gated monomers, rather than an order based solely on radical stabilization.[9]

Summary

1. Relative reactivities of six α-methylstyrenes toward the $\cdot SCH_2COOH$ radical derived from thioglycolic acid have been determined.

2. Reactivities lie in the order p-OCH_3 > p-CH_3 > p-H $\geqslant$ p-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.

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

The Use of S^{35} 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^{35} 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,[1] styrene,[2] and methyl methacrylate,[2] 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^{35}-containing mercaptan. Since the maximum penetration of the soft β-radiation from S^{35} 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.[3] Mathematically, this may be expressed in the form

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

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

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

where C is the "transfer constant,"[4,5] (1) may be rewritten as

$$R\frac{1 - [M]_1/[M]_0}{1 - [M]_2/[M]_0} = \frac{1 - ([M]_1/[M_0])^C}{1 - ([M]_2/[M]_0)^C} \qquad (3)$$

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,[6] 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

$$C = \log (1 - R + R[M]/[M]_0)/\log [M]/[M_0] \qquad (4)$$

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-

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(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).

(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.

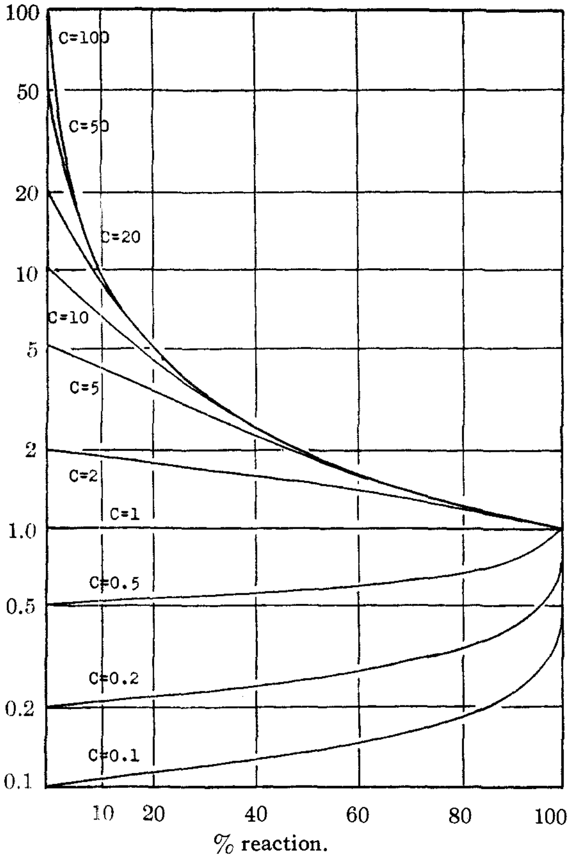


Fig. 1.—Variation of *R*, the relative activity of polymer samples, with % reaction for differing values of *C*, the transfer constant.

TABLE I

TRANSFER CONSTANTS OF *n*-BUTYL MERCAPTAN SYSTEMS AT 60°

Yield, %	*R*	*C*	
	Styrene[a]		
8.25	9.58	18.1	22 ± 3
1.25	21.5	24.9	
10.62	8.70	23.0	
8.68	9.93	21.8	
	Methyl methacrylate[a]		
7.48	0.653	0.667	0.67 ± 0.03
16.8	.702	.675	
23.8	.706	.679	
39.5	.713	.658	
	Methyl acrylate[b]		
27.3	1.45	1.58	1.69 ± 0.17
43.0	1.51	1.86	
21.2	1.59	1.71	
6.6	1.49	1.52	1.53 ± 0.04[c]
16.2	1.51	1.58	
12.2	1.45	1.49	
	Vinyl acetate[d]		
3.80	23.5	58	48 ± 14
4.12	19.6	39	

[a] 1 ml. mercaptan solution to 10 ml. monomer. [b] 1 ml. mercaptan solution to 10 ml. monomer, 10 ml. ethyl acetate. [c] At 30°. [d] 1 ml. mercaptan solution to 40 ml. monomer.

ments should not be carried to extents of reaction greater than the reciprocal of the anticipated transfer constant of the system. As a technique, the tracer method enjoys its greatest advantage in systems having a high transfer constant and in which the radioactive solvent is readily prepared, and should even compare favorably with titration of unreacted solvent[7,8] when the latter is possible. On the other hand in systems having low transfer constants (under ~ 0.1) measurement by molecular weight determination is certainly to be preferred.[4,9]

Results and Discussion.—Experimental results and calculated transfer constants are listed in Table I. Experimental errors given are, in general, standard deviations of the separate experiments. For methacrylate, however, agreement seems fortuitously good and the error is taken as 5% of the measured value. Transfer constants for styrene and methyl methacrylate are in good agreement with the values reported for *n*-amyl mercaptan with these monomers (20 and 0.8, respectively) by W. V. Smith[7] and for other straight-chain mercaptans by Gregg, Alderman and Mayo.[8] Measurements at two temperatures with the methyl acrylate system indicate that the reaction of chain growth has a lower activation energy than chain transfer (by 600 calories), but, since it has a smaller *PZ* factor, proceeds more slowly. Although this is the reverse of the situation observed with styrene and mercaptans,[8] differences are too small to have much real significance.

In an earlier paper[5] it was shown that a factor analogous to the "alternating effect" in copolymerization may be important in determining reactivity of olefins in simple free radical addition reactions. The data of this paper, taken with recent measurements of the absolute rates of the chain-growth reaction in vinyl polymerizations,[1,2] gives strong indication that similar forms are important in the conjugate reaction of chain transfer in which the radical from the olefin attacks the solvent, breaking a single bond. In Table II are listed rate constants for chain growth, transfer constants, and rate constants for reaction with *n*-butyl mercaptan for polymerizing styrene, methyl methacrylate, and vinyl acetate. Although in the general series of reactivities obtained from copolymerization studies methacrylate lies between styrene and vinyl acetate,[10] toward *n*-butyl mercaptan it has the lowest reactivity. In copolymerization[11] and addition of

(7) Smith, *ibid.*, **68**, 2059 (1946).

(8) Gregg, Alderman and Mayo, *ibid.*, in press.

(9) Gregg and Mayo, *ibid.*, **70**, 2373 (1948).

(10) Mayo, Lewis and Walling, *ibid.*, **70**, 1529 (1948).

(11) Walling, Briggs, Wolfstirn and Mayo, *ibid.*, **70**, 1537 (1948).

TABLE II

RATE CONSTANT FOR CHAIN GROWTH (k_p) AND REACTION WITH *n*-BUTYL MERCAPTAN (k_t) FOR THREE MONOMERS

Monomer	k_p^a	C	k_t
Styrene	207	22	4,550
Methyl methacrylate	367	0.67	246
Vinyl acetate	3700	48	178,000

[a] From Matheson, *et al.*,[2] in reasonable agreement with Bamford and Dewar[1c] (styrene) and Swain and Bartlett[1a] (vinyl acetate).

simple radicals to olefins[5] such anomalies have been explained on the basis of additional ionic forms in the transition state arising from electron transfer from radical to olefin or *vice versa*. In the present case, the analogous phenomenon would be contributions from non-bonded resonance structures such as

$$\underset{\text{I}}{R^{+}H\cdot{}^{-}S—R},\ \underset{\text{II}}{R^{+}H—S^{-}\cdot R},\ \underset{\text{III}}{R^{+}H—S\cdot{}^{-}R},\ \text{etc.}$$

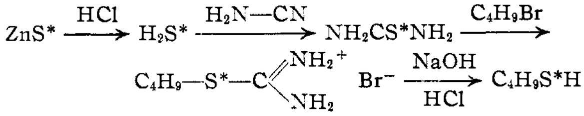
if an electron were transferred from the attacking radical, and

$$\underset{\text{IV}}{R^{-}H\cdot S^{+}—R},\ \underset{\text{V}}{R^{-}H^{+}\cdot S—R},\ \text{etc.}$$

if transfer were in the opposite direction. The heightened reactivity of styrene and vinyl acetate radicals (which are electron donors, rather than acceptors[10,11]) compared with methacrylate indicate that forms involving donation *to* the mercaptan are preferred, as might be expected from the relative electronegativities of sulfur and carbon. In short, in the case of a chain transfer reaction, as we have seen previously in copolymerization, certain structures increase the rates of both of two conjugate free radical reactions and give each more of an "ionic" character. Further confirmation is thus obtained for the suggestion made in previous papers from this laboratory that polar contributions to the transition state may be of importance in determining the effects of structure on reactivity in a great number of free radical reactions.

Experimental

Active *n*-Butyl Mercaptan.—This compound was prepared from active ZnS* by the sequence of reactions



$$ZnS^* \xrightarrow{HCl} H_2S^* \xrightarrow{H_2N—CN} NH_2CS^*NH_2 \xrightarrow{C_4H_9Br} C_4H_9—S^*—C\begin{matrix}\diagup\!\!\!\diagup NH_2^{+}\\ \diagdown NH_2\end{matrix}\ Br^- \xrightarrow[HCl]{NaOH} C_4H_9S^*H$$

Thiourea.—S^{35}, received originally as a trace constituent of potassium chloride supplied by the Clinton Laboratories of the Monsanto Chemical Company and subsequently diluted with inactive sulfur, was obtained from Dr. W. V. Smith of these Laboratories as a slurry of zinc sulfide in water containing some ammonia and zinc sulfate. Fifteen cc. of this suspension (containing approximately 2 mg. of sulfide sulfur and 30 microcuries of activity per cc.), 10 millimoles of inactive zinc sulfide, and 75 cc. of water were placed in a 500-cc. round-bottomed flask equipped with gas inlet tube, dropping funnel and reflux condenser. The gas inlet tube was attached to a hydrogen cylinder through a system consisting of a wash bottle containing sulfuric acid to act as a bubble counter and a side tube dipping into mercury serving as a safety valve. The exit tube of the condenser was connected to a Y-shaped reactor with a bottom limb of 10-cc. capacity containing a solution of 0.42 g. (10 millimoles) cyanamide (prepared from thiourea and mercuric oxide in ether, and purified by sublimation) in 5 cc. of 95% ethanol. The exit tube of the reactor led, in turn, to two wash-bottles in series each containing 10% zinc sulfate in 1:1 concd. ammonium hydroxide-water diluted five-fold.

After the entire system had been flushed with hydrogen, the reactor was cooled in liquid nitrogen and 60 cc. of 6 *N* hydrochloric acid added to the zinc sulfide slurry through the dropping funnel. Gradual heating of the slurry to boiling resulted in the smooth evolution of hydrogen sulfide and remaining traces were swept into the reactor by gently refluxing the mixture while slowly passing hydrogen through the system. Complete absorption was achieved, since no precipitate appeared in the wash-bottles. The reactor was next sealed off, warmed to −80°, shaken to insure solution of the hydrogen sulfide, and heated for twenty-four hours on the steam-bath. After cooling in liquid nitrogen, the reactor was opened and connected to a hydrogen source and two wash-bottles containing ammoniacal zinc sulfate. The reactor was then allowed to warm to room temperature, its contents refluxed for fifteen minutes, and finally swept slowly with hydrogen for an additional hour. Practically complete reaction was indicated since only a trace of precipitate appeared in the wash-bottles (pilot experiments in which the reactor was heated for three days at 60° gave a 67% yield of crystalline material), and, on cooling, beautiful needles of thiourea separated from the alcohol. For storage the thiourea was washed with additional alcohol into a 50-cc. volumetric flask.

Butyl Mercaptan.—In a 200-cc. flask equipped with dropping funnel and condenser which could be swiveled for either reflux or distillation was placed 10 cc. of the radioactive thiourea solution (*i. e.*, ~2 millimoles of thiourea), 0.76 g. (10 millimoles) of inactive thiourea and 3 cc. of butyl bromide, and the mixture refluxed for two and one-half hours under a hydrogen atmosphere. After cooling, the volatile material was distilled into a liquid nitrogen cooled trap under vacuum. With the condenser still in reflux position, hydrogen was readmitted and 10 cc. of *N* sodium hydroxide solution run in through the dropping funnel. The solution was then boiled for forty-five minutes to destroy the isothiourea. Next, the apparatus was arranged for distillation into a receiver consisting of a separatory funnel containing 10 cc. of chlorobenzene (chosen as an inert solvent with density greater than water), and 25 cc. of 0.5 *N* hydrochloric acid introduced through the dropping funnel.

Approximately half of the contents of the flask was now distilled, the receiver disconnected and shaken gently and the chlorobenzene layer run off into a small glass-stoppered bottle. The water layer was then extracted with the balance of 25 cc. of chlorobenzene and the chlorobenzene extracts all combined. Since experiments using inactive thiourea gave almost quantitative yields by this procedure, the chlorobenzene contained ~0.4 millimole mercaptan and 2 microcuries activity/cc. In the transfer experiments described in the next section the chlorobenzene solution was used directly without isolation or titration of the mercaptan since exact concentrations were not necessary. The absence of any contaminants which might interfere with the determination of transfer constants was shown by the good agreement of the constants for styrene and methyl methacrylate with those for *n*-amyl mercaptan and other normal mercaptans reported previously.

Transfer Experiments

Mixtures of freshly distilled monomer and mercaptan solution in mole ratios of 10 to 50:1, depending upon the expected transfer constant of the monomer, were placed in reaction tubes, degassed on a high vacuum line, sealed in absence of air, and heated for varying lengths of time in a 60° (or 30°) thermostat. In general, no catalyst was added. With styrene the thermal polymerization proceeded at a convenient rate, while methyl acrylate and methacrylate apparently contained enough adventitious catalyst to effect reaction. Vinyl acetate samples were polymerized by irradiating with a mercury vapor lamp. Samples and heating times were chosen to yield 100–300 mg. of polymer. Methyl methacrylate and acrylate polymers were worked up by precipitating three times from ethyl acetate with petroleum ether in a 50-ml. centrifuge tube. The polymers were then redissolved in approximately 5 cc. of ethyl acetate and transferred in portions to tared aluminum dishes 26 mm. in diameter and 3 mm. deep and the solvent evaporated under an infrared lamp. The centrifuge tubes were washed with additional benzene and the dishes dried under the lamp overnight (approx. 8 in. from a 250-watt bulb was found to yield a smooth bubble-free film). Blank experiments showed that this treatment was adequate to remove all solvent, and yields were determined by weighing the dishes. Relative polymer activities were then measured by placing the dishes covered by a mask with a hole approximately 20 mm. in diameter under the thin mica window of a Radiation Counter Laboratories Mark I Model 2 Geiger–Mueller counter attached to an Instrument Development Laboratories Scaling Circuit. For the styrene and vinyl acetate experiments, the polymer isolation procedure was modified in that the partially polymerized samples were transferred to a large side-arm test-tube and unreacted monomer distilled off *in vacuo* at room temperature. The polymer was redissolved (in chlorobenzene or toluene, respectively) and the solvent again distilled off. This procedure was repeated twice more and the residual polymer transferred to an aluminum dish for counting.

Actually, for the determination of the relative activity, *R*, theoretical activities of completely polymerized samples were calculated from a completely polymerized polystyrene sample, correcting for differences in mercaptan concentration in the reaction mixtures and polymer densities. Thus the measured activity of the styrene sample was multiplied by 1.06/1.19 for comparison with methacrylate since, because polymethacrylate has a greater density, the measured β-radiation is coming from a thinner layer of the polymer surface. Counts of relative activities were always extended to several thousand impulses to avoid significant random variations and comparisons of any set of polymers with the standard were always carried out consecutively since background count and sensitivity of the instruments varied from day to day.

Acknowledgment.—The writer wishes to thank Dr. Herbert N. Campbell for aid in operating the electronic apparatus.

Summary

1. A convenient method for the synthesis of radioactive mercaptans from zinc sulfide containing S^{35} has been worked out.

2. The transfer constants of *n*-butyl mercaptan with styrene, methyl methacrylate, methyl acrylate and vinyl acetate have been measured using radioactive mercaptan, and the advantages of tracer methods in polymer chemistry are discussed.

3. The results are shown to indicate that ionic forms in the transition state, similar to those involved in radical addition reactions, may be important in determining reactivity in radical displacement reactions as well.

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The Chlorination of Thiophene. II. Substitution Products; Physical Properties of the Chlorothiophenes; the Mechanism of the Reaction

BY HARRY L. COONRADT, HOWARD D. HARTOUGH AND GEORGE C. JOHNSON

The preceding paper[1] in this series reported the isolation and identification of chlorine addition products formed by the chlorination of thiophene. This paper describes the chlorine substitution products, reports their physical properties, and presents a mechanism for the reaction.

The substitution products formed by the chlorination of thiophene have been reported to be 2-chloro-,[2,3] 2,5-dichloro-,[2,3] 2,3,5-trichloro-,[2] and 2,3,4,5-tetrachlorothiophene.[2] In contrast with these results we have isolated and identified eight chlorine substitution products. The ninth and remaining possible substitution product, 3-chlorothiophene, was identified by infrared absorption spectrograms as present in small amounts.

The pure substitution products were separated by fractionation after the chlorine addition products had been removed. This prior removal or destruction of addition products generally was necessary because they decomposed into chlorothiophenes and hydrogen chloride during the course of the distillation and interfered with the fractionation. The method previously used[2,3,4] to destroy the addition products consisted of prolonged heating of the chlorination products with alcoholic potassium hydroxide. The preceding paper[1] described how addition products could be isolated from the reaction mixture. This had a pronounced effect on the ratio of the different substitution products.

The chlorine addition products were destroyed when chlorinated thiophene, like brominated thiophene,[5] was heated with solid sodium hydroxide or with potassium hydroxide. Calcium oxide was not effective. Other satisfactory procedures were prolonged pyrolysis or steam distillation of the reaction mixture from aqueous alkali or from a suspension of zinc or iron powder in water. Different

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[1] Coonradt and Hartough, THIS JOURNAL, **70**, 1158 (1948).

[2] Steinkopf and Köhler, *Ann.*, **532**, 250 (1937).

[3] Weitz, *Ber.*, **17**, 792 (1884).

[4] Steinkopf, "Die Chemie des Thiophens," Theodor Steinkopff, Dresden, 1941, p. 35.

[5] Blicke and Burckhalter, THIS JOURNAL, **64**, 477 (1942).