methacrylate, polymerization, inhibition, sulfinyl group.

INTRODUCTION

The activities of thiosulfinates and sulfoxides as retarders formed *in situ* during olefin autoxidation from disulfides and sulfides has been briefly recorded.[1] A fuller account of the activities of disulfides and derived thiosulfinates, covering substituent influence on rates of oxidation and retarder efficiency, draws attention to complexities to be met in dissecting structure/efficiency relationships arising from competing oxidation and decomposition reactions.[2] Thus it was shown that the retarder efficiency of added aryl disulfides improves with incorporation of electron donating substituents, but this change leads to an apparent anomaly that decrease in efficiency of derived thiosulfinates follows when added directly. Since as implied above, loss of thiosulfinate is possible at the temperature used for testing by further oxidation and decomposition, the present report compares the effects of disulfides and thiosulfinates on the polymerization of methyl methacrylate, thus providing conditions from which the further oxidation factor has been removed.

RESULTS AND DISCUSSION

Efficiencies of inhibition were measured dilatometrically, with rates of polymerization of methyl methacrylate as a 50% v/v solution in benzene at 60°, recorded as $R_p\%$ min^{-1}. Results for the uninhibited polymerization are illustrated in Figure 1 and for the polymerization inhibited by *p*-methylphenyl-*p*-methylbenzene thiosulfinate, a derivative with intermediate efficiency, in Figure 2. Results have been plotted as the result of a unimolecular reaction conforming to the expression, $xM \rightarrow M_x$.

A summary of results for a series of thiosulfinates, measured at two concentrations, together with some disulfides is given in Table I. Hitherto considerable attention has been given to ionic displacement reactions in oxygenated sulfur derivatives, including comparisons of the responses of the sulfenyl and sulfonyl sulfur atoms of thiosulfonates to a series of nucleophiles[3] and the combined acid/nucleo-

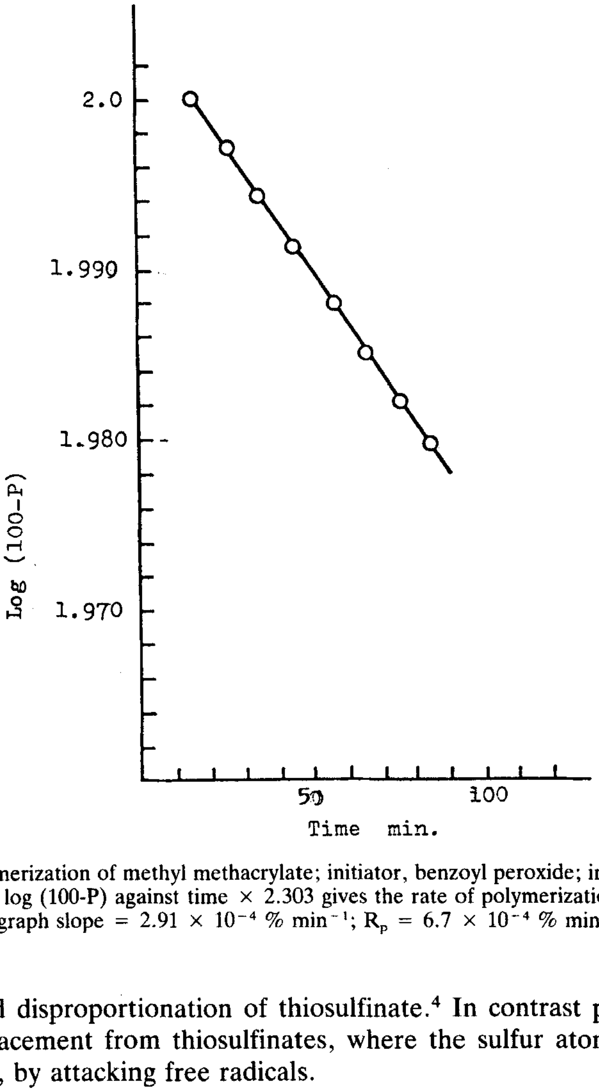


FIGURE 1 Polymerization of methyl methacrylate; initiator, benzoyl peroxide; inhibitor, none. The slope of the graph log (100-P) against time × 2.303 gives the rate of polymerization R_p as % min^{-1}. In this case, from graph slope = 2.91×10^{-4} % min^{-1}; $R_p = 6.7 \times 10^{-4}$ % min^{-1}.

philic catalyzed disproportionation of thiosulfinate.[4] In contrast present work is based on displacement from thiosulfinates, where the sulfur atom is at a lower oxidation level, by attacking free radicals.

Table I shows that aryl thiosulfinates at the higher concentration reduce the polymerization rate of methyl methacrylate by several orders of magnitude and that efficiency is controlled in a regular manner by substituents, in particular by electron donating effects on the divalent sulfur atom. Comparison of R_p values of the three methoxylated derivatives (III–V) shows that substitution on the sulfinyl side, as in V, reduces the polymerization rate only slightly below that of the parent unsubstituted derivative I. On the other hand a marked enhancement of efficiency follows substitution on the sulfenyl side as in III. Confirmation of only a slight contribution from a methoxyl group on the sulfinyl side comes with the doubly substituted derivative IV, where the effect is only of the same order as that of the mono-substituted derivative III.

These principles extend to the doubly substituted methyl derivative II, where the increase in efficiency is less than that of the equivalent methoxylated derivative

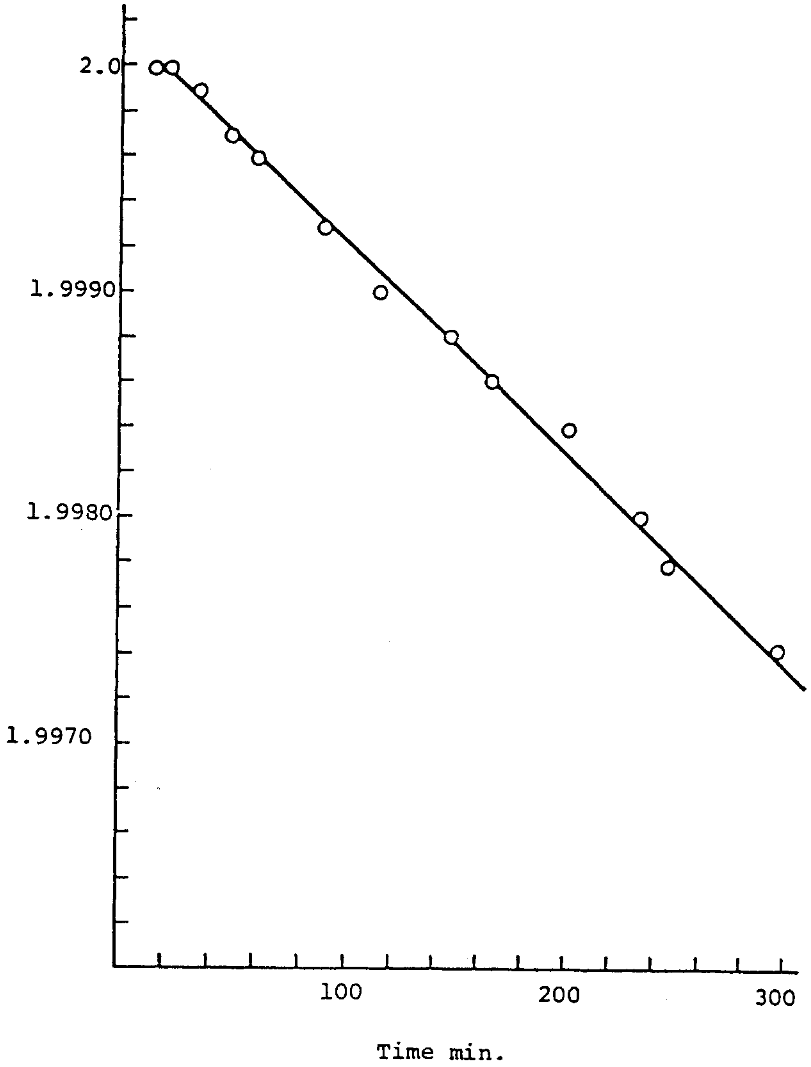


FIGURE 2 Polymerization of methyl methacrylate; initiator, benzoyl peroxide; inhibitor, *p*-methylphenyl-*p*-methylbenzene thiosulfinate. From graph slope = 6.1×10^{-6} % min^{-1}; $R_p = 1.4 \times 10^{-5}$ % min^{-1}.

in accordance with a lesser donating effect, and must be attributed primarily to the methyl substitution on the sulfenyl side. A restrictive influence by the sulfinyl group on the relay of substituent effects has been noted on several occasions. For instance comparisons of the capacities of a divalent sulfur atom ($n = 0$) and the sulfinyl group ($n = 1$) to relay substituent effects in the phenylmercaptoacrylic acids (X)[5] and phenylmercaptoacetic acids (X1)[6] illustrate this restrictive influence.

$$\text{Y } C_6H_4S(O)_nCH{=}CH\ COOH \quad \text{(X)} \qquad n = 0\text{–}2 \qquad m = 1\text{–}2 \qquad \text{Y } C_6H_4S(O)_n(CH_2)_mCOOH \quad \text{(X1)}$$

TABLE I

Effects of thiosulfinates and disulfides on polymerization of methyl methacrylate

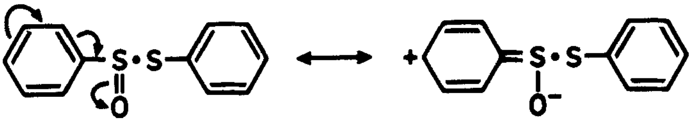
Additive			Concentration			
			$C = 1.3 \times 10^{-3}$ M		$C = 4 \times 10^{-4}$ M	
			Slope %/min	Rp %/min	Slope %/min	Rp %/min
None (Control)			2.91×10^{-4}	6.7×10^{-4}		
Thiosulfinates RSOSR¹						
	R	R¹				
(I)	C_6H_5	C_6H_5	9.8×10^{-6}	2.36×10^{-5}	3.27×10^{-5}	7.5×10^{-5}
(II)	$CH_3C_6H_4$	$C_6H_4CH_3$	6.1×10^{-6}	1.4×10^{-5}	2.55×10^{-5}	5.87×10^{-5}
(III)	C_6H_5	$C_6H_4OCH_3$	$3{,}74 \times 10^{-6*}$	8.6×10^{-6}	Init. 2.93×10^{-5} 3.7×10^{-5}	6.94×10^{-5} 8.5×10^{-5}
(IV)	$CH_3OC_6H_4$	$C_6H_4OCH_3$	$2.2 \times 10^{-6*}$	5.07×10^{-6}	2.68×10^{-5}	6.17×10^{-5}
(V)	$CH_3OC_6H_4$	C_6H_5	6.83×10^{-6}	1.57×10^{-5}	3.44×10^{-5}	7.92×10^{-5}
(VI)	C_2H_5	C_2H_5	2.86×10^{-5}	6.69×10^{-5}	-	-
Disulfides RSSR						
(VII)	C_2H_5	C_2H_5	2.8×10^{-4}	6.45×10^{-4}		
(VIII)	$CH_3OC_6H_4$	$C_6H_4OCH_3$	$3.04 \times 10^{-4**}$	7.0×10^{-4}		
(IX)	$CH_3OC_6H_4$	$C_6H_4OCH_3$	$1.2 \times 10^{-4***}$	2.76×10^{-4}		

* No polymer precipitated by methanol.
** $C = 1.36 \times 10^{-2}$.
*** Without initiator.
Comparison of VI and I. Ratio of times to 0.519% polymerization 30/1441 = 1/48.

The simplest explanation of the inhibition of polymerization may then be summated as the result of attack of a polymerizing methacrylate radical at the divalent sulfur, a point of higher electron density, as follows

$$\begin{aligned} P^\circ + \quad R.SO.S.R. &\rightarrow R.SO^\circ \quad + P.S.R. \\ 2\,R.SO^\circ &\rightarrow R.SO_2.S.R \end{aligned}$$

The failure of electron donating substituents on the sulfinyl side to influence rates means that effects do not reach the divalent sulfur atom, due to absorption either in the polarity of the SO group ($S{=}O \leftrightarrow S^+{-}O^-$) or in an overall conjugative affinity of the type



Thus although the sulfinyl group may not be the site of attack by the polymer radical, nevertheless the activity of thiosulfinates is completely dependent on its presence. Thermal homolysis of S—S bonds is easier in compounds of the type R.SO.X, as in thiosulfinates (X=S.R)[7] and sulfinyl sulfones ($X=SO_2.R$)[8] than in disulfides and disulfones ($R.SO_2.SO_2.R$). Possibly closer to present results photocatalyzed disproportionation of thiosulfinates to disulfide and thiosulfonate, as well as racemization of optically active sulfinamides,[9] occur readily. In each case the first step is homolysis of the SO.X bond (X=S.R or NH.R), with appropriate recombination reactions. Disproportionation of sulfinamides has been attributed to the influence of the sulfinyl group.[10]

In the present context it is proposed that attack of the polymer radical at the divalent sulfur atom leads to extrusion of a R.SO radical in which the odd electron is located in a S=O group.[11] It has been noted that the R.SO radical is isoelectronic with the $R.S_2$ radical and it has been found as predicted, that such radicals are more stable than R.S radicals.[12] With the R.SO radical generally less reactive disproportionation to thiosulfonate is a preferred course of reaction. From the decomposition of a sulfinyl sulfone in the presence of diphenylethylene, an active participant in free radical reactions, no product was found indicative of reaction with a R.SO radical[8] and no diversion of products was found with the inclusion of styrene in the decomposition of thiosulfinates.[8] By contrast there is much evidence for the participation of disulfides in free radical reactions with olefins. In a first step disulfides may act as radical acceptors with extrusion of a sulfenyl radical able to initiate or carry on chain processes as:

$$\begin{array}{llcl} R.S.S.R & + P^{\cdot} & \rightarrow & R.S.P. + R.S^{\cdot} \\ R.S^{\cdot} & + C{=}C & \rightarrow & R.S.C{-}C^{\cdot} \end{array}$$

The disulfides are thereby acting as chain transfer agents so that their inactivity as retarders might be better described as "apparent" rather than "real." In contrast the inactivity of thiosulfonates is real. As a common end product of thermal and photocatalyzed decompositions of thiosulfinates and sulfinyl sulfones emphasis must be placed on their greater stability. It is clear that in any process where R.SO radicals may be generated there is a strong driving force for their removal from the system as thiosulfonates. The stability of thiosulfonates relative to thiosulfinates thus provides an illustration of the theorem that stability and reactivity are inversely related. Relative stability is probably one factor contributing to the anomalous behaviors of alkyl and aryl disulfides and their derived thiosulfinates as antioxidants[2] and now to differences in effects on the polymerization of methyl methacrylate.

As discussed elsewhere[2] comparisons of S—S bond strengths show the value for dialkyl disulfides, about 75 kcal/mol, greater than that for aryl derivatives by about 10 kcal/mol. This difference is maintained in the thiosulfinates where the S—S bond energies are lower, of the order 46 ± 4.6 kcal/mol for methyl methanethiosulfinate and about 34.5 kcal/mol for aryl derivatives.[7] The resulting easier fission of the S—S bond of aryl thiosulfinates, favored also by the properties of the sulfinyl

TABLE II

Polymerization of methyl methacrylate at 60°, methyl methacrylate 19.94 g, benzene 18.64 g. These weights have the same volume 22.3 ml at 60°; initiator, benzoyl peroxide 1.94×10^{-3} mol/L, inhibitor, none.

Readings

Time mins.	sec.	Cathetometer reading-cm.	Δ cm.	P%	(100-P)	Log (100-P)
15	45	11.099	—	—	100	2.0000
25	30	10.564	0.535	0.69	99.31	1.9969
35	5	10.059	1.040	1.34	98.66	1.9942
45	25	9.523	1.576	2.02	97.98	1.9912
56	30	8.962	2.137	2.75	97.25	1.9879
66	20	8.420	2.679	3.45	96.55	1.9847
76	10	7.927	3.172	4.08	95.92	1.9819
85	27	7.537	3.562	4.59	95.41	1.9795

P, the extent of polymerization was derived from the change in meniscus level by multiplying by the dilatometer constant, in this case 1.288, which incorporated the change in specific volume with polymerization, (24.68% for 100% methyl methacrylate polymerization) and the area of the cross section of the capillary.

TABLE III

Polymerization of methyl methacrylate at 60°, methyl methacrylate 19.92 g, benzene 18.64 g; initiator, benzoyl peroxide 2.01×10^{-3} mol/L, inhibitor, *p*-methylphenyl-*p*-methylbenzenethiosulfinate 1.37×10^{-3} mol/L.

Readings

Time mins.	Cathetometer reading-cm.	Δ cm.	P%	(100-P)	Log (100-P)
13	11.865	—	—	100	2.0000
22	11.863	0.002	0.003	99.99	2.0000
33	11.845	0.020	0.026	99.97	1.9999
48	11.812	0.053	0.07	99.93	1.9997
59	11.797	0.068	0.088	99.91	1.9996
87	11.744	0.121	0.156	99.84	1.9993
113	11.694	0.171	0.22	99.78	1.9990
145	11.650	0.215	0.276	99.724	1.9988
164	11.615	0.250	0.32	99.68	1.9986
200	11.558	0.307	0.395	99.605	1.9984
231	11.512	0.353	0.454	99.546	1.9980
245	11.482	0.383	0.49	99.51	1.9978
295	11.399	0.466	0.60	99.40	1.9974
352	11.295	0.570	0.735	99.265	1.9968
410	11.194	—	—	—	—

radical as discussed above, become contributing factors to the superiority of aryl thiosulfinates as inhibitors of vinyl polymerization. Subsequent studies using variously sulfur isotope-labeled thiosulfinates followed by examination of isolated polymer, have confirmed the sulfenyl sulfur as the point of attack by the polymerizing radical.[13]

EXPERIMENTAL

Thiosulfinates were prepared by condensation of a sulfinyl chloride with a thiol[14] and thiosulfonates by decomposition of anhydrous sulfinic acids.[15] Disulfides were obtained by oxidation of thiols. All derivatives were recrystallized to satisfactory melting point and elemental analysis. Methyl methacrylate (Kallodoc) in small batches (500 ml) was freed from inhibitor by shaking with 10% sodium hydroxide solution (3 × 100 ml) then with water (3 × 100 ml). The dry (Na_2SO_4) monomer was distilled under reduced pressure under nitrogen, collecting the fraction b.pt. 40°–45/110–100 mm. The material was stored at low temperature protected from light. Benzoyl peroxide initiator was recrystallized several times from ether. Benzene solvent for polymerizations was A.R. reagent dried over sodium.

Procedure. Polymerization rates were measured dilatometrically. The standardized dilatometer consisted on a tubular bath (13.5 × 2.5 cm, about 50 ml capacity) provided with a neck of statndard bore capillary tubing into which the level of contents rose at 60°. A standard joint fixed to the open end allowed sealing *in vacuo* for each determination. A small pimple at the bottom of the bulb when punctured allowed contents to flow freely from the dilatometer after each determination. The monomer was introduced by bulb to bulb distillation *in vacuo* into a solution of the initiator and inhibitor in benzene in the dilatometer. This procedure served to remove any polymer in the inhibitor-free monomer formed during storage. At most only a thin film was left on the sides of the flask after distillation. The mixture was degassed several times by alternate freezing, evacuating the thawing. Finally the dilatometer was sealed *in vacuo*.

Polymerization rates were determined by completely immersing the dilatometer in a large thermostatted bath at 60 ± 0.1°, measuring the volume changes with a cathetometer. Translation of readings to polymerization rates is illustrated in Tables II and III.

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