Anal. Calcd. for $C_5H_{11}ClN_2OS$: C, 32.87; H, 6.07; S, 17.55. Found: C, 33.04; H, 6.12; S, 17.82.

The picrate was obtained as small yellow crystals, m.p. 142–144°, from ethyl acetate.

Anal. Calcd. for $C_{11}H_{13}N_5O_8S$: C, 35.20; H, 3.49; S, 8.54. Found: C, 35.42; H, 3.60; S, 8.80.

The hydrochloride did not give a nitroprusside test for mercapto. Its infrared spectrum (potassium bromide) did not contain a mercaptan band at 3.9 μ and showed a strong band at 6.10 μ. The picrate (potassium bromide) similarly did not give a mercaptan band and exhibited a single strong band at 6.10 μ, analogously to the picrate of the $C_{12}H_{16}N_2OS$ intermediate rather than to the picrate of the mercaptan IVa.

Bis[2-(2-oxazolin-2-ylamino)ethyl] Disulfide (Vb).—To 0.6 g. of the $C_5H_{10}N_2OS$ hydrochloride in 6 ml. of water was added 3 ml. of 10% sodium hydroxide, and the solution was allowed to stand for 4 days with intermittent aeration. The white crystalline precipitate that separated amounted to 0.37 g. (78% yield), m.p. 131–133°. Crystallization from ethyl acetate afforded 0.32 g. (67%) of glistening plates, m.p. 133.5–135.5°.

Anal. Calcd. for $C_{10}H_{18}N_4O_2S_2$: C, 41.36; H, 6.25; S, 22.08; mol. wt., 290. Found: C, 41.54; H, 6.30; S, 22.02; mol. wt. (vapor pressure osmometer), 288.

The picrate separated from ethanol-acetone as fine yellow crystals, m.p. 202–204°.

Anal. Calcd. for $C_{22}H_{24}N_{10}O_{16}S_2$: C, 35.30; H, 3.23; S, 8.56. Found: C, 35.62; H, 3.38; S, 8.42.

In the infrared the base showed the strong bands at 6.0 and 6.6 μ and the picrate the strong bands at 5.85–5.9 and 6.1 μ, characteristic of the disulfides.

Vb from Rearrangement.—In the usual manner, equimolar quantities of 2-thioöxazolidone, 2-bromoethylamine, and sodium ethylate were refluxed in ethanol for 3 hr. After the product had been allowed to stand in solution at pH 9–10 for 5 days, there was obtained a 28% yield of crude picrate that melted from 170 to 182° but that gave an infrared spectrum similar to that of the dipicrate of Vb. The yield of twice-crystallized picrate, m.p. 199–201°, was 11.5%. Identity to Vb dipicrate was demonstrated after further purification, and a crystalline base identical to Vb was recovered from the picrate.

Without sodium ethylate, Vb dipicrate was obtained in very low yield.

Acknowledgment.—We are indebted to Dr. Gerald O. Dudek of Harvard University and Dr. Paul R. Shafer of Dartmouth College for the n.m.r. spectra, to Dr. M. Kent Wilson of Tufts University for some of the infrared spectra, and to Mr. Carmine DiPietro of these laboratories for the microanalyses.

The Base-catalyzed Oxidation of Mercaptans. III. Role of the Solvent and Effect of Mercaptan Structure on the Rate Determining Step[1,2]

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n-Butyl mercaptan has been oxidized in dimethylformamide (DMF)–methanol and diethyleneglycol dimethyl ether (diglyme)–methanol mixtures at 23.5 ± 0.2° using sodium methoxide as the base. The relative rates of oxidation of the mercaptan decreased at the same rate in the two solvent systems as the quantity of methanol was increased in each solvent mixture suggesting that similar transition states are involved in both systems. A series of ion pair complexes which ultimately involve an intimate ion pair complex between methanol and the sodium mercaptide are suggested as possible explanations for the observed results. In addition, benzyl mercaptan, thiophenol, *p*-aminothiophenol, *p*-nitrothiophenol, and cyclohexyl mercaptan were oxidized under a variety of conditions. The observed results indicate that the rate determining step is reaction of the anion ($RS^{\ominus}$) with oxygen.

Until recently, most studies on the base-catalyzed oxidation of mercaptans (thiols) to disulfides with molecular oxygen have been limited to an aqueous sodium hydroxide media.[3] Some structural effects of mercaptans on the rate of oxidation in this medium have been observed[4] but the results have been somewhat difficult to interpret since solubilities and salting-out effects vary for the mercaptans studied. Barringer[5] has reported that N,N′-disubstituted-*p*-phenylenediamines are capable of accelerating this coupling reaction. The use of various transition metal phthalocyanines and other organic chelates in basic media has also been recommended.[6] In the latter case, the rate-limiting step appears to be diffusion of oxygen and the mercaptide ion to the surface of the catalyst.[7] We have recently observed in these laboratories[1] that various dipolar and ethereal solvents greatly enhanced the homogeneous, base-catalyzed oxidation rate of *n*-butyl mercaptan with molecular oxygen.

The present study was undertaken to determine how the addition of a hydroxylic material (methanol) to an aprotic base–solvent system would effect the rate of oxidation of *n*-butyl mercaptan. Further, it also seemed of interest to ascertain how the rate of oxidation varied with the structure of the mercaptan since this would provide information on the rate determining step in this reaction.

Results

One-tenth of a mole of *n*-butyl mercaptan was oxidized in DMF–methanol and diglyme–methanol mixtures at 23.5 ± 0.2° under a constant oxygen pressure of one atmosphere. 0.2 mole of sodium methoxide was used in each oxidation reaction. Each reaction was carried out to about 30% completion. The amount of mercaptan converted to the disulfide was determined from the amount of oxygen consumed as a function of time according to the derived first-order rate expression. The apparent first-order rate constants obtained for the oxidation of *n*-butyl mercaptan to the disulfide in each hydroxylic–aprotic solvent mixture are summarized in Table I and calculated relative to the rate obtained in

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[1] T. J. Wallace and A. Schriesheim, *J. Org. Chem.*, **27**, 1514 (1962).

[2] T. J. Wallace, J. M. Miller, H. Pobiner, and A. Schriesheim, *Proc. Chem. Soc.*, 384 (1962).

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[4] J. Xan, E. A. Wilson, L. D. Roberts, and N. H. Horton, *J. Am. Chem. Soc.*, **63**, 1139 (1941).

[5] C. M. Barringer, *Ind. Eng. Chem.*, **47**, 1022 (1955).

[6] W. K. T. Gleim and P. Urban, U. S. Patent 714,937 (Feb. 13, 1958).

[7] T. J. Wallace, A. Schriesheim, and D. L. Baeder, unpublished results.

TABLE I

OXIDATION OF *n*-BUTYL MERCAPTAN IN DMF–METHANOL AND DIGLYME–METHANOL SOLUTIONS AT 23.5 ± 0.2°

	Volume % solvent	$k \times 10^3$, min.$^{-1}$	k Relative to methanol
DMF	100	1077	334
	75	368	114
	50	68.6	21.3
	25	9.16	2.8
	10	3.93	1.2
Diglyme	100	323	100
	75	138	43
	50	36.5	11
	35	6.21	1.9
Methanol	100	3.22	1.00

100% methanol. A plot of k relative DMF/k relative diglyme *vs.* the volume per cent of methanol in each reaction mixture (Fig. 1) gives a linear relationship which decreases with increasing amounts of methanol.

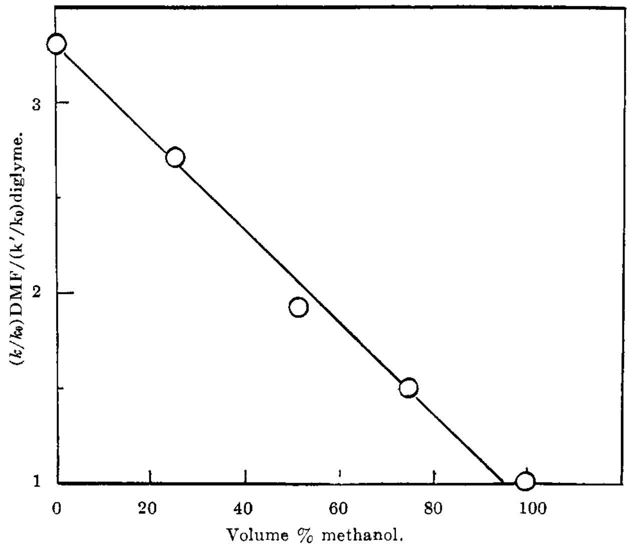

Fig. 1.—A plot of (k/k_0) DMF/(k'/k_0) diglyme *vs.* volume % methanol; k_0 = rate in methanol; k = rate in DMF solutions; k' = rate in diglyme solutions.

Due to the paucity of information on structural effects in the oxidation of sulfur anions a second aspect of this research was concerned with how the rate of oxidation is influenced by the structure of the mercaptan. Benzyl mercaptan, thiophenol, *p*-aminothiophenol, *p*-nitrothiophenol, and cyclohexyl mercaptan were oxidized in several solvents at 23.5 ± 0.2° to their corresponding disulfides. In each reaction, an excess of either sodium methoxide or potassium *tert*-butoxide was used. The specific conditions employed and the results obtained are summarized in Table II. Results previously obtained with *n*-butyl mercaptan are also included for convenience of comparison. Thiophenol oxidized at a considerably slower rate than *n*-butyl and benzyl mercaptans under the reaction conditions listed. Cyclohexyl mercaptan and *p*-aminothiophenol are oxidized some four- to tenfold faster than thiophenol. *p*-Nitrothiophenol was not oxidized over a 20-hr. period.[8]

TABLE II

VARIATION OF THE RATE OF OXIDATION WITH MERCAPTAN STRUCTURE

Mercaptan	Solvent	Base	$k \times 10^3$, min.$^{-1}$	pK_a[a]
n-C_4H_9SH	CH_3OH	NaOMe	3.22	11.5
n-C_4H_9SH	*tert*-C_4H_9OH	KOtBu	34.7	
n-C_4H_9SH	DMF	NaOMe	1077	
C_6H_5SH	CH_3OH	NaOMe	0.23	6.5
C_6H_5SH	*tert*-C_4H_9OH	KOtBu	8.19	
C_6H_5SH	DMF	NaOMe	76.6	
$C_6H_{11}SH$	CH_3OH	NaOMe	0.88	..
p-NH_2—C_6H_4SH	CH_3OH	NaOMe	2.53	..
p-NO_2—C_6H_4SH	CH_3OH	NaOMe	N.R.	..
$C_6H_5CH_2SH$	CH_3OH	NaOMe	5.57	9.4

[a] All pK_a values listed were taken from the following sources: M. M. Kreevoy, *et al.*, *J. Am. Chem. Soc.*, **82**, 4899 (1960); D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257 (1940).

Discussion

To date, no detailed study on the mechanism of mercaptan oxidation in basic media has been attempted. In the present study, a mechanism, which takes into account both the rate determining step and the role of the solvent in this reaction, is proposed and discussed in detail.

In the present investigation, the oxidation of mercaptans was studied under such conditions that the reaction rate became independent of the rate of agitation. Thus, it may be assumed that the rate of diffusion of oxygen gas into the solution did not control the chemical reaction rate. In the base-solvent systems employed the oxidation of a mercaptan to its corresponding disulfide may be described by the following mechanistic paths.

Ionization
$$RSH + B^{\ominus} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RS^{\ominus} + BH \tag{1}$$

Oxidation
$$RS^{\ominus} + O_2 \xrightarrow{k_3} RS\cdot + \dot{O}_2{}^{-} \tag{2}$$

$$RS^{\ominus} + \dot{O}_2{}^{-} \xrightarrow{k_4} RS\cdot + O_2{}^{-2} \tag{3}$$

Dimerization
$$2RS\cdot \xrightarrow{k_5} RSSR \tag{4}$$

Base regeneration
$$O_2{}^{-2} + BH \xrightarrow{k_6} OH^{\ominus} + B^{\ominus} + {}^1/_2O_2 \tag{5}$$

The above reaction scheme yields an over-all stoichiometry in agreement with the experimental results of this study.

$$2RSH + {}^1/_2O_2 + B^{\ominus} \longrightarrow RSSR + HO^{\ominus} + BH \tag{6}$$

Since, in these experiments, the base, $B^{\ominus}$, was employed in excess with respect to mercaptan concentration, the interconversion of alkoxide ions into hydroxide ions is not expected to influence appreciably the reaction kinetics. Further, it has been demonstrated that even in 1 *N* sodium hydroxide solution the ratio of $(RS^{\ominus})$/(RSH) (see equation 1) is at least 2×10^3 for all mercaptans investigated.[3] Based on this mechanism, the rate of oxygen consumption is given by

$$\frac{d(O_2)}{dt} = -k_3(RS^{\ominus})(O_2) + {}^1/_2k_6(O_2{}^{\ominus}) \tag{7}$$

where the bracketed quantities denote the concentrations of the various species in the solution. Assuming that the $O_2{}^{-2}$ and $\dot{O}_2{}^{\ominus}$ ions are present in steady state concentrations, the rate equation reduces to

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[8] A similar result in dimethyl sulfoxide-*tert*-butyl alcohol was recently communicated: G. A. Russell, A. J. Moye, and K. Nagpal, *J. Am. Chem. Soc.*, **84**, 4154 (1962).

$$\frac{d(O_2)}{dt} = \frac{-k_3}{2}(RS^{\ominus})(O_2) \qquad (8)$$

The concentration of mercaptide ions is determined by the ionization equilibrium constant $K = k_1/k_2$.

$$(RS^{\ominus}) = K\frac{(RSH)(B^{\ominus})}{(BH)} \qquad (9)$$

The stoichiometric concentration of mercaptan, C_{RSH}, is given by

$$C_{RSH} = (RS^{\ominus}) + (RSH) \qquad (10)$$

thus

$$(RSH) = C_{RSH} - (RS^{\ominus}) \qquad (11)$$

Substituting into the equilibrium expression for (RSH) and simplifying the relationship between C_{RSH} and $(RS^{\ominus})$ is given by equation 12.

$$(RS^{\ominus}) = \frac{C_{RSH}}{[1 + \frac{1}{K}(BH)/(B^{\ominus})]} \qquad (12)$$

hence

$$\frac{d\,(O_2)}{dt} = \frac{-k_3}{2}\,\frac{C_{RSH}(O_2)}{[1 + 1/K\,(BH)/(B^-)]} \qquad (13)$$

With an alkoxide as the base, it is evident from equation 13 that the rate of oxidation is inversely proportional to the concentration of added alcohol, BH (when no alcohol is added the oxidation would be inhibited to a small extent in its latter stages because of alcohol formed during the reaction). For low levels of conversion the concentration of BH may be considered to be constant, *i.e.*, (BH) = (BH) initial. Thus, for highly acidic species and a given initial base concentration $[1 + (BH)/K(B^-)] = 1$ and

$$\frac{d\,(O_2)}{dt} = \frac{-k_3}{2}\,C_{RSH}(O_2) \qquad (14)$$

From the over-all stoichiometry, each mole of RSH requires $^1/_4$ mole of O_2. Therefore,

$$\frac{d\,(RSH)}{dt} = 4\,\frac{d\,(O_2)}{dt} = -2k_3\,C_{RSH}\,(O_2) \qquad (15)$$

The equilibrium concentration of oxygen in the solution can be expressed as

$$O_2 = K_S P_{O_2} \qquad (16)$$

where K_s = constant and P_{O_2} = partial pressure of oxygen gas. Thus, the rate of mercaptan disappearance is given by

$$\frac{d\,(RSH)}{dt} = -2k_3K_sC_{RSH}P_{O_2} \qquad (17)$$

which under constant oxygen pressure yields upon integration

$$\ln\frac{(RSH)}{(RSH)\text{ initial}} = -kt \qquad (18)$$

where t = duration of oxidation and $k = [2k_3K_sP_{O_2}]$. Thus, at a given initial base concentration, a constant alcohol concentration, and a constant partial pressure of oxygen the rate equation simplifies to a first-order rate expression which is in agreement with the observed results and proposed mechanistic speculations.

The mercaptans investigated in the present study are relatively acidic species and in the base-solvent systems listed the ratio of the concentration of the anion, $RS^{\ominus}$, to the concentration of the unionized mercaptan should be greater than 2×10^3.[3] Thus, for low levels of conversion it is reasonable to assume that the rate determining step is reaction of the anion with oxygen (equations 2 and 3). An examination of the results in Table II indicates that the structure of the anion plays a key role in the rate determining step of this reaction. For example, *p*-nitrothiophenol forms the most stable anion and it is not oxidized. The thiophenolate ion, which is resonance stabilized by interaction of the electron pair on the sulfur atom with the π system of the benzene ring, is less reactive toward oxygen than either the cyclohexyl mercaptide of *p*-aminothiophenolate ions. In the latter case, resonance interactions would lead to decreased stability of the resulting ion. This reactivity sequence may be rationalized by assuming that reaction of the anion with oxygen is rate limiting. The reverse order of reactivity would be observed if ionization of the mercaptan was rate limiting. This is substantiated by the results obtained with *n*-butyl and benzyl mercaptans. Both mercaptans are less acidic than thiophenol and *p*-nitrothiophenol and their resulting anions are not resonance stabilized. However, they are oxidized at a relatively rapid rate. A similar reactivity sequence has recently been observed by Russell and co-workers[8] for the oxidation of carbanions, *i.e.*, the most stable carbanion is the most difficult to oxidize.

Previous studies on solvent effects in the oxidation of mercaptans indicated that the rate of oxidation of *n*-butyl mercaptan was 35 to 300 times faster in various ethereal and dipolar, aprotic solvents than in methanol.[1] These results were rationalized on the basis of a specific cation solvation of the sodium cation initially associated with the mercaptide ion in an ion-pair intermediate. Further, an *sp*³ complex involving *s–p* overlap between the oxygen atom of the solvent and the empty 3-*s* orbital of the sodium cation was suggested. Thus, it seemed reasonable to presume that any species capable of interacting with both the aprotic solvent and the sodium mercaptide would lead to a decreased rate of oxidation.

The results show that the relative rates of oxidation in DMF and diglyme $((k/k_0)\text{DMF}/(k/k_0)\text{diglyme})$ decrease linearly as a function of the volume per cent of added methanol in each solvent mixture. This suggests that similar transition states are involved in both solvents. It seems reasonable to assume that initially the transition state consists of an "external" ion-pair involving the aprotic solvent (DMF) and the sodium mercaptide (Figure 2). Depending upon the quantity of methanol added, the transition state can be transformed into an "intermediate" ion-pair complex composed of sodium mercaptide–solvent–methanol (Figure 3) which in the presence of excess methanol can exist as an "intimate" ion-pair involving sodium mercaptide–methanol (Figure 4). Based on the rate determining step, the energy difference between reactants and transition state must be less for the nonhydrogen-bonded system than it is for the hydrogen-bonded case where methanol is present.

Similar explanations have been advanced concerning the greater catalytic activity of potassium *tert*-butoxide ($K^{\oplus\ominus}Ot$–Bu) in dimethyl sulfoxide as opposed to *tert*-butyl alcohol or dimethyl sulfoxide–*tert*-butyl alcohol mixtures.[9,10] However, this is the

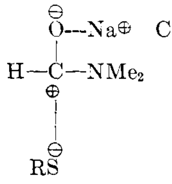

Figure 2

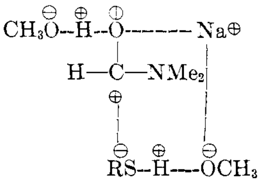

Figure 3

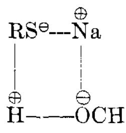

Figure 4

first reported case in which the fate of the reacting entity, RS$^{\ominus}$Na$^{\oplus}$, can be spectulated on with any reasonable certainty.

Experimental

Reagents.—The following materials were distilled under a nitrogen atmosphere through a 14-in. silvered column equipped with a tantalum-wire spiral: *n*-butyl mercaptan (Matheson Coleman, and Bell, b.p. 96–98°, $n^{20}\text{D}$ 1.4411), cyclohexyl mercaptan [Columbia Organic Chemicals, b.p. 62–65° (12 mm.), $n^{20}\text{D}$ 1.4925] benzyl mercaptan [Evans Chemetics Inc., b.p. 70° (3 mm.), $n^{20}\text{D}$ 1.5776], and thiophenol [Matheson Coleman and Bell, b.p. 75° (5 mm.) $n^{20}\text{D}$ 1.5805]. *p*-Aminothiophenol, *p*-nitrothiophenol and *p*-aminophenyl disulfide (Kek Labs) were used without further purification. All mercaptans were stored under a nitrogen atmosphere in a cold box.

Purification of Solvents.—Dimethylformamide, diglyme, *tert*-butyl alcohol, and methanol were dried over indicating Drierite and then distilled over 13X Linde Molecular Sieves to remove any water that was present. The sieves had previously been calcined under nitrogen at 750° for 4 hr. All solvents were stored in a nitrogen dry box.

Synthesis and Identification of Disulfides.—Each authentic disulfide was prepared according to the method described in Vogel.[11] One-tenth mole of each mercaptan was added to 50 ml. of a 15% sodium hydroxide solution in a flask equipped with a stirrer and nitrogen bubbler. Iodine (11.0 g.) was added over a 2-hr. period and each reaction mixture was then stirred overnight. *n*-Butyl and cyclohexyl disulfide were purified by distillation under reduced pressure through a 14-in. silvered column equipped with a tantalum wire spiral. Boiling points and indices of refraction agreed with those tabulated in Reid.[12] Phenyl and benzyl disulfides, when recrystallized from methanol, had respective melting points of 62 and 74° (reported[12] 62 and 74°, respectively). The yields of all disulfides varied between 65 and 80%.

In the isolation of disulfides from the oxidation reactions, the reaction mixture was neutralized with hydrochloric acid, diluted with an equal volume of water, and the disulfide removed by extraction with petroleum ether. The disulfides were purified as above and the physical properties agreed with the literature values. In addition, the infrared spectrum of each disulfide was identical to the synthesized materials. In the case of the phenyl, *p*-aminophenyl, and benzyl disulfides mixture melting points with the authentic disulfides showed no depression.

Preparation of Reaction Mixtures and Actual Oxidation Experiments.—All base-solvent systems were made up to the appropriate molarity in a specially adapted heavy-walled 500-ml. erlenmeyer flask in a nitrogen drybox. Each solvent contained 0.20 mole of the desired alkoxide base. One-tenth mole of each mercaptan was then added, the reaction flask sealed, and transferred to the oxidation apparatus which consisted of a polyethylene gas balloon, wet-test meter, drying tower, and a water-cooled condenser. Kinetic measurements were determined from the rate of oxygen consumption as a function of time using the previously derived first-order rate expression. This method of analysis as well as a detailed description of the apparatus employed have been discussed in detail previously.[1,13,14]

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Telomerization by Free Radical Mercaptan Chain Transfer. I. Styrene and Ethanethiol[1]

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One- and two-unit telomers (only) have been obtained from styrene using ethanethiol as a free radical chain transfer agent in the liquid phase. Reversibility of telomer formation under the conditions studied was found to be slight. Chain transfer constants for one- and two-unit telomers and also long chain polymers have been determined. The significance of the increase of transfer constant with chain length is discussed.

The formation of short chain polymer fragments (telomers and cotelomers) by free radical chain transfer has been known for some time. However, its potential versatility as a synthetic tool has thus far received little application owing in part to separation problems and in part to lack of fundemental data on chain transfer in very short chains. A number of workers[3] have studied haloalkane agents and determined chain transfer constants for a few monomers measuring the relative rate of displacement (equation 1) to propagation (equation 2) for short chains containing n units. (Here M refers to monomer units and A and

$$\text{B—M}_n\cdot + \text{A—B} \xrightarrow{k_{dn}} \text{B—M}_n\text{—A} + \text{B}\cdot \qquad (1)$$

$$\text{B—M}_n\cdot + \text{M} \xrightarrow{k_{pn}} \text{B—M}_{n+1}\cdot \qquad (2)$$

B to fragments of the transfer agent, A–B. The sym-

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(2) Presented in part at the 141st National Meeting of the American Chemical Society, Division of Polymer Chemistry, Washington, D. C., March, 1962, and taken in part from the thesis of James C. Wang.

(3) (a) For a review and earlier references, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 243–259 and 313–326; (b) J. C. Robb and E. Senogles, *Trans. Faraday Soc.*, **58**, 708 (1962); (c) W. J. Kirkham and J. C. Robb, *ibid.*, **57**, 1757 (1961); (d) J. C. Robb and D. Vofsi, *ibid.*, **55**, 558 (1959); (e) W. I. Bengough and R. A. M. Thomson, *ibid.*, **57**, 1928 (1961); (f) **56**, 407 (1960).