+ XO + M, is given by an expression of the type E8

$$k_1 = \frac{PZ}{(s-1)!}\left(\frac{E^0}{RT}\right)^{s-1} e^{-E^0/RT} \quad \text{(E8)}$$

and if the equilibrium constant is given by an expression of the form

$$K = Ae^{-E^0/RT}$$

(which is approximately true), then the recombination constant will be given by

$$k_2 = k_1/K = \frac{1}{A}\cdot\frac{PZ}{(s-1)!}\left(\frac{E^0}{RT}\right)^{s-1}$$

with a similar expression for k_8. The factor A is about the same for the two reactions. From a simple viewpoint the PZ factors would also be about equal. With $s = 3$ the ratio of the $(E^0/RT)^{s-1}$ terms contributes a factor of about 9 to k_8/k_2. The rest of the difference in the rates of the O + NO + M and O + O_2 + M reactions remains unexplained.

Acknowledgments.—The support of this work by the Office of Naval Research is gratefully acknowledged. We thank Professor S. W. Benson and Dr. O. R. Wulf for helpful discussions and Professor R. M. Badger for the loan of the spectrograph. We are much indebted to Dr. R. E. Duff for making his computing codes available to us. W. M. Jones expresses his appreciation to the California Institute of Technology for its hospitality, to the Los Alamos Scientific Laboratory for its support while on leave and to Dr. J. H. Sullivan for many helpful discussions.

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The Reactivity of Phenols toward Peroxy Radicals. I. Inhibition of the Oxidation and Polymerization of Methyl Methacrylate by Phenols in the Presence of Air[1]

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RECEIVED OCTOBER 26, 1961

In an effort to elucidate the mechanism by which phenols retard vinyl polymerization in the presence of air, the action of twenty phenols upon the polymerization of methyl methacrylate has been studied. Induction periods and rates of polymerization have been measured dilatometrically. Addition of a phenol increases the length of the inhibition period over that due to oxygen alone. A kinetic scheme has been developed which accords well with the experimental results. On this basis it is concluded that phenols act as anti-oxidants, as is often found to be the case in other free-radical reactions. The phenol prevents oxygen from becoming depleted too rapidly, thus extending the inhibition period by maintaining a reasonably high oxygen concentration level for a longer time than would normally be the case. Relative efficiencies of several phenols have been determined and these results correlated with other kinetic studies of oxidation inhibition by phenols.

Introduction

While phenols have long been used as stabilizers for vinyl monomers, their mechanism of action is still not clear. It has usually been assumed that the phenols act by destroying peroxides that can initiate polymerization, or by being oxidized to quinoid products that can inhibit polymerization.[2-5] It has been found in the present work that these mechanisms of stabilization do not appear to be generally valid. An alternative mechanism which appears to be in better accord with the experimental facts has been set forth.

A defect common to the previous theories is the lack of attention given to the role of oxygen in the stabilization process. Oxygen itself is well-known as a polymerization inhibitor.[6] Schulz and Henrici[7] have recently studied the oxygen-inhibited polymerization of methyl methacrylate by a simple dilatometric technique in which the length of the well-defined inhibition periods were used to estimate the rate of oxidation of the monomer during the inhibition periods. They assumed an exactly alternating copolymerization of methyl methacrylate and oxygen during the inhibition period. The greatly decreased rate of polymerization during the inhibition period was found to be caused chiefly by a large decrease in the kinetic chain-length relative to the chain-length found in normal polymerization. Since essentially all of the oxygen is used up during the inhibition period, the rate of oxidation was taken to be equal to the initial concentration of oxygen divided by the length of the inhibition period. This is very convenient for studying inhibition-period rates since the length of this period is a quantity easily measured.

Mayo and Miller[8] have carried out a much more complete study of the same system. They used the complete copolymerization equations in their study and so obtained much more detailed information about the various steps as well as their change with time. For conditions corresponding to those of Schulz and Henrici, some expected differences were found. In spite of these differences, the assumptions of Schulz and Henrici are probably a fair approximation during the larger part of the inhibition period. It appears reasonable

(1) Taken from a portion of the Ph.D. thesis of R. G. C. Inquiries should be addressed to J. L. I. The financial support of the Research Corporation and of the University of Hawaii Research Committee is gratefully acknowledged.

(2) C. Walling and E. R. Briggs, *J. Am. Chem. Soc.*, **68**, 1141 (1946).

(3) B. A. Dolgoplosk and D. Sh. Korotkina, *Zhur. Obshchei Khim.*, **27**, 2226 (1957). Consultants Bureau (C. B.) Translation, p. 2285.

(4) B. A. Dolgoplosk and G. A. Parfenova, *ibid.*, **27**, 3083 (1957). C. B. Translation, p. 3122.

(5) G. P. Belonovskaya, Zh. D. Vasyutina and B. A. Dolgoplosk, *Zhur. Priklad. Khim.*, **32**, 1824 (1958). C. B. Translation, p. 1863.

(6) F. A. Bovey and I. M. Kolthoff, *Chem. Revs.*, **42**, 491 (1948).

(7) G. V. Schulz and G. Henrici, *Makromol. Chem.*, **18/19**, 437 (1956).

(8) F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **80**, 2493 (1958).

to consider that Schulz and Henrici's approach actually reflects an *average* behavior over the whole of the inhibition period. In order to treat even more complex systems which result when phenols (or other compounds) are added to the reaction mixture, it is convenient to use the equations and simplifying assumptions of Schulz and Henrici.

Experimentally it is found that the addition of phenols significantly increases the length of the inhibition period for oxygen-inhibited polymerization of methyl methacrylate. Boardman and Selwood[9] have demonstrated that the rate of oxidation of styrene is decreased by the addition of phenolic antioxidants. In view of the fact that phenols are known to have little effect on the rate of polymerization in the absence of oxygen,[2-5,10] it appears a reasonable postulate that phenols act simply as antioxidants in the inhibition of vinyl polymerization in the presence of oxygen. If a chain-carrying peroxy radical reacts with a phenol to produce a new radical which then terminates another oxidation chain, two kinetic chains have been broken which would have reacted with many oxygen molecules. The role of the phenols in the inhibition or stabilization process is simply to prevent the oxygen from being consumed rapidly and thus to maintain the oxygen concentration at a level high enough to cause inhibition for a longer time.

The effects of concentration of each of a series of phenols on the length of the inhibition period for the 2,2′-azobis-(isobutyronitrile)-initiated polymerization of methyl methacrylate in the presence of air at 44.4° have been measured. With the basic assumption that the problem to be considered was the *average* behavior during the inhibition period, it has been possible to derive an equation useful for the kinetic analysis of the experimental results. Since one of the results of the kinetic analysis is the relative reactivity of the phenols or other addends toward peroxy free radicals, the present approach should also prove useful for other reaction systems.

Kinetic Analysis.—Following Schulz and Henrici[7] it is assumed that steady state conditions obtain during the inhibition period. It is also assumed that the rate of oxidation of the manomer is given by the negative of the initial oxygen concentration divided by the length of the inhibition period. Neglecting alternative oxygen-consuming reactions, this is tantamount to using the average rate of oxidation in the kinetic equations. Since it is known that the phenols have little effect in the absence of oxygen,[10] it is apparent that the length of the inhibition period must still be determined by the rate of depletion of oxygen from the solution. There may still be appreciable phenol concentrations present at the end of the inhibition period.

Derivation of the Kinetic Equations.—The kinetic scheme assumed is:

$$\mathrm{I} \longrightarrow \mathrm{R} \text{ with rate } = r_i \quad (1)$$

$$\mathrm{O_2} + \mathrm{R} \longrightarrow \mathrm{RO_2} \qquad k_o(\mathrm{O_2})(\mathrm{R}) \quad (2)$$

$$\mathrm{RO_2} + \mathrm{M} \longrightarrow \mathrm{R} \qquad k_p(\mathrm{RO_2})(\mathrm{M}) \quad (3)$$

$$\mathrm{RO_2} + \mathrm{RO_2} \longrightarrow \text{products} \qquad k_t(\mathrm{RO_2})^2 \quad (4)$$

$$\mathrm{RO_2} + \mathrm{X} \longrightarrow \mathrm{Z} \qquad k_x(\mathrm{RO_2})(\mathrm{X}) \quad (5)$$

$$\mathrm{RO_2} + \mathrm{Z} \longrightarrow \text{products} \qquad k_c(\mathrm{RO_2})(\mathrm{Z}) \quad (6)$$

$$\mathrm{Z} + \mathrm{Z} \longrightarrow \text{products } (+ \mathrm{X}) \qquad k_z(\mathrm{Z})^2 \quad (7)$$

Here I is an initiator molecule, R an initiator or polymer chain-carrying radical, O_2 an oxygen molecule, RO_2 a peroxy radical, M a monomer molecule, X a retarder molecule, and Z a retarder radical. In equation 7 the symbol for the retarder molecule in parentheses signifies that a molecule of retarder may or may not be regenerated by this reaction. The first four reactions in this scheme are those found to be the most important in Schulz and Henrici's work.[7] The additional three reactions are assumed to be the most significant reactions caused by the addition of an antioxidant to the system.

The absence from the kinetic scheme of the usual propagation and termination reactions of the polymethyl methacrylate radical implies that these reactions are swamped because of the great reactivity of these radicals toward molecular oxygen.

Applying the steady state condition, these relations are obtained

$$\mathrm{d(R)}/\mathrm{d}t = 0 = r_i - k_0(\mathrm{O_2})(\mathrm{R}) + k_p(\mathrm{RO_2})(\mathrm{M}) \quad (8)$$

$$\mathrm{d(RO_2)}/\mathrm{d}t = 0 = k_0(\mathrm{O_2})(\mathrm{R}) - k_p(\mathrm{RO_2})(\mathrm{M}) - 2k_t(\mathrm{RO_2})^2 - k_x(\mathrm{RO_2})(\mathrm{X}) - k_c(\mathrm{RO_2})(\mathrm{Z}) \quad (9)$$

$$\mathrm{d(Z)}/\mathrm{d}t = 0 = k_x(\mathrm{RO_2})(\mathrm{X}) - k_c(\mathrm{RO_2})(\mathrm{Z}) - 2k_z(\mathrm{Z})^2 \quad (10)$$

Adding equations 8, 9 and 10

$$r_i = 2k_t(\mathrm{RO_2})^2 + 2k_c(\mathrm{RO_2})(\mathrm{Z}) + 2k_z(\mathrm{Z})^2 \quad (11)$$

This equation merely states that the rate of chain initiation is equal to the rate of termination of the kinetic chains.

It is convenient first to consider the relations that hold when no phenols are present. Discarding the last two terms in equation 11 and solving for (RO_2), gives

$$(\mathrm{RO_2})_0 = r_i^{1/2}/(2k_t)^{1/2} \quad (12)$$

where (RO_2) is the peroxy radical concentration for a given r_i when there is no retarder present. From equation 8 and the observation that in the absence of phenols, r_i is small in comparison with the other two terms of the equation,[7] we have

$$-\mathrm{d(O)_2}/\mathrm{d}t = k_0(\mathrm{O_2})(\mathrm{R}) = k_p(\mathrm{RO_2})(\mathrm{M}) \quad (13)$$

The basic definition of the average rate of disappearance of oxygen is

$$-\mathrm{d(O_2)}/\mathrm{d}t = (\mathrm{O_2})_0/T \quad (14)$$

where $(O_2)_0$ is the initial oxygen concentration and T is the length of the inhibition period. Combining with equations 12 and 13, we have

$$T_0^{-1} = k_p(2k_t)^{-1/2}(\mathrm{M})(\mathrm{O_2})_0^{-1}r_i^{1/2} \quad (15)$$

where T_0 is the length of the inhibition period for a given r_i in the absence of phenols. This equation is equivalent to the result obtained by Schulz and Henrici.[7]

Returning now to the case where the retarder is also present, it follows, using equation 8, that

$$(\mathrm{RO_2})/(\mathrm{RO_2})_0 = KT_0/T \quad (16)$$

(9) H. Boardman and P. W. Selwood, *J. Am. Chem. Soc.*, **72**, 1372 (1950).

(10) R. G. Caldwell and J. L. Thrig, *J. Polymer Sci.*, **46**, 507 (1960).

where the zero subscripts signify quantities corresponding to a given r_i when no phenols are present, and K is a correction factor (close to unity under our conditions but evaluated in each case) given by the expression

$$K = [(O_2)_0 - r_i T]/[(O_2)_0 - r_i T_0] \quad (17)$$

where the subscript zero on the oxygen concentration represents the initial oxygen concentration. From equations 10, 11, 12 and 16, we have

$$r_i[1 - (K^2T_0^2/T^2)] = 2k_x(RO_2)(X) - 2k_z(Z)^2 \quad (18)$$

At this point it is convenient to make an assumption about the principal mode of chain termination by Z radicals. It has become apparent that cross-termination between unlike radicals is favored over mutual-termination between like radicals provided the concentration relationships are not too unfavorable.[11] Thus it is plausible to assume that reaction 6 is more important than reaction 7.

Using this assumption and equation 18, it follows that

$$r_i[1 - (K^2T_0^2/T^2)] = -2d(X)/dt \quad (19)$$

The deduction of equation 19 follows exactly (within the assumed kinetic scheme) if a molecule of retarder is either regenerated in reaction 7 or if reaction 7 is completely negligible. It is only approximate if no X is regenerated in reaction 7 and depends on the validity of the assumption made about the relative importance of the different modes of disappearance of Z from solution.

The average rate of reaction of the phenols during the inhibition period can be taken to be the concentration consumed divided by the length of the inhibition period. This is expressed by

$$-d(X)/dt = [(X)_0 - (X)_T]/T = [(X)_0/T][1 - (X)_T/(X)_0] \quad (20)$$

where $(X)_0$ is the initial retarder concentration and $(X)_T$ is the retarder concentration at the end of the inhibition period. If most Z's disappear by cross-termination, the average retarder concentration during the inhibition period can be related to the initial and final retarder concentrations by the expression

$$(\bar{X})/(X)_0 = [1 - (X)_T/(X)_0]/\ln [(X)_0/(X)_T] \quad (21)$$

Combining equations 19 and 20, the final relation necessary to calculate the average value of the phenol concentration during the inhibition period is given by

$$(X)_T/(X)_0 = 1 - r_i/2(X)_0[(T^2 - K^2T_0^2)/T] \quad (22)$$

Invoking once again the assumption that reaction 6 is more important than reaction 7, and using equation 10, we write

$$(Z) = (k_x/k_c)(X) \quad (23)$$

By substituting this result back into the equation and using equations 12 and 16, after rearranging we have our final kinetic equation in a form suitable for plotting

$$r_i(\bar{X})^{-2}[1 - (K^2T_0^2/T^2)] = 2^{1/2}k_x k_i^{-1/2}[KT_0 r_i^{1/2}T^{-1}(\bar{X})^{-1}] - 2k_z k_x^2 k_c^{-2} \quad (24)$$

It must be remembered here that $\bar{X}$ represents the average value of X during the inhibition period and is calculated by use of equations 21 and 22.

If the kinetic scheme assumed is correct and if only data from experiments in which there is some phenol left in solution at the end of the inhibition are used, a plot of the quantity on the left-hand side of equation 24 against the quantity in brackets on the right-hand side of the equation should yield a straight line for any given phenol. Since the value of k_x is the most natural index of the reactivity of retarder molecules toward peroxy radicals, the ratio of the k_x constants for two different compounds can be taken as a measure of their relative reactivity. In the present work phenol, itself, was taken as the reference compound. The reactivities of the other phenols were all measured relative to that of phenol. These relative efficiencies E were then obtained simply by taking the ratio of the slopes obtained by plotting equation 24 for a series of phenols to that obtained for phenol.

Another quantity of interest may be obtained from the plot for a single compound. A quantity ϕ is defined which gives a measure of the tendency of the retarder radicals and peroxy radicals to cross-terminate rather than to terminate mutually.[11]

$$\phi = k_0/2k_t^{1/2}k_z^{1/2} \quad (25)$$

If ϕ is greater than one, the tendency is for the radicals to cross-terminate, if less than one, the tendency is toward mutual-termination. From the plot of equation 24 the value of ϕ for any phenols can be obtained from the relation

$$\phi = {}^1/_2(\text{slope})(-\text{intercept})^{-1/2} \quad (26)$$

In view of the approximations made, and of the fact that the intercepts were found to be very small, this quantity is much less certain than the relative efficiencies toward reaction with peroxy radicals.

The Stoichiometric Equation.—A slight generalization of equation 19 is possible if it is noted that the coefficient "2" on the right-hand side of the equation represents the number of kinetic chains stopped per molecule of phenol which reacts. Thus we may write

$$r_i[1 - (K^2T_0^2/T^2)] = -N\,d(X)/dt \quad (27)$$

where N is the number of chains stopped per retarder molecule.

In the special case where retarder exhaustion takes place right at the end of the inhibition period, the average rate of reaction of the retarder can be written approximately as

$$-d(X)/dt = (X)_0/T \quad (28)$$

Substituting equation 28 into equation 27, and rearranging gives

$$(T^2 - K^2T_0^2)/T = N(X)_0/r_i \quad (29)$$

For convenience this is called the stoichiometric equation. A plot of this equation should give a straight line through the origin with a slope equal to N, the number of kinetic chains stopped per retarder molecule.

Alternative Kinetic Schemes.—Using average rates and retarder concentrations during the inhibition period, it is possible to derive kinetic

(11) See, *e.g.*, C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 145–147.

equations corresponding to alternative reaction schemes. Two such were worked through in detail but proved to be less simple and not quite so general as the one described above.[1] One scheme assumed that the reaction proceeds through an addition-complex structure for the retarder radical, Z. In the other a combination of hydrogen-atom-abstraction and addition-complex-formation mechanisms was postulated.

Results[12]

Results in the Absence of Phenols.—The results found in the absence of added phenols were found to be very similar to those found by Schulz and Henrici.[7] In all experiments the methyl methacrylate was initially saturated with air at atmospheric pressure. At 44.4°, the reciprocal of the inhibition period length before the methyl methacrylate began to polymerize at the normal polymerization rate was found to be given accurately by the expression

$$T_0^{-1} = 0.236\,(\mathrm{AIBN})^{1/2} \qquad (30)$$

where T_0 is the length of the inhibition period in minutes, and (AIBN) is the molar concentration of the polymerization initiator, 2,2′-azobis-(isobutyronitrile). The rate of the unretarded polymerization after this period was established as

$$r_0 = 30.1\,(\mathrm{AIBN})^{1/2} + 0.13 \qquad (31)$$

where r_0 is the rate of polymerization in %/hr.

Results in Hydroquinone Experiments.—Since hydroquinone has been widely used as a vinyl monomer stabilizer and since some experimental results are available for benzoquinone[10] (the presumed product of hydroquinone-free radical reactions) under similar experimental conditions, special attention was paid to this phenol. When hydroquinone was added to the reaction mixture at concentrations from 5×10^{-5} to 3×10^{-4} molar, at an AIBN concentration of about 3×10^{-2} molar, the inhibition periods were increased from about 25 min. to 65–180 min. The rates of polymerization after the inhibition periods were found to be retarded relative to normal polymerization rates.

From previous results obtained from retardation studies of AIBN-initiated polymerization of methyl methacrylate by benzoquinone under similar experimental conditions,[10,13] it is possible to calculate the retarding effect of any given concentration of benzoquinone. It was found that under the present experimental conditions the hydroquinone appeared to be essentially consumed at the end of the inhibition periods (see below). It is a plausible assumption that the final product of the peroxy radical-hydroquinone reaction is benzoquinone. This is also suggested by the yellow coloring of the solutions observed after the inhibition periods in the hydroquinone experiments. This assumption is also subject to check by the following method: if hydroquinone is completely converted to benzoquinone during the inhibition periods, we may calculate how much retardation would be expected from the resulting benzoquinone concentrations. If the assumption is correct, the calculated amounts of retardation should agree with the retardations observed after the end of the inhibition periods in the hydroquinone experiments.

Below are listed the fractional degrees of retardation (relative to the unretarded rates for the same initiator concentrations). The first value in the following number pairs is the fractional degree of retardation observed in the hydroquinone experiments; the second is the value calculated from the experimental benzoquinone results[10]: 0.90–0.87, 0.79–0.76, 0.65–0.65, 0.67–0.63, and 0.81–0.77. This general agreement suggests strongly that the reaction product is indeed benzoquinone.

It is of interest to check what the effect of benzoquinone is on the length of the inhibition period and whether its retardation after the inhibition period is the same as for the previous experiments carried out in the complete absence of air. With a benzoquinone concentration of 1.62×10^{-4} molar, and an initiator concentration of 2.49×10^{-2} molar, the length of the inhibition period was observed to be 27.3 min., and the fractional degree of retardation after the inhibition period was 0.64. The length of the inhibition period in the absence of added retarder was calculated to be 26.9 min. from equation 30. The fractional degree of retardation calculated from the previous benzoquinone results in the absence of air was 0.62. The length of the inhibition period appears to be unchanged within the normal experimental error. It will be noted that the calculated fractional degree of retardation for benzoquinone in the absence of air is slightly lower than that observed in the present work. This effect is also apparent above in the comparison of the observed and calculated fractional degrees of retardation in the hydroquinone experiments. This may be due to the slightly different experimental conditions for the two different kinds of experiments. Benzoquinone, then, has no appreciable effect on the length of the inhibition period and its normal retardation behavior is not significantly changed.

Estimation of Auxiliary Quantities.—In order to apply the basic kinetic equations, which include the factor K to the experimental data, it is necessary to estimate several auxiliary quantities. The value of the initial oxygen concentration is needed, but since it appears only in a correction term which is close to unity, the exact value is not important. The value used was 2.2×10^{-3} molar taken from the equation given by Mayo and Miller[8] for the solubility oxygen in methyl methacrylate as a function of its partial pressure. They state that the solubility is only slightly temperature dependent and used a value from this equation for their own work at 50°. This value is also close to that used by Schulz and Henrici[7] for the oxygen concentration in methyl methacrylate in equilibrium with air at 50°. Since the results are not at all sensitive to the exact value used in the present work, the estimate adopted was considered satisfactory.

Another necessary quantity is the rate of initiation r_1. This was obtained from the empirical

(12) For a more complete presentation of these results, see: R. G. Caldwell, Ph.D. Thesis, University of Hawaii, 1960.

(13) J. L. Kice, *J. Am. Chem. Soc.*, **76**, 6274 (1954).

TABLE I

KINETIC DATA ON RETARDATION OF POLYMERIZATION BY RETARDERS IN THE PRESENCE OF OXYGEN

Retarder	Retarder, mole/l.	Initiator, mole/l.	T, min.	T_0, min.	r/r_0
p-Benzoquinone	1.62×10^{-4}	2.49×10^{-2}	27.3	26.9	0.643
Hydroquinone	5.09×10^{-5}	3.08×10^{-2}	67.3	24.15	.896
	1.02×10^{-4}	3.08×10^{-2}	111.4	24.15	.789
	1.53×10^{-4}	3.08×10^{-2}	140.8	24.15	..
	2.03×10^{-4}	3.08×10^{-2}	192.2	24.15	..
	1.35×10^{-4}	2.42×10^{-2}	180.0	27.2	.654
	1.49×10^{-4}	3.03×10^{-2}	158.0	24.4	.666
	1.17×10^{-4}	4.76×10^{-2}	85.3	19.4	.810
	2.71×10^{-4}	3.43×10^{-2}	220.3	22.9	.523
α-Naphthol	8.99×10^{-5}	3.43×10^{-2}	71.4	22.9	..
(1-Naphthol)	4.48×10^{-5}	3.11×10^{-2}	48.4	24.0	.982
	8.96×10^{-5}	3.11×10^{-2}	76.5	24.0	.956
	1.345×10^{-4}	3.11×10^{-2}	103.0	24.0	..
	1.79×10^{-4}	3.11×10^{-2}	127.3	24.0	..
β-Naphthol	2.39×10^{-4}	3.43×10^{-2}	51.3	22.9	.947
(2-Naphthol)	2.02×10^{-4}	3.55×10^{-2}	46.75	22.5	.957
	4.04×10^{-4}	3.55×10^{-2}	65.2	22.5	.936
	6.06×10^{-4}	3.55×10^{-2}	78.0	22.5	..
	8.08×10^{-4}	3.55×10^{-2}	87.7	22.5	..
Phenol	8.105×10^{-4}	3.44×10^{-2}	49.2	22.9	.926
	1.62×10^{-3}	3.44×10^{-2}	75.8	22.9	.874
	2.43×10^{-3}	3.44×10^{-2}	98.4	22.9	.835
	3.24×10^{-3}	3.44×10^{-2}	120.8	22.9	.668
Catechol	2.81×10^{-5}	2.89×10^{-2}	41.2	24.9	.987
	5.61×10^{-5}	2.89×10^{-2}	61.3	24.9	.945
	8.42×10^{-5}	2.89×10^{-2}	82.2	24.9	..
Resorcinol	7.975×10^{-4}	3.04×10^{-2}	119.2	24.3	.839
	1.595×10^{-3}	3.04×10^{-2}	170.8	24.3	.801
	2.39×10^{-3}	3.04×10^{-2}	206.8	24.3	.801
Pyrogallol	2.78×10^{-5}	3.11×10^{-2}	39.7	24.0	.972
	5.34×10^{-5}	3.26×10^{-2}	56.0	23.5	.926
	8.01×10^{-5}	3.26×10^{-2}	75.2	23.5	.912
Phloroglucinol	1.33×10^{-4}	3.51×10^{-2}	30.4	22.6	.905
	2.66×10^{-4}	3.51×10^{-2}	36.3	22.6	.854
	3.98×10^{-4}	3.51×10^{-2}	40.5	22.6	.839
1,2,4-Trihydroxybenzene	4.585×10^{-5}	4.31×10^{-2}	53.8	20.4	.906
(1,2,4-Benzenetriol)	9.17×10^{-5}	4.31×10^{-2}	88.0	20.4	.789
	1.38×10^{-4}	4.31×10^{-2}	123.3	20.4	..
1,4-Naphthalenediol	1.26×10^{-5}	4.49×10^{-2}	21.1	20.0	1.01
	2.52×10^{-5}	4.49×10^{-2}	22.5	20.0	0.992
	3.78×10^{-5}	4.49×10^{-2}	24.3	20.0	..
1,5-Naphthalenediol	1.51×10^{-5}	3.22×10^{-2}	33.6	23.6	.998
	3.02×10^{-5}	3.22×10^{-2}	44.4	23.6	.981
	4.53×10^{-5}	3.22×10^{-2}	58.2	23.6	..
1,6-Naphthalenediol	3.84×10^{-5}	3.68×10^{-2}	41.5	22.1	.986
	7.67×10^{-5}	3.68×10^{-2}	63.4	22.1	.949
	1.15×10^{-4}	3.68×10^{-2}	84.9	22.1	.956
2,3-Naphthalenediol	3.61×10^{-5}	4.12×10^{-2}	35.2	20.9	.931
	7.23×10^{-5}	4.12×10^{-2}	49.3	20.9	.875
	1.08×10^{-4}	4.12×10^{-2}	63.3	20.9	.843
2,7-Naphthalenediol	1.84×10^{-4}	3.29×10^{-2}	54.7	23.4	.971
	3.68×10^{-4}	3.29×10^{-2}	72.8	23.4	.941
	5.52×10^{-4}	3.29×10^{-2}	82.9	23.4	..
o-Hydroxybiphenyl	1.69×10^{-4}	4.60×10^{-2}	28.75	19.7	.948
(*o*-Phenylphenol)	3.38×10^{-4}	4.60×10^{-2}	39.5	19.7	.895
	5.07×10^{-4}	4.60×10^{-2}	50.8	19.7	..
p-Hydroxybiphenyl	3.01×10^{-4}	4.15×10^{-2}	62.3	20.8	.923
(*p*-Phenylphenol)	6.02×10^{-4}	4.15×10^{-2}	100.2	20.8	.954
	9.03×10^{-4}	4.15×10^{-2}	128.9	20.8	..
p,*p*′-Dihydroxybiphenyl	1.015×10^{-4}	4.14×10^{-2}	71.2	20.8	.917
(*p*,*p*′-Biphenol)	2.03×10^{-4}	4.14×10^{-2}	127.3	20.8	.863
	3.04×10^{-4}	4.14×10^{-2}	176.2	20.8	..

p-Methoxyphenol	8.20×10^{-5}	5.10×10^{-2}	51.3	18.8	.873
	1.64×10^{-4}	5.10×10^{-2}	87.2	18.8	.785
	2.46×10^{-4}	5.10×10^{-2}	120.5	18.8	.697
p-Nitrophenol	5.67×10^{-3}	2.525×10^{-2}	26.9	26.7	1.000
	2.27×10^{-2}	2.47×10^{-2}	31.8	26.9	0.969
	3.40×10^{-2}	2.47×10^{-2}	35.6	26.9	0.965

equation given by Ferington and Tobolsky.[14] In order to use this equation, it was necessary to estimate the relative probability of termination by disproportionation to that of combination for polymethyl methacrylate free radicals. This was done by fitting the data given by Bevington and his coworkers[15] to an Arrhenius-type equation and then calculating the value for 44.4°. At this temperature termination by disproportionation was found to be 3.72 times as probable as termination by combination. Using this value in combination with Ferington and Tobolsky's equation, the following relation was obtained

$$r_i = 6.59 \times 10^{-8} r_0^2 \qquad (32)$$

where r_i is the rate of initiation in moles liter^{-1} min.$^{-1}$ and r_0 is the rate of polymerization in %/hr. calculated from equation 31.

Results on the Relative Efficiencies of Phenols with Peroxy Radicals.—The phenols were studied at concentrations in the range 10^{-5} to 10^{-3} molar except for *p*-nitrophenol whose inactivity required concentrations over 10^{-2} molar. The inhibition periods found ranged from about 20 to 220 min.

The results for the experiments in the presence of the phenols were similar to those found in their absence. The ends of the inhibition periods were just as sharply defined as those in the absence of the phenols. Polymerization rates following the inhibition periods were all retarded somewhat. The significance of the fractional degrees of retardation in these cases where there is still some phenol present at the end of the inhibition period is obscured by the possibility of reaction between the phenols and the polyperoxides formed by the copolymerization of methyl methacrylate and oxygen. The primitive kinetic data are summarized in Table I.

The fundamental kinetic equation 24 is plotted in Fig. 1 for phenol itself. Figure 2 is a similar plot for α-naphthol, a compound of greatly different reactivity. The fit is seen to be satisfactory. Several of the phenols could not be treated in this manner because apparently they were consumed completely during the inhibition period under our experimental conditions. The compounds that could not be so plotted were: 1,5-naphthalenediol, 1,2,4-trihydroxybenzene and 1,4-naphthalenediol. Hydroquinone appeared to be just on the borderline of being completely consumed during the inhibition period. While an accurate plot could not be obtained, the data from several of the runs were used to estimate its efficiency. Since *p*-nitrophenol was found to be such a weak inhibitor, the intercept could not be obtained with any accuracy, but the value of its efficiency was obtained. All the other phenols gave plots that fitted the equation as well as the representatives shown in Figs. 1 and 2. The results of the kinetics analysis for all the phenols are summarized in Table II.

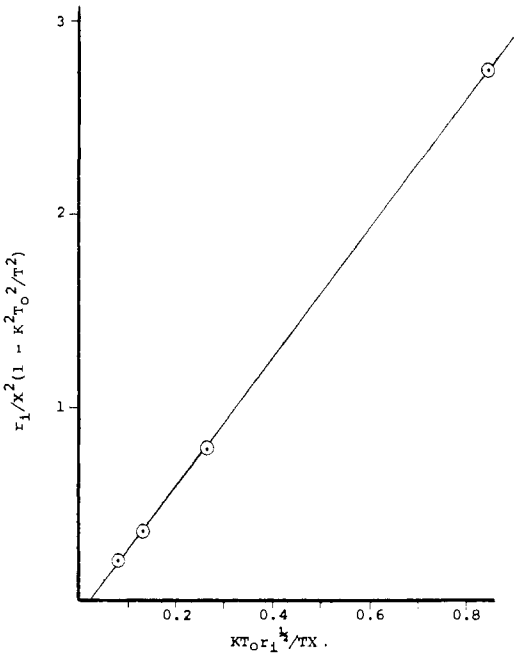

Fig. 1.—Plot of kinetic equation for phenol inhibition of polymerization in presence of oxygen.

It is apparent from this table that all ø values are greater than unity as would be expected if the tendency toward cross-termination is preferred. Due to the many uncertainties, however, the absolute ø values shown probably do not have much significance.

Stoichiometric Equation.—Those phenols essentially used up during the inhibition period are plotted according to the stoichiometric equation 29 in Fig. 3. One phenol which was used up entirely during the inhibition period and still could not be plotted according to the stoichiometric equation was 1,4-naphthalenediol. It or its semiquinone radical is apparently attacked by molecular oxygen strongly enough so that it has almost no effect on the length of the inhibition period under the present experimental conditions.

The theoretical slope corresponding to two kinetic chains stopped per phenol molecule is also shown in Fig. 3. The results for hydroquinone and 1,5-naphthalenediol are seen to fall fairly close to the theoretical line. Several of the hydroquinone points fall below the line. These represent the runs which were used to estimate the efficiency of hydroquinone. In these runs hydroquinone was evidently not quite consumed.

(14) T. E. Ferington and A. V. Tobolsky, *J. Colloid Sci.*, **10**, 536 (1955).

(15) J. C. Bevington, H. W. Melville and R. P. Taylor, *J. Polymer Sci.*, **14**, 463 (1954).

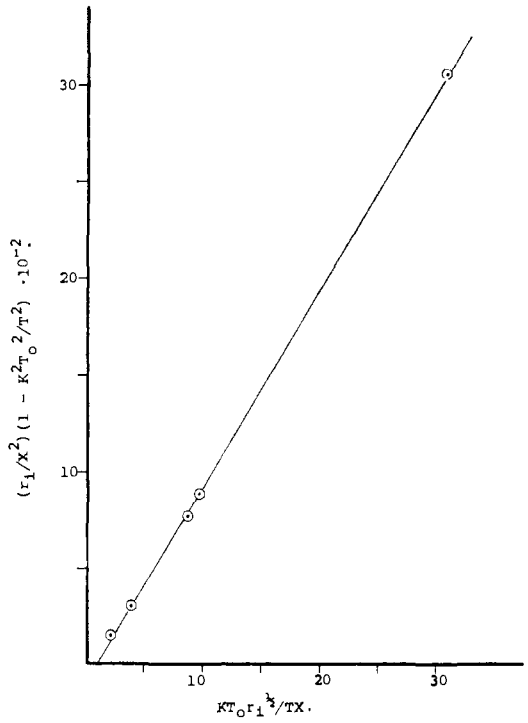

Fig. 2.—Plot of kinetic equation for α-naphthol inhibition of polymerization in presence of oxygen.

The results for 1,2,4-trihydroxybenzene are seen to fall above the line corresponding to two chains stopped per molecule. The slope of the line through the points corresponds to about 2.5 kinetic chains stopped per molecule. This is not surprising since there are three hydroxyl groups on this phenol. This shows that for quinols with more than two hydroxyl groups, the results of the kinetic analysis using equation 24 will be in error since the assumption that two kinetic chains are stopped per molecule is implicit in its derivation. Such a disagreement should be expected when the product of the reaction between a phenol molecule and two chain radicals can still stop further kinetic chains as the pyrogallol results also show. By this reasoning it is seen that the results for molecules like resorcinol might also be in error. For the less reactive phenols, however, this error should be negligible since so little phenol is actually consumed during the inhibition period.

The fact that the other more reactive quinols fall near the theoretical line suggests that attack by molecular oxygen must not be important. Since these are the most reactive phenols, oxygen attack on the remaining ones must also be negligible.

Discussion

The Mechanism of Stabilization of Vinyl Monomers by Phenols in the Presence of Oxygen.—From the preceding results the role of the phenols in the stabilization of methyl methacrylate monomer appears fairly certain. Due to the different natures of other vinyl monomers with regard to oxidation,[16] the present mechanism cannot be assumed to hold for *all* vinyl monomers. It appears reasonable, however, to expect that the mechanism might hold for a number of others. Henrici-Olivé and Olivé[17] have found that the mechanism of polymerization inhibition of styrene by oxygen is the same as that for methyl methacrylate found by Schulz and Henrici[7] using the same experimental method. This appears reasonable, for the polystyrylperoxy free radical toward phenols should not differ greatly from the polymethyl methacrylate peroxy radical. It would be desirable to ob-

(16) See, *e.g.*, F. R. Mayo, A. A. Miller and G. A. Russell, *J. Am. Chem. Soc.*, **80**, 2500 (1958).

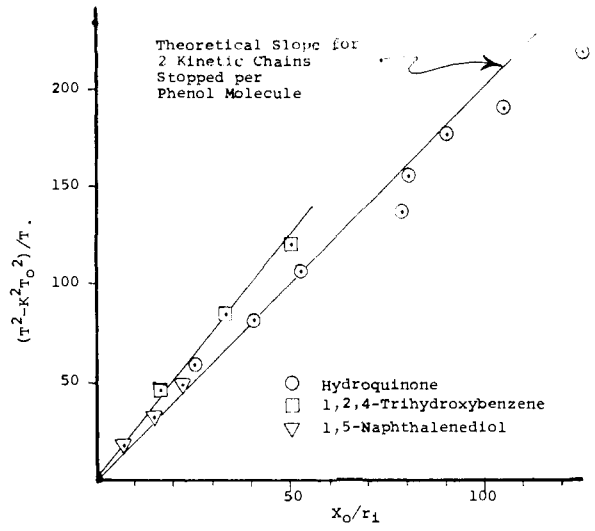

Fig. 3.—Plot of stoichiometric equation for phenols completely consumed during inhibition period.

TABLE II

SUMMARY OF RESULTS OF KINETIC ANALYSIS

Phenol	E	ϕ
p-Nitrophenol	0.006	..
Phenol	1.00	7
Phloroglucinol	2.47	1.5
o-Hydroxybiphenyl (*o*-Phenylphenol)	2.62	5
Resorcinol	3.18	3
β-Naphthol (2-Naphthol)	4.44	4
p-Hydroxybiphenyl (*p*-Phenylphenol)	5.42	8
2,7-Naphthalenediol	6.11	3
α-Naphthol (1-Naphthol)	31.0	5
2,3-Naphthalenediol	34.2	3
p,p'-Dihydroxybiphenyl	35.5	13
Catechol	36.4	5
p-Methoxyphenol	39.8	7.5
Pyrogallol	41.7	10
Hydroquinone	44	..
1,6-Naphthalenediol	45.4	4
1,5-Naphthalenediol	2 Chains stopped per molecule	
1,2,4-Trihydroxybenzene	2.5 Chains stopped per molecule	
Hydroquinone	2 Chains stopped per molecule	
1,4-Naphthalenediol	Ineffective under present conditions	

(17) G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **24**, 64 (1957).

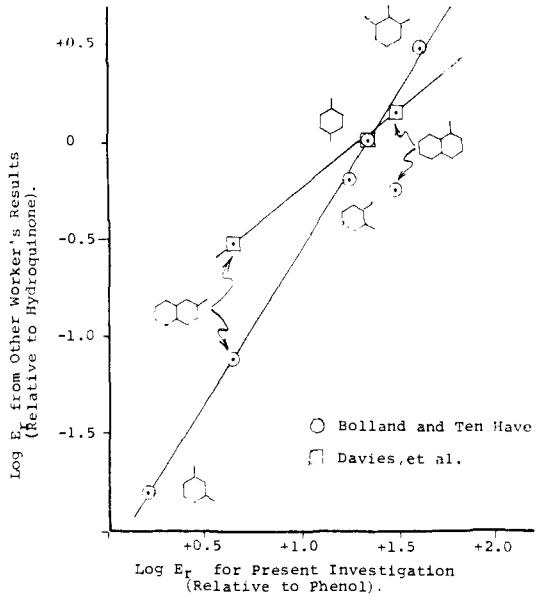

Fig. 4.—Comparison of present results for relative efficiencies of phenols toward reaction with peroxy radicals with results of other workers.

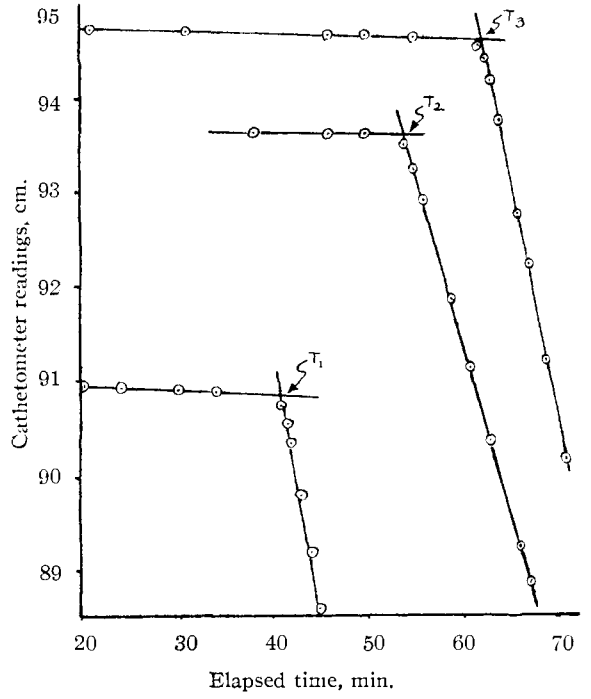

Fig. 5.—Sample plots of primitive kinetic data for phenolic inhibition experiments in the presence of air: 1, 1,6-naphthalenediol; 2, 1,2,4-trihydroxybenzene; 3, *p*-hydroxybiphenyl.

tain further experimental data with other monomers.

The fact that the kinetic behavior of the phenols in the present study seem to fit an antioxidation scheme very well lends strong support to our postulate as to their mechanism of action. It is also significant that the alternative reaction schemes discussed previously are also antioxidation schemes, differing only in the mechanism of antioxidation behavior.

Comparison of Present Results with Antioxidation Efficiencies of Phenols.—It has been observed that the relative reactivities of various peroxy radicals are very similar.[18] If the major variation in the reactivities is caused by the difference in the activation energies of the different reactions, the results of different workers using different systems may be compared. This can be done by plotting the log of the relative reactivities (corrected for symmetry properties of the various phenols in the transition state[19]) obtained by one worker against the log of the relative efficiencies obtained by others. This should result in a straight line plot if the above condition holds.

Relative reaction efficiencies are usually stated as ratios of rate constants for the reaction. In the present work the relative efficiencies are not strictly speaking, given by rate constant ratios because of the averaging process used in the derivation of the kinetic equation. If, however, the present approach is valid, the relative efficiencies obtained should be similar to those obtained by other workers using traditional kinetic methods.

In Fig. 4 the relative efficiencies for the reaction of several phenols toward polymethyl methacrylate peroxy radicals are compared with the results obtained by two other groups of workers.

The symmetry corrections of Bolland and Ten Have[20] have been applied to all three sets of data. Only α-naphthol falls off the line in the plot of Bolland and Ten Have's results[20] on the relative inhibitory effects of phenols upon the oxidation of ethyl linoleate. The results obtained by Davies and co-workers[18] on the phenolic inhibition of the oxidation of tetralin are also plotted with the exception of their result for phenol, itself, since they state that it did not satisfy their conditions for a satisfactory kinetic treatment.

The success of the comparison supports strongly the validity of the present kinetic approach. The correlation also serves to strengthen the conclusion that the phenols were acting in a straightforward manner as antioxidants in the present work.

Correlation of Reactivity and Structure of the Phenols.—A detailed discussion of the correlation between the reactivity of the phenols toward polymethyl methacrylate peroxy radicals and their electronic structure will be reserved for Part II of this series where a variety of molecular orbital treatments are utilized to discuss the possible transition states for the reaction of the phenols and peroxy radicals. It is sufficient here to remark briefly on the results listed in Table II.

It is apparent from Table II that the phenols having a quinone oxidized form are generally more reactive toward radical attack than the remaining phenols. It should be remembered, however, that to compare the purely *chemical* reactivities of the phenols, it is necessary to separate out the symmetry contributions to the measured reactivities.[19] If the

(18) D. S. Davies, H. L. Goldsmith, A. K. Gupta and G. R. Lester, *J. Chem. Soc.*, 4926 (1956).

(19) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(20) J. L. Bolland and P. Ten Have, *Discussions Faraday Soc.*, **2**, 252 (1947).

reaction proceeds through an initial attack on a hydroxyl group, the relative efficiencies of the phenols should be divided by the number of equivalent "most reactive" hydroxyl groups. In this case the reduced relative efficiencies of the quinols are lowered considerably.

Phloroglucinol is seen to be less reactive than resorcinol (even with no symmetry corrections). This is due presumably to the well-known tendency for phloroglucinol to exist in its tautomeric keto form.

The electron-withdrawing *p*-nitro group is seen to greatly deactivate phenol toward peroxy radical attack. The electron-donating *p*-methoxy group greatly activates phenol. These results infer that polar resonance forms in which electronic charge is transferred from the phenol to the peroxy radical are of importance in the transition state of the reaction.

Experimental

Materials.—Methyl methacrylate monomer was purified as described elsewhere.[10] 2,2'-Azobis-(isobutyronitrile) was recrystallized several times from methanol before use. Phenol, itself, was distilled using an air condenser. After a large fraction had been distilled, one drop (boiling at 178°) was collected in a weighed flask. The flask plus the phenol was reweighed and the solution used for the phenol experiments was then made up directly in the same flask.

Dilatometric Procedure.—A weighed amount of initiator and a weighed amount of phenol were added to a small flask. Twenty-five ml. of methyl methacrylate, previously saturated with air at room temperature, was pipetted into the flask and the temperature noted. The initiator and phenol were dissolved and mixed by shaking. A dilatometer of about 20 ml. capacity was then filled from the flask.

The dilatometer was then inserted into a constant-temperature bath held at 44.4° by an infrared lamp which was filtered by an added red-glass filter. The temperature of the bath was held constant to within 0.005°. The bath was located in a darkroom and the dilatometer was illuminated by a red safe-light during the run.

After the solution had come almost up to temperature, the dilatometer was removed briefly from the bath and the liquid in the capillary adjusted to the mark. The time necessary to make this adjustment was usually less than 15 sec. The zero time was taken to be the time of the initial insertion of the dilatometer into the bath. Periodic readings of the level of the liquid in the capillary were made with a cathetometer until about 30 min. after the easily-observed end of the inhibition period. Typical plots of the dilatometric measurements are shown in Fig. 5.

The procedure and necessary monomer constants for calculating polymerization rates are described elsewhere.[15]

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

The Amine Induced Chloroacetolysis of Trityl Chloride in Carbon Tetrachloride. A 2:1 Acid–Amine Adduct as a Reactant

BY L. J. ANDREWS AND R. M. KEEFER

RECEIVED JANUARY 19, 1962

The kinetics of reaction of chloroacetic acid with trityl chloride in carbon tetrachloride in the presence of β-bromoallyl-*n*-hexylamine have been investigated. When the acid to amine ratio is 2:1, the chloroacetolysis is first order with respect to the salt, $Am(HA)_2$. When the acid to amine ratio is between 2 and unity, the medium contains both $Am(HA)_2$ and Am.HA; apparently the latter is present predominantly in dimeric form and is a much less effective reactant than $Am(HA)_2$. When their total acid to total amine ratios are greater than 2, the media contain free acid, and the reactions then occur via a path which is rate dependent on the concentrations both of $Am(HA)_2$ and the free acid. There is some evidence that reactive aggregates, $Am(HA)_x$ (where $x > 2$), may also be present in solutions in which the acid is in large excess of the amine.

As part of an investigation of polar processes in non-polar media, the acetolysis and chloroacetolysis reactions of trityl chloride in carbon tetrachloride have been studied recently.[1,2] To prevent the accumulation of hydrogen chloride in the medium and thus insure that ester formation proceeds to completion one of two amines (β-bromoallyl-*n*-hexylamine or tri-*n*-butylamine), has been added to the initial reaction mixture as the carboxylic acid salt. Since these amines both form salts with carboxylic acids and hydrogen chloride which are appreciably soluble in carbon tetrachloride, it has proved feasible to conduct spectrophotometric studies of the kinetics of the amine induced reactions.

It has been convenient to study the acetolysis reaction at room temperature only with the acetic acid concentration relatively high (>0.5 *M*) and in large excess of that of the amine ($CH_2{=}CBrCH_2NHC_6H_{13}$-*n*). Under these conditions the reaction is first order with respect to the amine salt and of an apparent order higher than first with respect to the acid. The salt is presumed to function, in the form of an ion-pair,[3] as a nucleophile, in the rate determining step, while the acid must promote reaction through electrophilic solvation of the departing chloride of the trityl chloride molecule.

The chloroacetolysis reaction is relatively rapid around 25° even when the acid concentration is relatively low (0.2 *M* or less) and not much larger than that of the amine (either $CH_2{=}CBrCH_2NHC_6H_{13}$-*n* or $(n\text{-}C_4H_9)_3N$). Qualitatively the rate of the reaction is dependent both on the free acid and the amine salt concentration, but the variations in rate with changes in acid and amine concentration cannot satisfactorily be explained on the assumption that the salt which participates as a reactant is a 1:1 amine-acid adduct. Rather, kinetic evidence has been obtained that when sufficient acid is available, aggregates of the type $R_3N(RCOOH)_x$, where $x > 2$, must form. The formation of such association products of carboxylic acids and their 1:1 acid–amine salts in non-polar media has also

(1) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **83**, 3708 (1961).

(2) R. M. Keefer and L. J. Andrews, *ibid.*, **84**, 941 (1962).

(3) R. M. Fuoss and C. A. Kraus, *ibid.*, **77**, 4474 (1955).