

Identical experiments with solutions of vesicant-treated and untreated tobacco mosaic virus gave similar results. After the action of Duponol C on the vesicant-treated virus, a value of 0.01 mg. of vesicant residues per 7 mg. of virus was obtained.

These results demonstrate that the restoration of phenol color value in vesicant-treated pepsin and tobacco mosaic virus by the action of Duponol C is not accompanied by any appreciable degree of cleavage of vesicant residues from the proteins.

**Dimethyl  $\beta$ -Phenoxyethyl Sulfonium Iodide.**—This salt was prepared by treatment of methyl  $\beta$ -phenoxyethyl sulfide with methyl iodide under the conditions described by Crane and Rydon.<sup>10,17</sup>

**Methyl  $\beta$ -Phenoxyethyl  $\beta$ -Butylmercaptoethyl Sulfonium Diliturate.**—Methyl  $\beta$ -phenoxyethyl sulfide (1.68 g.) and butyl-H (3.0 g.) were dissolved in 20 cc. of 95% ethanol. After four days, the mixture was diluted with 3 volumes of water and centrifuged. The upper layer was removed and treated with 3 volumes of a saturated aqueous solution of dilituric acid (5-nitrobarbituric acid). The light yellow prisms which separated were collected and washed with cold methanol and cold acetone. The product (1.5 g.) was purified by one recrystallization from acetone and two recrystallizations from methanol. The recrystallizations were carried out at a maximum temperature of 25° on account of the instability of the compound. The purified sulfonium salt melted on the hot stage with decomposition and evolution of gas at 120–130°.

*Anal.* Calcd. for  $C_{16}H_{25}OS_2 \cdot C_4H_2O_5N_3$ : N, 9.18; S, 14.01. Found: N, 9.18; S, 13.85.

**Phenol Color Reactions of the Sulfonium Compounds.**—The phenol color reactions of the sulfonium compounds are summarized in Table I. A very small amount of color was produced by the action of the phenol reagent at pH 8 on the sulfonium compounds; the amount of color produced remained unchanged after preliminary treatment

with Duponol C. However, considerable color was produced with the phenol reagent after the compounds had been treated with alkali.

**Acknowledgment.**—The authors would like to take this opportunity to express their appreciation to Dr. Mary Elizabeth Wright for invaluable aid in the preparation of this manuscript.

### Summary

A study has been made of the decreased chromogenic power toward Folin's phenol reagent at pH 8 displayed by pepsin and tobacco mosaic virus which had been treated with *n*-butyl  $\beta$ -chloroethyl sulfide (butyl-H). After treatment with sodium dodecyl sulfate (Duponol C), the vesicant-treated and untreated proteins give the same amount of color with the phenol reagent. Moreover, no significant amount of vesicant residues is liberated by the action of Duponol C on the vesicant-treated proteins.

It is concluded that the increase in the amount of phenol color from these vesicant-treated proteins after the action of Duponol C is not due to the cleavage of vesicant residues from the tyrosine or tryptophan groups of the proteins. It is further concluded that the decreased chromogenic power of vesicant-treated proteins toward the phenol reagent at pH 8 is not due to reaction of the vesicant with the tyrosine or tryptophan groups in the proteins.

(17) Crane and Rydon, *J. Chem. Soc.*, 766 (1947).

NEW YORK, N. Y.

RECEIVED FEBRUARY 9, 1948

[CONTRIBUTION NO. 78 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

## The Reaction of $\alpha$ -Methylstyrenes with Thioglycolic Acid

BY CHEVES WALLING, DEXTER SEYMOUR AND KATHERINE P. WOLFSTIRN

Studies of the relative reactivities of meta- and para-substituted styrenes<sup>1</sup> and  $\alpha$ -methylstyrenes<sup>2</sup> with free radicals derived from copolymerizing monomers have been useful in determining the nature of the "alternating effect" in copolymerization. An entirely similar approach may be made to the study of the nature of the attack of solvent radical on monomer in the chain transfer reaction.<sup>3</sup> This paper presents an investigation of the relative reactivities of six meta and para substituted  $\alpha$ -methylstyrenes toward the radical  $\cdot\text{SCH}_2\text{COOH}$  derived from thioglycolic acid.

Since the transfer constant for an  $\alpha$ -methylstyrene with thioglycolic acid is very large,<sup>4</sup> when two  $\alpha$ -methylstyrenes are heated with thioglycolic

acid in the presence of a free-radical catalyst, virtually the only reaction by which styrenes will be consumed will be by reaction with the  $\cdot\text{SCH}_2\text{COOH}$  radical (to give, eventually,  $\beta$ -phenylpropylmercaptoacetic acid), and the kinetic equations will be identical with those for the system of two  $\alpha$ -methylstyrenes and maleic anhydride.<sup>2</sup> *I.e.*,  $d[M_1]/d[M_2] = k_1[M_1]/k_2[M_2]$  where  $M_1$  and  $M_2$  represent the two styrenes and  $k_1$  and  $k_2$  the rate constants for their reaction with the mercaptide radical.<sup>5</sup> Calculations of relative reactivities including the determination of experimental errors were, accordingly, carried out as described previously.<sup>2</sup>

### Experimental

**Materials.**—Thioglycolic acid was obtained by fractionating commercial material. Its physical constants were b. p. 79–80 (1 mm.), m. p. –17.5 to –15.5°. The  $\alpha$ -

(1) Walling, Briggs, Wolfstirn and Mayo, *THIS JOURNAL*, **70**, 1537 (1948).

(2) Walling, Seymour and Wolfstirn, *ibid.*, **70**, 1544 (1948).

(3) Mayo, *ibid.*, **65**, 2324 (1943).

(4) The styrene radical reacts with ethyl thioglycolate 58 times as readily as with styrene. Cf. Gregg, Alderman and Mayo, *ibid.*, in press. Since  $\alpha$ -methylstyrene shows relatively little tendency to polymerize with itself, its transfer constant with thioglycolic acid is presumably even larger.

(5) It is of interest that the equation describing chain transfer, in general, is a special case of the copolymerization equation in which the "monomer reactivity ratio" for the solvent is zero and the "transfer constant" is the reciprocal of the "monomer reactivity ratio" for the monomer considered.

methylstyrenes were portions of the same samples used in the maleic anhydride work.<sup>2,6</sup>

**Technique.**—Experiments were carried out using 0.1 mole of mixed styrenes, 0.05–0.1 mole of thioglycolic acid, and 0.14–0.18 millimole of benzoyl peroxide. Techniques of polymerization, isolation of unreacted monomers, and analysis were identical with those used with the maleic anhydride systems.<sup>2</sup> Results are listed in Table I.

TABLE I  
REACTION OF MIXED SUBSTITUTED  $\alpha$ -METHYLSTYRENES ( $M_1$  AND  $M_2$ ) WITH THIOGLYCOLIC ACID (S) AT 60°. (ALL QUANTITIES IN MILLIMOLLES)

$[M_1]_0$	$[M_2]_0$	$[S]_0$	Time, hr.	$[M_1]$	$[M_2]$
$\alpha$ -Methylstyrene ( $M_1$ )– $\alpha$ , $p$ -dimethylstyrene ( $M_2$ )					
49.2	49.8	49.8	31.8	39.7	33.9
32.3	65.7	98.4	31.8	17.74	13.01
64.9	32.6	98.5	31.8	37.7	8.05
$\alpha$ , $p$ -Dimethylstyrene ( $M_1$ )– $p$ -fluoro- $\alpha$ -methylstyrene ( $M_2$ )					
49.0	46.0	49.0	14.0	36.0	42.6
32.0	59.0	98.0	10.2	15.31	50.0
66.0	27.0	98.0	10.2	37.3	24.1
28.0	46.0	97.0	15.5	1.33	30.3
$\alpha$ , $p$ -Dimethylstyrene ( $M_1$ )– $p$ -bromo- $\alpha$ -methylstyrene					
49.0	49.0	49.7	6.75	30.4	36.6
33.0	63.0	99.3	6.75	9.80	47.4
66.0	32.0	98.5	6.75	40.3	23.9
$\alpha$ , $p$ -Dimethylstyrene ( $M_1$ )– $m$ -bromo- $\alpha$ -methylstyrene ( $M_2$ )					
33.0	66.0	98.0	6.75	11.50	49.3
65.0	38.0	98.0	8.5	33.50	24.0
25.8	42.6	49.0	15.5	8.63	24.8
$\alpha$ , $p$ -Dimethylstyrene ( $M_1$ )– $p$ -methoxy- $\alpha$ -methylstyrene ( $M_2$ )					
56.0	42.0	49.0	3.25	47.2	5.12
34.0	44.5	101	0.50	32.4	14.30
68.0	21.5	101	0.25	65.2	2.87

### Discussion

Relative reactivities of the six  $\alpha$ -methylstyrenes toward the mercaptide radical from thioglycolic acid are listed in Table II, together with relative reactivities toward the maleic anhydride type radical, included for comparison. In each case, reactivities have been referred to  $\alpha$ -methylstyrene as unity even though the actual comparison was

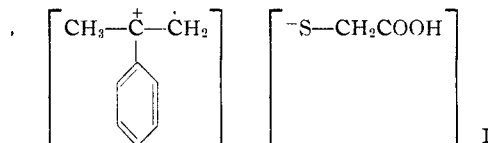
TABLE II  
RELATIVE REACTIVITIES OF  $\alpha$ -METHYLSTYRENE TOWARD THIOGLYCOLIC ACID AND MALEIC ANHYDRIDE-TYPE RADICALS

Substituent	Reactivities toward	
	Thioglycolic acid radical	Maleic anhydride radical <sup>2</sup>
$p$ -OCH <sub>3</sub>	215 $\pm$ 100	18.5
$p$ -CH <sub>3</sub>	2.28 $\pm$ 0.54	1.72
None	1.00	1.00
$p$ -F	0.51 $\pm$ 0.13	0.72
$p$ -Br	0.90 $\pm$ 0.56	0.73
$m$ -Br	0.96 $\pm$ 0.56	0.96

(6) Seymour and Wolfstirn, *ibid.*, **70**, 1177 (1948).

with  $\alpha$ , $p$ -dimethylstyrene. Experimental errors have been taken as the standard deviation of separate experiments and are somewhat greater than those reported for the maleic anhydride study.<sup>2</sup> While they could doubtless be reduced by further refinement of technique, accuracy is ample for the discussion which follows.

Copolymerization studies<sup>1,2</sup> have shown that the reactivity of styrene toward carbonyl conjugated radicals is increased by substituents in the order  $p$ -CH<sub>3</sub> <  $p$ -OCH<sub>3</sub> < N(CH<sub>3</sub>)<sub>2</sub>, and that the effect of each substituent increases with the tendency of the monomer from which the attacking radical was derived to alternate in copolymerization with styrene. Table II indicates a similar effect of substitution on reactivity toward the  $\cdot$ SCH<sub>2</sub>COOH radical, but even greater than that encountered toward maleic anhydride, the most powerfully "alternating" radical studied.<sup>7</sup> In the copolymerization experiments, the effect was suggested as arising from the presence of special (chiefly non-bonded) resonance forms in the transition state in which an electron had been donated from the styrene to the carbonyl-conjugated molecule. Similar structures such as (I) can be postu-



lated here and stabilization anticipated both from the many structures available to the styrene carbonium-ion radical and the electronegativity of sulfur (the mercaptide ion is an even weaker base than the enolate ion postulated as stabilizing the transition state in the copolymerization reaction<sup>1,2</sup>).

Heretofore, discussions of radical addition reactions have been directed entirely toward a consideration of the resonance stability of the radicals produced.<sup>8</sup>

However, in view of our knowledge of copolymerization phenomena,<sup>9</sup> important contributions of polar resonance forms to the transition state in the attack of other free radicals on double bonds should probably be anticipated whenever the radical may gain stability by electron donation or acceptance. Thus, for example, in the attack of a bromine atom on a double bond, contributions involving the bromide ion should be important, and relative reactivities of olefins in the free radical chain additions of both bromine and hydrogen bromide should parallel those observed toward the radicals from mercaptans and carbonyl conju-

(7) In this paper no competitive experiments using  $p$ -dimethylamino- $\alpha$ -methylstyrene were attempted as it was presumed that the ratio of reactivities would be too great to measure.

(8) See, for example, Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944; Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

(9) For recent summaries, see Mayo, Lewis and Walling, *THIS JOURNAL*, **70**, 1529 (1948); *Trans. Faraday Soc.*, in press.

gated monomers, rather than an order based solely on radical stabilization.<sup>9</sup>

### Summary

1. Relative reactivities of six  $\alpha$ -methylstyrenes toward the  $\cdot\text{SCH}_2\text{COOH}$  radical derived from thioglycolic acid have been determined.

2. Reactivities lie in the order  $p\text{-OCH}_3 > p\text{-CH}_3 > p\text{-H} \geq p\text{-halogen}$  and closely parallel

those toward the maleic anhydride type radical observed in copolymerization. Results are interpreted in terms of contributions of non-bonded resonance forms to the transition state.

3. The possibility that contributions of polar (probably non-bonded) forms to the transition state may be important in a variety of free radical reactions is discussed.

PASSAIC, NEW JERSEY RECEIVED FEBRUARY 18, 1948

[CONTRIBUTION NO. 79 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

## The Use of S<sup>35</sup> in the Measurement of Transfer Constants

BY CHEVES WALLING

The use of radioactive tracer elements as a method of end-group analysis should provide an elegant means of following chain transfer with solvents in polymerizing systems. This paper describes the measurement of the transfer constant of *n*-butyl mercaptan containing S<sup>35</sup> with styrene, methyl methacrylate, methyl acrylate and vinyl acetate. While the work was undertaken primarily to gain experience in the use of radioisotopes in polymer chemistry, the results, taken with recent measurements of the absolute rate of the chain-growth step in polymerization of vinyl acetate,<sup>1</sup> styrene,<sup>2</sup> and methyl methacrylate,<sup>2</sup> give further evidence of the importance of ionic forms in the transition state of free radical reactions.

**Method.**—The fundamental measurement employed in this work has been the comparison of the radioactivity of samples of polymer carried to different degrees of conversion in the presence of the same amount of S<sup>35</sup>-containing mercaptan. Since the maximum penetration of the soft  $\beta$ -radiation from S<sup>35</sup> in ordinary polymers is under 0.2 mm., for thicker films of identical area (as obtained by the technique described below) measured activity is proportional to the concentration of —SR groups in the polymer and independent of film thickness.<sup>3</sup> Mathematically, this may be expressed in the form

$$\frac{[S]_0 - [S]_1}{[M]_0 - [M]_1} \bigg/ \frac{[S]_0 - [S]_2}{[M]_0 - [M]_2} = R \quad (1)$$

where  $R$  is the ratio of measured activities of polymer from two experiments and  $[M]$  and  $[S]$  are concentrations of monomer and solvent (mercaptan), respectively, present initially (subscript zero) and at the end of the two experiments (subscripts one and two). Recalling that the usual integrated form of the transfer equation is given by

$$\log [S]/[S]_0 = C \log [M]/[M]_0 \quad (2)$$

(1) (a) Swain and Bartlett, *ibid.*, **68**, 2381 (1946); (b) Burnett and Melville, *Proc. Roy. Soc. (London)*, **A189**, 456 (1947); (c) Bamford and Dewar, *ibid.*, **192A**, 309 (1948).

(2) Matheson, Bevilacqua, Aver and Hart, unpublished work from this laboratory.

(3) See, for example, Henriques, Kistiakowsky, Margnetti and Schneider, *Ind. Eng. Chem., Anal. Ed.*, **18**, 349 (1946).

where  $C$  is the "transfer constant,"<sup>4,5</sup> (1) may be rewritten as

$$R \frac{1 - [M]_1/[M]_0}{1 - [M]_2/[M]_0} = \frac{1 - ([M]_1/[M]_0)^C}{1 - ([M]_2/[M]_0)^C} \quad (3)$$

Using data giving  $R$  and yields from two experiments,  $C$  may, in principle, be obtained by graphical solution of (3). However, in cases where the transfer constant of the system is greater than unity,<sup>6</sup> the calculation can be greatly simplified by choosing as one of the samples for the determination of  $R$  a polymer which has been carried to complete conversion. Here, equation (3) reduces to

$$C = \log (1 - R + R[M]/[M]_0) / \log [M]/[M]_0 \quad (4)$$

Since the only quantities needed for the determination of transfer constants by the tracer technique are yields and relative activities, measurements of absolute amounts of transfer agent or molecular weights are unnecessary. The chief requirement is the use of enough mercaptan for measurement of its activity yet little enough so that material is produced which can be handled as polymer (rather than the simple addition product). Some judgment is required, also, in the selection of the extent of reaction to which monomer-solvent mixtures are carried before polymer isolation, particularly when a high transfer constant is anticipated. In Fig. 1 is plotted the variation of  $R$  with per cent. reaction for various values of  $C$ , and it will be seen that the rapid consumption of active solvents with large transfer constants makes high conversion experiments useless for evaluating  $C$ . This phenomenon, of course, applies to *any* method of measuring transfer constants and a useful generalization is that experi-

(4) Mayo, *THIS JOURNAL*, **65**, 2324 (1943).

(5) Walling, Seymour and Wolfstirn, *ibid.*, **70**, 2559 (1948).

(6) Even in cases where the transfer constant is less than unity (so that complete inclusion of the mercaptan in the polymer is not assured, even when polymerization is carried to completion) equation (4) may be employed by using a reference sample of a different monomer carried to complete reaction. Also, it is frequently advantageous (when the transfer constant differs widely from unity) to employ a reference sample prepared in the presence of a different (but known relative) mercaptan concentration.