Reduction of *o*-Tolunitrile to *o*-Xylylamine.—A solution of 7.6 g. (0.2 mole) of lithium aluminum hydride in 300 ml. of ether is placed in a one-liter, three-necked flask equipped with a reflux condenser, dropping funnel and mechanical stirrer. Openings are protected from atmospheric moisture, until completion of the reaction, by calcium chloride tubes. Through the dropping funnel, a solution of 23.4 g. (0.2 mole) of *o*-tolunitrile in 200 ml. of ether is introduced at a rate such as to produce gentle reflux. Shortly after completing the addition, sufficient water is added dropwise, and with cooling of the flask in ice-water, to decompose the excess hydride. There is then added 500 ml. of a 20% solution of sodium potassium tartrate. The clear mixture is transferred to a separatory funnel and after separating the ether layer, the aqueous layer is extracted with two 100-ml. portions of ether. From the combined ether extracts there is obtained, after drying over calcium sulfate, an 88% yield of *o*-xylylamine, b. p. 134° (85 mm.), $n^{20}\mathrm{D}$ 1.5412. The product was further characterized by conversion to *o*-xylylbenzamide,[5] m. p. 88°.

Gilman–Schulze Color Test.—The test was carried out in the following manner. Ten drops of a 1% solution of Michler ketone in thiophene-free benzene are added to 1 ml. of an ethereal solution of lithium aluminum hydride. Thirty seconds later, 1 ml. of water and then 8 drops of a 0.2% solution of iodine in glacial acetic acid are added. Two layers appear and the lower aqueous layer is blue or purple depending upon the concentration of the hydride solution. This test was used to determine the stoichiometry of the reaction of lithium aluminum hydride with *p*-tolunitrile by adding successive portions of the latter to a known quantity of the hydride in ether solution and withdrawing a small sample of the solution after each addition for testing as described above. The test was positive when the quantity of nitrile, in terms of moles per mole of lithium aluminum anhydride, was 1.65 and 1.87, and negative with amounts of 2.09 and 2.31. The combining ratio was thus indicated as lying between 1.87 and 2.09.

Summary

The reduction of alkyl halides to hydrocarbons, nitriles to primary amines, aromatic nitro and azoxy compounds to azo compound, aliphatic nitro compounds to primary amines, and miscellaneous other reductions by lithium aluminum hydride are described.

CHICAGO, ILLINOIS RECEIVED APRIL 30, 1948

---

[5] Krober, *Ber.*, **23**, 1027 (1890), m. p. 88°.

[CONTRIBUTION NO. 77 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Chain Transfer in the Polymerization of Styrene. V. Polymerization of Styrene in the Presence of Mercaptans

BY R. A. GREGG, D. M. ALDERMAN[1] AND FRANK R. MAYO

Chain transfer is the process whereby a polymerizing free radical removes an atom from some molecule, forming an inactive polymer molecule and a new radical.[1a] The ratio of the rate constants for radical reaction with solvent and with monomer is called the transfer constant,[2] *C*, and measures the reactivity of the solvent toward the radical. The polymerization of styrene in carbon tetrachloride[3] showed the transfer constant to be independent of the solvent concentration and of the average length of the radicals except for the very shortest[4] radicals. Application of the same methods to hydrocarbons showed that the relatively unreactive substituted benzyl radical in polymerizing styrene is excellent for determining small differences in reactivities of hydrocarbons.[5] The present work shows some effects of structure on the reactivities of mercaptan[6] hydrogen atoms in chain transfer.

Two methods were used to determine the transfer constants of the mercaptans. In the first, the transfer constant, *C*, is given by[2,3]

$$1/\bar{P} = C[\mathrm{SX}]/[\mathrm{M}] + 1/\bar{P}_0 \tag{1}$$

where $\bar{P}$ is the degree of polymerization of the polymer formed at solvent and monomer concentrations [SX] and [M]; $\bar{P}_0$ is a constant equal to the degree of polymerization in the absence of solvent. Experimentally, [SX]/[M] must remain sensibly unchanged and $\bar{P}$ must be large in comparison with unity.[3,4] In the second method, the rates of disappearance of monomer and solvent are measured, from which[6]

$$\frac{\mathrm{d}\log[\mathrm{SX}]}{\mathrm{d}\log[\mathrm{M}]} = C \tag{2}$$

assuming that essentially all chains are terminated by chain transfer. The method is applicable to both catalyzed and uncatalyzed reactions at any conversion, but modification is necessary when the number of moles of monomer and solvent reacting are nearly equal.[4]

---

[1] Deceased, October 16, 1944.

[1a] Flory, THIS JOURNAL, **59**, 241 (1937).

[2] Mayo, *ibid.*, **65**, 2324 (1943).

[3] Gregg and Mayo, *ibid.*, **70**, 2373 (1948).

[4] Mayo, *ibid.*, **70**, 3689 (1948).

[5] Gregg and Mayo, *Trans. Faraday Soc.*, in press.

[6] *Cf.* also W. V. Smith, THIS JOURNAL, **68**, 2059 (1946).

Experimental

Materials.—The styrene was crystallized and distilled as described earlier.[3] *t*-Butyl mercaptan was fractionated through a 50-cm. helices packed column, b. p. 63.9–64.4° at 763 mm., n^{20}_D 1.4228. Eastman Kodak Co. ethyl thioglycolate was likewise fractionated under nitrogen, b. p. 43.1° at 8 mm., n^{20}_D 1.4582, and stored in evacuated tubes in the refrigerator until used. Dodecyl mercaptan, f. p. −6.7° to −7.0° and n^{20}_D 1.4589, was prepared from pure lauryl bromide by the thiourea method.[7] We are indebted to Dr. L. W. Hartzel for the preparation of 3-ethoxypropanethiol from 3-ethoxypropyl bromide[8] by the thiourea method.[7] Fractionation of the product gave 3-ethoxypropanethiol, b. p. 55–57° at 25 mm., in 52.5% yield.

Anal. Calculated for $C_5H_{12}OS$: S, 26.67. Found: S, 26.9, 27.2; mercaptan by silver nitrate titration, 98.6%.

Procedure.—Weighed amounts of reactants in flamed Pyrex ampoules were thoroughly degassed and sealed under high vacuum. An individual sample was used for each experiment. The samples were allowed to react at 60 ± 0.05° and 100 ± 0.1°. For transfer constant determinations from degrees of polymerization, the polymers were precipitated in methanol and dried as previously described.[3] Intrinsic viscosities were determined in benzene at 30° and degrees of polymerization calculated from the equation[3]

$$\overline{M}_n = 184{,}000[\eta]^{1.40} = 104\overline{P} \qquad (3)$$

The transfer constants were then calculated by Equation (1).

For the second method either or both of two procedures were used to determine monomer concentration. The polymer was isolated as above or the styrene concentration was determined from the refractive index, a refractive index difference of 0.000577 at 20° being taken equal to 1% polymerization by weight. The mercaptan was titrated amperometrically with silver nitrate essentially according to the method of Kolthoff and Harris.[9] The reaction sample or an aliquot of 5 to 20 g. was precipitated in about 50 cc. of ammoniacal ethanol containing ammonium nitrate.[9] The polymer was separated by centrifuging, dissolved in a little benzene, and reprecipitated in a second portion of ethanol solution to free it of entrapped mercaptan. For conversion in excess of 10% a third solution and precipitation were used to insure complete removal of free mercaptan from the polymer. The combined ethanolic mercaptan solutions were titrated with 0.005 *N* silver nitrate using a rotating platinum electrode and the half-cell described by Kolthoff and Harris.[9] Fouling of the electrode by polymer is eliminated and the mercaptan is determined in one titration by the present method. Less satisfactory procedures were used in most of the titrations of dodecyl mercaptan which was studied initially.

Products from Styrene–Dodecyl Mercaptan Reaction.—Equimolar quantities of dodecyl mercaptan and styrene were distilled under high vacuum into a reaction tube; the mixture was thoroughly degassed, and the tube sealed under high vacuum. After twenty-two and one-half hours at 60°, the mixture was distilled to give approximately 9% styrene, 33% dodecyl mercaptan and 36–39% addition product with b. p. 192–195° at 1.5 mm. and n^{20}_D 1.5028–1.5035. It is probably β-phenylethyl dodecyl sulfide.

Anal. Calcd. for $C_{20}H_{34}S$: S, 10.46. Found: S, 10.4, 10.6.

The residue analyzed 6.61, 6.76% S corresponding to 2.66 styrene units per mercaptan.

Discussion of Results

Table I lists degrees of polymerization of polystyrenes prepared in the presence of dodecyl, *t*-butyl and 3-ethoxypropyl mercaptans. The transfer constants are calculated by Equation (1). Figures 1–4 plot the rates of styrene and mercaptan consumption using each of four mercaptans.[10] The transfer constants are calculated from the slopes of the lines, according to Equation (2). Table II lists all transfer constants together with experimental activation energies and frequency factors. The value of the transfer constant of a given mercaptan at one temperature should be the same by the two methods.

TABLE I

POLYMERIZATION OF STYRENE IN THE PRESENCE OF MERCAPTANS

TRANSFER CONSTANTS FROM DEGREES OF POLYMERIZATION

[RSH]/[Styrene] × 10^5	Time, hr.	Yield, %	k_2[a] × 10^4	[η]	$1/\overline{P}$ × 10^5	C[b]
1. Dodecyl mercaptan at 60°						
1.66	13.2	1.12	0.98	1.50	32.0	13.2
2.69	13.2	1.12	.98	0.915	63.9	19.6
6.02	19.6	1.54	.92	.731	87.7	12.9
6.02	16.4	1.30	.91	.739	86.5	12.7
2. *t*-Butyl mercaptan at 60°						
7.6	23.7	2.10	1.06	1.30	39.1	3.8
19.0	23.7	2.08	1.05	0.788	79.0	3.7
38.1	17.0	1.45	1.00	0.498	150.3	3.7
3. *t*-Butyl mercaptan at 100°						
5.25	0.9	1.90	25.0	1.40	35.2	2.0
14.56	0.9	2.10	27.6	0.933	62.4	2.6
31.02	0.9	2.36	31.1	0.694	94.4	2.2
4. 3-Ethoxypropanethiol at 60°						
2.1	14.8	1.26	1.02	1.30	39.1	13.8
4.4	14.8	1.20	0.95	0.832	73.2	14.3

[a] Second order rate constant in liters $mole^{-1}$ $hour^{-1}$. [b] $1/\overline{P}_0$ taken as 10.1 and 24.8 × 10^{-5} at 60° and 100°, respectively, for calculations by Equation (1).

TABLE II

TRANSFER CONSTANTS[a] OF MERCAPTANS WITH STYRENE

Equation 1 60°	Equation 1 100°	Equation 2 60°	Equation 2 100°	$E_t - E_g$[b] (kcal./mole)	A_t/A_g
t-Butyl mercaptan					
3.7 ± 0.5	2.3 ± 0.5	3.6 ± 0.3	3.2 ± 0.3	−0.7	1.2
Dodecyl mercaptan					
14.8 ± ?	....	18.7 ± 1	....		
3-Ethoxypropanethiol					
14.1 ± ?	....	21.0 ± 1	13.7 ± 1	−2.6	0.40
Ethyl thioglycolate					
....	....	58 ± 4	....		

[a] Estimated possible errors given for each value. [b] Calculated from Equation (2) values using Arrhenius equation $C = Ae^{-E/RT}$ where A is the ratio, A_t/A_g, for chain transfer and chain growth, and E is the difference in experimental activation energies, $E_t - E_g$.

Table II shows excellent agreement between the two methods for *t*-butyl mercaptan but not for 3-ethoxypropanethiol. The discrepancy arises from

---

[7] Organic Syntheses, Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 36.

[8] Hurd and Fowler, THIS JOURNAL, **61**, 249 (1939).

[9] Kolthoff and Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

[10] These polymerization data are not listed in tables. Second order rate constants for styrene consumption were very close to those listed in Table I except in the presence of ethyl thioglycolate where the values were somewhat lower.

the assumption in Equation (1) that the solvent: monomer ratio remains constant. For as little as 2% reaction of the styrene, more than one-third of the 3-ethoxypropanethiol will have reacted while the styrene:*t*-butyl mercaptan ratio will

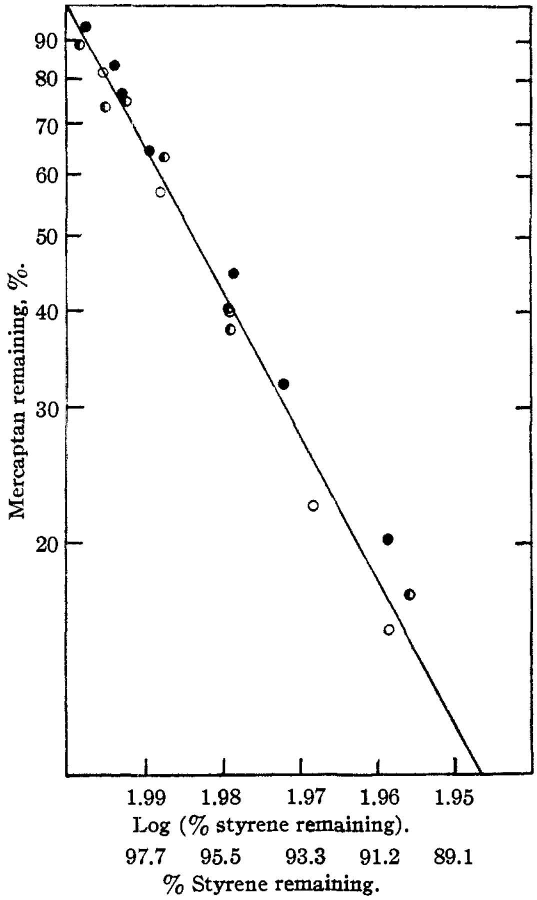


Fig. 1.—Dodecyl mercaptan in styrene at 60°: 0.311% mercaptan, ●; 1.991% mercaptan, ◐; 0.446% in benzene solution ○.

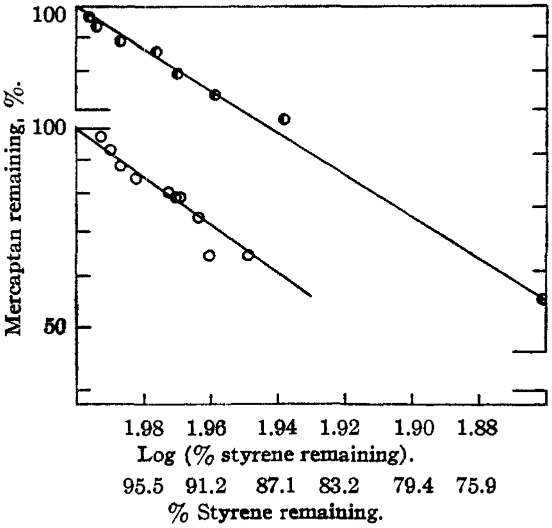


Fig. 2.—*t*-Butyl mercaptan in styrene: 0.103% mercaptan at 100°, ◐; 0.103% mercaptan at 60°, ○.

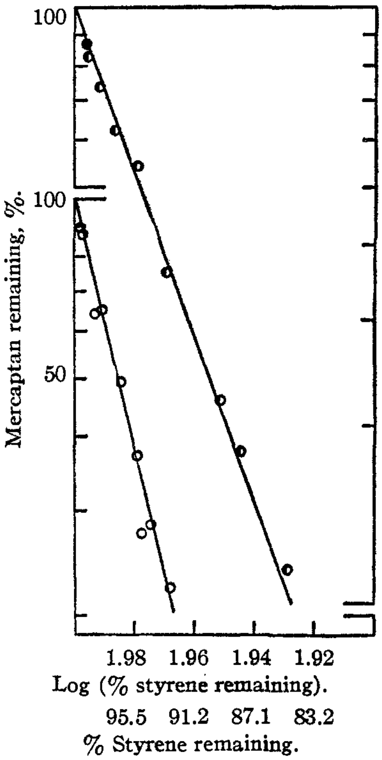


Fig. 3.—3-Ethoxypropanethiol in styrene: 0.122% mercaptan at 100°, ◐; 0.122% mercaptan at 60°, ○.

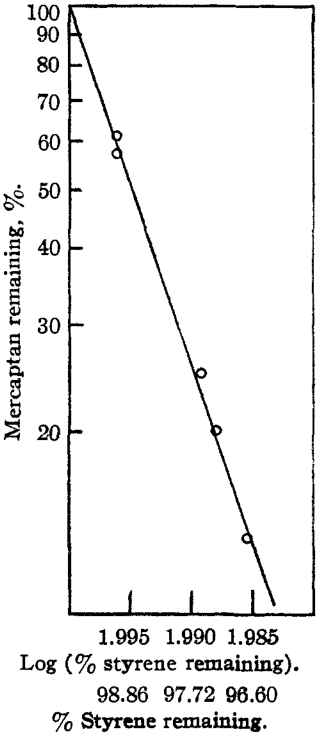
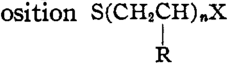


Fig. 4.—Ethyl thioglycolate in styrene at 60°.

have remained sensibly constant. Hence, experimental difficulties make it practical to use Equation (1) only for solvents having transfer constants of about 5 or less.

Table II shows that alkoxyl group substitution does not change the activity of primary mercaptans and, together with other work, that transfer constants of primary mercaptans are independent of their molecular weight.[11] Thus, *n*-amyl mercaptan has a transfer constant of 20,[6] and *n*-butyl mercaptan of 22 ± 3.[12] The tertiary mercaptan is much less reactive than the primary mercaptans while ethyl thioglycolate is by far the most reactive mercaptan known.

Previous work[2,3,5] has shown that transfer constants of relatively unreactive solvents increase with increasing temperature. For the mercaptans, the transfer constants decrease with increasing temperature and the activation energy for chain transfer is lower than for chain growth.

Transfer theory demands the production of a series of compounds of composition  $S(CH_2\underset{\underset{R}{|}}{C}H)_nX$ from an unsaturate $RCH{=}CH_2$ and a solvent SX, where X is removed by radical transfer, and *n* is 1 or greater. The proportions of the products will depend on the nature and concentrations of reactants but in general the mole fraction of *n*-mer must decrease as *n* increases. Mercaptan addition products with $n = 1$ have long been known. The present work showed that the reaction of equal moles of styrene and dodecyl mercaptan gave a product with $n = 1$ and a smaller amount of mixed products averaging $n = 2.7$. With this system, separation of the products by distillation could not be made sufficiently precise to enable calculation of the transfer constants of the individual radicals. A later paper will describe the separation of the reaction products of low molecular weight mercaptans with styrene and the calculation of the transfer constants of the individual radicals. These phenomena have been described previously in detail for carbon tetrachloride[3,4] in which case the pure 1:1 compound has not been isolated.

Summary

The abilities of four mercaptans to supply a hydrogen atom to the substituted benzyl radical in polymerization have been compared by two methods, by their effect in reducing the molecular weight of the polymer and by the relative rates of reaction of monomer and mercaptan. Results by the two methods are in agreement. Mercaptans possess a high activity toward radicals, the substituted benzyl radical preferring transfer with the mercaptan to reaction with styrene. α-Methyl group substitution decreases and α-carboethoxy substitution increases the reactivity of a mercaptan toward radicals.

PASSAIC, NEW JERSEY RECEIVED APRIL 5, 1948

---

[11] In emulsion polymerization, the decreased water solubility of higher molecular weight mercaptans decreases their effective regulating ability. The converse may be true for alkoxy substituted mercaptans; *cf.* W. V. Smith, THIS JOURNAL, **68**, 2064 (1946).

[12] Walling, *ibid.*, **70**, 2561 (1948).

[CONTRIBUTION NO. 48 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Kinetics of Heterogeneous Reactions with Special Reference to Catalytic Hydrogenation

BY JOHN F. FUZEK AND HILTON A. SMITH

A great many articles have been published dealing with the kinetics of certain catalytic reactions.[1] Most of the measurements have involved the reaction of gaseous materials on catalytic surfaces, reaction rate constants having been calculated from the pressure drops in the systems used.

A critical examination of the kinetics of such reactions leads to the conclusion that the rate constants calculated in this manner depend on the volume of the gaseous system used. In spite of this, comparison of such experimental constants with equations which do not involve the volume of the system are made. A true constant is obtained only when the rate equation is in the form

$$\frac{dp_x}{dt} = \frac{k}{V} p_x^a$$

rather than the usual

$$\frac{dp_x}{dt} = k' p_x^a$$

where p is the pressure of the gas x, and a is the reaction order.

It is of some interest to compare experimental results of catalytic reactions using gaseous systems of different volumes. On examining the literature, it was noted that sometimes the volume of the system studied for a given reaction was not even specified, and reliable data taken for different volumes were not found. Therefore, for sake of such comparison, several catalytic hydrogenation reactions were run both at high and low pressures using nickel and platinum catalysts.

---

[1] Hinshelwood, "The Kinetics of Chemical Change," Oxford University Press, Oxford, England, 1940, Chapter VIII; Pease, "Equilibrium and Kinetics of Gas Reactions," Princeton University Press, Princeton, New Jersey, 1942, Chapter IX; Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Chapter VII.