

aggregates is the protonated base, while the anion is the carboxylate ion, X^- , the simple homoconjugate ion, HX_2^- , or the more complex homoconjugate ion, $X(HX)_2^-$.

Infrared studies do not show evidence for hydrogen bonding between the protonated cation and the anion of the ion pair as has been noted in other solvents.^{16a-d} In mixtures of bases, strong interaction can occur between the ion pairs BH^+X^- and $B'H^+X^-$, suggesting

that ionic aggregates containing different cations are more stable than aggregates containing several identical cations.

Acknowledgments. This research has been financially supported by the U. S. Army Research Office (Durham). The authors wish to express their appreciation to Mr. John Belisle for his help in performing the preliminary DVP experiments.

Inhibition of the Oxidation and Polymerization of Methyl Methacrylate. II. Effect of Aromatic Amines¹

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The action of aromatic amine retarders upon the polymerization of methyl methacrylate in the presence of air has been studied. Induction periods and polymerization rates have been determined dilatometrically. The results confirm and extend the conclusions of a previous study of the action of phenols under the same conditions. The amines display a wider range of reactivities than did the phenols. Of the 28 amines tested, 21 were amenable to the same kinetic treatment as used previously. This is an antioxidation scheme, from the success of which it is concluded that most of these terminators, like phenols, act by slowing down the depletion of oxygen in the system, thus extending the length of the inhibition period. Relative efficiencies have been determined for most of the amines. Highly reactive amines, however, appear to react directly with molecular oxygen in competition to their interaction with chain-carrying peroxy radicals.

Introduction

In an earlier study² (called part I) a report was made of the effect of phenols upon the polymerization of methyl methacrylate in the presence of air. It was demonstrated that the oxygen inhibition of methyl methacrylate is prolonged by the presence of phenolic substances which led to the conclusion that their action is one of retarding the initial autoxidation thus delaying the exhaustion of oxygen from the system. The importance of this mechanistic point has led us to extend our studies to an examination of the effect of aromatic amines under similar conditions to confirm the conclusion reached earlier and to extend the range of reactivities observed with the phenols.

Although aromatic amines as a class should be expected to be somewhat more reactive in autoxidation processes than phenols taken as a group, quantitative kinetic data bearing on this are considerably less

abundant in the literature for amines compared with phenols.

A third, and perhaps most important, rationale for this study is the continuing high degree of interest in the whole problem of autoxidation inhibition and its relation to polymerization retardation. Current efforts directed toward answering the central mechanism question, π -complex formation or labile hydrogen atom abstraction, seem to favor the latter hypothesis. Thus we have new studies of the kinetic isotope effect,³⁻⁷ transfer constant measurements,⁸⁻¹⁰ and solvent effects,¹¹ but certain of the problems posed by Hammond and co-workers¹²⁻¹⁴ remain unresolved. A very recent reminder by Lloyd and Lange¹⁵ points out that: "The state of the theory consequently lacks predictive power; we cannot be sure, for any new substrate-retarder system, which mechanism to invoke until we have obtained empirical knowledge of that particular system."

A direct, frontal attack upon the problem, that of measuring rate effects of phenols upon polymerization in the absence of oxygen, did not permit an unequivocal choice to be made because of the very small rate differences observed compared with those obtained for minute amounts of quinone impurities likely to be present.¹⁶ At the present moment it seems altogether

(1) Taken from a portion of the Ph.D. thesis of W. R. Y. 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) R. G. Caldwell and J. L. Ihrig, *J. Am. Chem. Soc.*, **84**, 2878 (1962).

(3) R. A. Bird, G. A. Harpell, and K. E. Russell, *Can. J. Chem.*, **40**, 701 (1962).

(4) J. A. Howard and K. U. Ingold, *ibid.*, **40**, 1851 (1962).

(5) J. A. Howard and K. U. Ingold, *ibid.*, **41**, 1744 (1963).

(6) K. U. Ingold, *ibid.*, **41**, 2807 (1963).

(7) J. R. Shelton and D. N. Vincent, *J. Am. Chem. Soc.*, **85**, 2433 (1963).

(8) M. P. Godsay, G. A. Harpell, and K. E. Russell, *J. Polymer Sci.*; **57**, 641 (1962).

(9) S. C. Barton, R. A. Bird, and K. E. Russell, *Can. J. Chem.*, **41**, 2737 (1963).

(10) L. R. Mahoney and F. C. Ferris, *J. Am. Chem. Soc.*, **85**, 2345 (1963).

(11) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044, 1250 (1964).

(12) C. E. Boozer and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 3861 (1954).

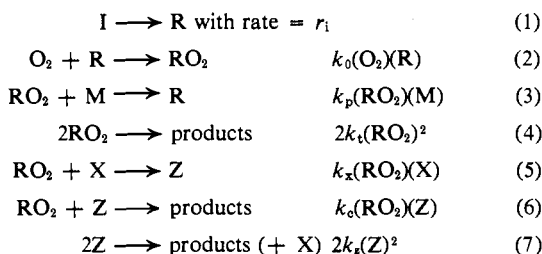
(13) G. S. Hammond, C. E. Boozer, C. E. Hamilton, and J. N. Sen, *ibid.*, **77**, 3238 (1955).

(14) G. S. Hammond and U. S. Nandi, *ibid.*, **83**, 1217 (1961).

(15) W. G. Lloyd and C. E. Lange, *ibid.*, **86**, 1491 (1964).

likely that no one simple reaction scheme of up to ten steps will be able to reconcile all of the data on so complicated a reaction as autoxidation inhibition. As kinetic data on a variety of systems accumulates, however, it should be possible to classify the different cases according to related mechanism type. From this vantage point the correctness of the basic criterion itself (labile hydrogen or π -complex) may profitably be re-examined.

Kinetic Analysis. As before, a kinetic scheme was used which is an extension of that proposed by Schulz and Henrici.¹⁷ The detailed derivation of the pertinent equations and discussion of the assumptions employed will be found in part I.² The essential reaction steps are



Again, I represents an initiator molecule; R is a radical chain carrier derived either from initiator decomposition or monomer polymerization; M, X, and O₂ are monomer, retarder, and oxygen molecules; RO₂ is a peroxy radical of any molecular size; and Z is a retarder radical.

In this scheme the terminator X, which functions as an autoxidation inhibitor, may or may not be regenerated in reaction 7. Z radicals produced in reaction 6 are assumed not to react directly with oxygen, thus permitting an extension of the period in which inhibition of polymerization by oxygen occurs. A terminator more successful in competing for RO₂ radicals will bring about a longer inhibition period than will a less effective one with the same initial oxygen supply.

To obtain a tractable kinetic expression, it is assumed that: (a) steady-state radical concentrations exist during the inhibition period; (b) average concentration values of O₂ and X may be used; and (c) reaction 7 is unimportant as a mode of Z disappearance. A check upon this last is the presence of rate constant k_z in the final expression. For cases of terminators where this is not justified, k_x values obtained are only approximate. With the aid of these assumption, we obtain

$$r_i(\bar{X})^{-2} [1 - (K^2T_0^2/T^2)] = 2^{1/2}k_xk_t^{-1/2} [KT_0r_i^{1/2} \times T^{-1}(\bar{X})^{-1}] - 2k_zk_x^2k_c^{-2} \quad (8)$$

where T is the length of the inhibition period; T_0 is the length of that period for a given r_i in the absence of added terminator; and K is a parameter, evaluated in each case, given by the expression

$$K = [(O_2)_0 - r_iT]/[(O_2)_0 - r_iT_0] \quad (9)$$

Here (O₂)₀ refers merely to the initial oxygen concentration.

It remains to provide a way to compute the average concentration of X. In part I it was assumed that the

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

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

average value of (X) is that which corresponds to the average rate of its disappearance

$$(\bar{X}) = [-d(X)/dt]/k_x(RO_2) \quad (10)$$

from which

$$(\bar{X})/(X)_0 = [1 - (X)_T/(X)_0]/\ln [(X)_0/(X)_T] \quad (11)$$

and

$$(X)_T/(X)_0 = 1 - r_i/2(X)_0[T^2 - K^2T_0^2/T] \quad (12)$$

are obtained, where (X)_T is the terminator concentration at the end of the inhibition period.

From the definition of (\bar{X}) in eq. 10 it can be seen that this method will always yield a value of (\bar{X}) lower than the true average, but that it will be a good approximation whenever (X)_T/(X)₀ is less than 0.6. In this case, which obtained for most of the phenols studied previously, $-d(X)/dt$ does not change appreciably during the inhibition period. For the more reactive amines of the present work, a better approximation is obtained when (\bar{X}) is simply set equal to (X)₀/2. This proved satisfactory for all of the amines studied except the very weakest in reactivity, such as aniline and 2-naphthylamine, for which the former method of computing (\bar{X}) was used.

Another equation of some significance may be obtained from the kinetic treatment² as a step in the derivation of eq. 8. It is

$$r_i[1 - (K^2T_0^2/T^2)] = -2d(X)/dt \quad (13)$$

where the factor of 2 on the right side represents the number of kinetic chains stopped by each X molecule. Where X is nearly depleted at the end of the inhibition period, a special case, we have the so-called "stoichiometric equation" of the first paper generalized by replacing the assumed 2 with N .

$$(T^2 - K^2T_0^2)/T = N(X)_0/r_i \quad (14)$$

Previously the equation was used to determine the stoichiometric factor N for a number of phenolic substances. The usefulness of eq. 14 for amine antioxidants will be discussed later.

In order to apply the kinetic equations, it is necessary to have values of r_i and (O₂)₀. Since the experimental conditions were deliberately chosen to be the same as those of the previous phenol study, the same values of r_i and (O₂) were appropriate

$$r_i = (6.59 \times 10^{-8})r_0^2 \quad (15)$$

$$(O_2)_0 = 2.2 \times 10^{-3} M \quad (16)$$

where r_0 is the over-all rate of polymerization in the absence of added terminator.

Experimental

Materials. Purification of methyl methacrylate monomer and 2,2'-azobis(isobutyronitrile) initiator (AIBN) have been described elsewhere.^{2,16}

Aniline, N-methylaniline, and N,N'-dimethylaniline (Eastman White Label) were distilled under a stream of argon at a pressure slightly greater than atmospheric. Center fractions of 2 ml., representing less than 1% of

the distillate, were sealed in glass ampoules and stored under refrigeration. All three were colorless liquids.

o-Phenylenediamine and *p*-phenylenediamine (Eastman White Label) were recrystallized repeatedly from hot water containing a little sodium hydrosulfite until their appearances and melting points showed no improvement. They appeared as tan plates and very pale pink plates, respectively, with the melting ranges 101.8–102.1° and 138.5–141.0° (uncor.). The literature values are 102 and 139.7°. (Melting points are recorded in this section only when some doubt exists as to the purity or identity of the material. For example, they are indicated whenever a material obtained here is not accurately described by literature reports, or when it was obtained by synthetic methods in this laboratory.)

m-Phenylenediamine dihydrochloride (Eastman White Label) was treated with 5% sodium hydroxide in aqueous solution and allowed to stand overnight in a refrigerator. The resulting colorless needles were recrystallized from ether–ligroin.

1-Naphthylamine and *2*-naphthylamine (Eastman White Label) were each recrystallized three times from ligroin and benzene–ligroin, respectively, with good yields of colorless crystals.

1,2-Diaminonaphthalene (Aldrich Chemical Co.) was recrystallized three times from hot water containing a small amount of sodium hydrosulfite.

1,4-Diaminonaphthalene was prepared by reduction of 4-nitro-1-naphthylamine (K and K Laboratories) with sodium hydroxide and zinc dust in aqueous ethanol. The diamine was extracted from the reaction mixture and recrystallized twice from hot water containing a little sodium hydrosulfite. The yellow-green needles melted with discoloration in a vacuum at 121.4–122.6° (cor.). The diacetylamine was prepared in this laboratory by D. C. Carty, who also observed its (cor.) melting point (310° dec.).

1,5-Diaminonaphthalene (Aldrich) was recrystallized from absolute ethanol and sublimed at 170° (2 mm.) to obtain colorless crystals melting at 192° (uncor.). The literature value is 189.5°.

1,7-Diaminonaphthalene hydrochloride (K and K), an almost black material, was recrystallized from ethanol with a very small yield of colorless crystals. Treatment with 5% sodium hydroxide precipitated the diamine which was extracted with ether and reprecipitated with ligroin. Subsequent recrystallization from benzene yielded very pale pink crystals.

1,8-Diaminonaphthalene (Aldrich) was recrystallized three times from aqueous ethanol with the aid of decolorizing charcoal to yield pink needles.

2,3-Diaminonaphthalene (Aldrich) and *2,7*-diaminonaphthalene (Light and Co.) were recrystallized twice from hot water containing a little sodium hydrosulfite and once from ligroin–ether. Both appeared as slightly brown plates.

2-Aminoanthracene (Aldrich) was recrystallized twice from absolute ethanol. The resulting yellow needles produced a greenish fluorescence in both ethanol and MMA.

2-Aminobiphenyl (Aldrich) and *4*-aminobiphenyl (Chemicals Procurement Laboratories) were recrystallized twice from aqueous ethanol, yielding pale pink and pale yellow crystals, respectively.

Diphenylamine (Eastman White Label) was recrystallized three times from ligroin, producing colorless plates with an uncorrected melting point of 52.7–53.0°. The literature value is 53°.

p-Hydroxydiphenylamine (Light) was recrystallized three times from chlorobenzene–ligroin, yielding light tan needles melting at 69.3–69.5° (uncor.). The literature value is 70°.

2-Aminochrysene (Chemical Procurement Laboratories) and *2*-aminofluorene (Frinton Laboratories) were each recrystallized twice from ethanol.

4-Nitro-1-naphthylamine (K and K) was used as received in the form of bright yellow crystals.

2,3,4,5-Tetraphenylpyrrole was prepared by the method of Davidson.¹⁸ The colorless, silky needles were recrystallized from ethanol and melted at 213–214°, as reported by Davidson.

N,N'-Diphenyl-*p*-phenylenediamine (Matheson Coleman and Bell), technical grade, was recrystallized three times from chlorobenzene–ligroin to yield colorless crystals melting at 147.3–148.0° (uncor.). The literature value is 147–149°.

N,N- and *N,N'*-Dimethyl-*p*-phenylenediamine were obtained from the dihydrochloride (Matheson, 98% minimum) and from the dioxalate (Chemicals Procurement Laboratories), respectively, by neutralizing the aqueous solutions with sodium hydroxide, extracting with ether, and recrystallizing from ligroin. Finally, the colorless crystalline amines were obtained by subliming at 8 mm. pressure and 80°.

N,N,N',N'-Tetramethyl-*p*-phenylenediamine dihydrochloride (Eastman White Label) was treated with 5% sodium hydroxide in aqueous solution to precipitate the free base. After drying, the amine was sublimed at 60° (2 mm.) to yield colorless crystals.

Dilatometric Procedure. Reaction rates were followed dilatometrically using simple vessels consisting of bulbs of about 20-ml. capacity with a stopcock on one end and selected capillary tubes of about 10 in. on the opposite end. Details of calibration and the necessary monomer constants for calculating polymerization rates are described elsewhere.¹⁹

To charge the dilatometers, AIBN and the amine were weighed into separate glass-stoppered flasks to which monomer was added by pipet at measured temperatures. Aliquots of the resulting solution and of pure monomer, again at known temperatures, were pipetted into clean flasks, one for each run, according to a convenient scheme for obtaining desired concentrations. These new solutions were saturated with air by hand pumping into the solutions through a fritted-glass dispersion tube at the same time the solutions were shaken vigorously. The solutions were drawn into the dilatometers through the capillaries and the stopcocks closed. They were then placed in a constant temperature bath at 44.40° which was controlled to within 0.005° by an infrared lamp. It was necessary to locate the bath in a photographic dark room illuminated only by a red safelight and the infrared lamp. Early runs in an open laboratory illuminated by daylight or by fluorescent fixtures were very erratic until the bath was moved.

(18) D. Davidson, *J. Org. Chem.*, 3, 361 (1938).

(19) W. R. Yates, Ph.D. Thesis, University of Hawaii, 1964.

After attainment of thermal equilibrium, the dilatometers were removed for a rapid adjustment of the capillary liquid level and immediately reinserted. Zero time was taken to be the time of first insertion into the bath and has little meaning in the absolute sense under the experimental conditions of this work. Fortunately, the kinetic analysis is not at all sensitive to small uncertainties in the absolute zero time. The capillary levels were read with a cathetometer to the nearest 0.005 cm., and times were determined by stopwatch to 0.05 sec. Typical plots of the primitive data are shown in Figure 1. The end of the inhibition periods were found to be a little less sharp than with phenols present, but the "elbow" was still easily determined in most cases.

Results

Table I summarizes the results of quantitative significance obtained in this study. The last column in the table reports the "degree of retardation," defined as the ratio of the measured rate for a given run with added amine to the rate expected if no amine had been present. This latter quantity, r_0 , was calculated in each case by means of the empirical relationship relating unretarded rates with initiator concentrations.

For two other amines, *N,N*-dimethylaniline and 2,3,4,5-tetraphenylpyrrole, very slight retardation was noted qualitatively. With *p*-phenylenediamine and with the 1,4-, 1,5-, 1,7-, and 1,8-diaminonaphthalenes, it was not possible to obtain the right combination of AIBN and amine concentrations to permit reliable measurements of the length of the inhibition period, T . With amine concentrations akin to those in Table I, the inhibition periods were too long. Cutting these back to minute levels, with or without increasing the initiator concentration, resulted merely in such a broad rounding of the "elbow" (as shown in Figure 1) that the extrapolated intersection of the two straight-line portions of the curve became too uncertain to have kinetic significance. Of the amines tested, then, 21 out of 28 may be said to have produced satisfactory results for the purposes of this survey.

Discussion

For each of these compounds in Table I a straight-line plot of eq. 8 was obtained. These plots were entirely comparable with those obtained in the phenol study, examples of which are to be found in that report. The natural indicator of reactivity of a given terminator toward peroxy radicals in this system is the rate constant k_x which is obtained from the slope of the plot, providing k_t can be evaluated. However, since a rather bold averaging technique was necessary in order to derive a tractable kinetic expression for this highly complex reaction, little significance can be attached to the *absolute* values of rate constants thus obtained. Rather these slopes should be used as measures of the relative reactivities of the amines, especially since k_t should not be highly dependent upon the presence and nature of the added terminator.

From these considerations, we define the relative reactivity E of a terminator as the numerical value of the slope of its kinetic plot. This is equivalent to comparing k_x for a given terminator with that of a hypothetical amine displaying a slope, $k_x/(2k_t)^{1/2}$,

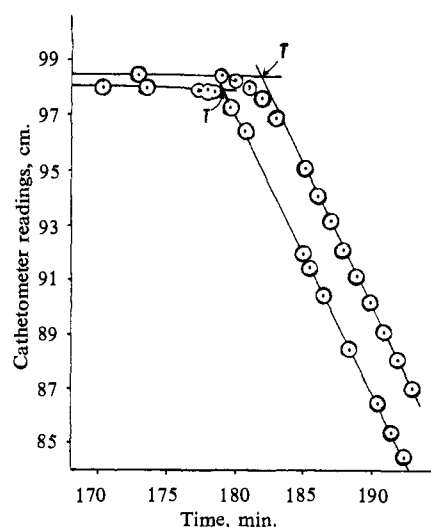


Figure 1. Sample plots of primitive dilatometric kinetic data.

of unity. Table II lists the values of E so obtained for the amines employed in this study in order of increasing reactivity.

A similar table for aromatic hydroxy compounds is to be found in part I wherein E was taken to be the reactivity ratio of each one compared to the reference substance, phenol. To place both sets of compounds on the same reactivity scale, the results for the phenols need only be multiplied by 3.3, the slope of the plot for phenol itself.

The much-discussed "phi-factor" of copolymerization theory,²⁰ defined as $\phi = k_c/2k_t^{1/2}k_z^{1/2}$, can be obtained from the slope and intercept of the kinetic plot for a given amine. As usually interpreted, a value of $\phi < 1$ indicates that termination occurs predominantly through reaction between like radicals. If $\phi > 1$ the tendency is toward cross-termination which was assumed to be the predominant process in the kinetic derivations of this study and of the previous one. Since the intercepts of the amine plots were all very small, θ could not be determined quantitatively with any accuracy. (This is to be expected as k_z is relatively insignificant.) However, it is worth noting that for all but four of the amines listed in Table I ϕ exceeded unity. The exceptions were: *o*-phenylenediamine, *p*-hydroxydiphenylamine, *N,N*-dimethyl-*p*-phenylenediamine, and *N,N'*-diphenyl-*p*-phenylenediamine. The fact that $\phi > 1$ for 17 cases supports the assumption that reaction 7 is of little importance in systems of this kind.

The "stoichiometric eq." 14 may be used to obtain the number of kinetic chains N stopped per amine molecule consumed, if the amine is approximately depleted at the end of the inhibition period. For those terminators whose behavior is described by eq. 8, N should be 2 which seems to be the case of several of the amines. Some indicated a trend in N toward 2 as the amine came to be more nearly consumed in a progression of experiments with different initial amine concentrations. This is not unexpected, of course, but insufficient knowledge of the reaction details is

(20) C. H. Bamford, W. G. Barb, A. D. Jenkins, and P. F. Onyon, "The Kinetics of Vinyl Polymerization by Radical Mechanisms," Butterworths Scientific Publications, London, 1958, Chapter 6; J. C. Bevington, "Radical Polymerization," Academic Press, London, 1961, p. 143.

Table I. Summary of Kinetic Results Using Amine Retarders in the Presence of Oxygen

Retarder	r_0 , % hr. ⁻¹	Retarder, mole/l.	Initiator, mole/l.	T , min.	T_0 , min.	r/r_0
None	3.34	1.07×10^{-2}	39.6
	4.31	1.86	31.7
	4.36	1.92	30.6
	5.07	2.69	26.2
	6.82	5.20	19.0
Aniline		6.36×10^{-4}	1.82×10^{-2}	116.0	31.4	0.955
		3.95	2.13	77.0	29.0	0.967
		2.73	1.95	70.3	30.4	0.996
		2.05	2.21	54.8	24.5	0.960
		1.78	2.22	53.9	28.4	0.986
1-Naphthylamine		1.40	1.99	49.8	30.0	0.999
		1.11	2.25	42.7	28.3	1.01
		8.35×10^{-5}	2.24×10^{-2}	124.6	28.3	0.848
		3.44	1.88	76.2	30.9	0.901
		2.16	1.90	57.7	30.8	0.944
2-Naphthylamine		8.72×10^{-6}	2.34	35.5	27.7	0.976
		1.37×10^{-4}	1.86×10^{-2}	91.0	31.1	0.966
		1.12	1.90	78.3	30.8	1.01
		8.62×10^{-5}	1.94	66.3	30.4	0.982
		5.88	1.99	53.6	30.0	1.00
2-Aminoanthracene		3.63×10^{-4}	3.14×10^{-2}	275.0	23.9	0.806
		1.65	3.57	141.1	22.4	0.928
		1.33	2.77	139.8	25.5	0.894
		8.65×10^{-5}	3.74	~85	21.9
		5.72	2.97	72.4	24.9	0.988
2-Aminobiphenyl		4.28×10^{-4}	2.37×10^{-2}	61.3	27.5	0.972
		1.49	2.76	37.8	25.5	1.01
		5.22	2.89	29.2	24.9	0.985
		3.34×10^{-4}	2.52×10^{-2}	134.6	26.7	1.00
		1.61	1.73	109.8	32.2	0.998
4-Aminobiphenyl		1.16	2.93	63.9	24.7	0.994
		3.53×10^{-5}	1.90	46.0	30.8	1.01
		4.07	3.08	37.3	24.2	1.03
		1.79	1.92	38.4	30.6
		1.81×10^{-4}	3.31×10^{-2}	292.0	23.3	0.909
<i>o</i> -Phenylenediamine		1.24	3.40	192.2	23.0	0.961
		6.34×10^{-5}	3.48	106.4	22.7	0.956
		4.83	2.02	133.6	30.0	0.991
		1.03×10^{-3}	2.51×10^{-2}	395.5	26.7	0.862
		4.70×10^{-4}	2.85	240.1	25.1	0.883
<i>m</i> -Phenylenediamine		2.94	2.17	227.8	28.8	0.923
		2.46	2.99	144.1	24.5	0.925
		1.80	2.22	148.2	28.4	0.936
		1.22	2.25	106.7	28.3	0.957
		4.19×10^{-4}	2.41×10^{-2}	522.1	27.3
1,2-Diaminonaphthalene		4.57	2.58	637.7	26.4
		2.22	2.55	300.6	26.5
		1.80	2.58	217.5	26.4
		1.40	2.09	239.3	29.3
		1.50	3.08	170.0	24.1
2,3-Diaminonaphthalene		1.02	2.14	168.2	29.0
		8.28×10^{-5}	2.16	146.7	28.8
		2.67×10^{-4}	1.61×10^{-2}	477.2	33.4	0.812
		1.49	1.79	260.3	31.7	0.914
		9.33×10^{-5}	1.87	168.8	31.0	0.943
2,7-Diaminonaphthalene		6.37	1.92	122.8	30.6	0.973
		4.27×10^{-4}	5.16×10^{-2}	160.8	18.7	0.746
		1.01	2.25	105.7	28.3	0.975
		6.68×10^{-5}	2.29	75.2	28.0	0.979
		5.17	2.31	63.1	27.9	0.999
Diphenylamine		6.92×10^{-4}	2.81×10^{-2}	504.6	25.3	0.688
		5.35	2.82	444.2	25.2	0.815
		4.91	4.07	291.0	21.0	0.778
		3.84	3.12	336.8	24.0	0.815
		3.42	4.25	229.2	20.6	0.887
<i>p</i> -Hydroxydiphenylamine		3.49	5.97	172.0	17.3	0.733
		3.22	4.73	202.4	19.5	0.749
		5.33×10^{-4}	3.82×10^{-2}	454.1	21.7	0.551
		2.42	4.35	194.5	20.3	0.763
		1.27	4.55	106.7	19.9	0.871
N-Methylaniline		8.24×10^{-4}	5.06×10^{-2}	109.4	18.8
		3.10	4.75	69.4	19.4
		1.59	4.90	50.7	19.2
N,N-Dimethyl- <i>p</i> -phenylenediamine		8.11×10^{-5}	4.98	36.3	19.0
		1.06×10^{-3}	5.16×10^{-2}	548.5	18.7	0.941
		4.82×10^{-4}	5.86	318.2	17.5	0.871

Table I (Continued)

Retarder	r_0 , % hr. ⁻¹	Retarder, mole/l.	Initiator, mole/l.	T , min.	T_0 , min.	r/r_0
N,N'-Dimethyl- <i>p</i> -phenylenediamine		3.12	6.07	206.9	17.2	0.873
		2.53	6.14	171.1	17.1	0.989
		3.68×10^{-4}	4.63×10^{-2}	~230	19.7
		1.62	5.26	133.9	18.5	0.866
N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine		1.08	5.44	91.9	18.2	0.906
		8.76×10^{-5}	5.51	78.3	18.0	0.934
		8.58×10^{-4}	4.55×10^{-2}	245.2	19.9	0.852
		4.99	4.61	240.7	19.9	0.852
N,N'-Diphenyl- <i>p</i> -phenylenediamine		2.86	5.68	138.6	17.8	0.854
		2.09	5.15	122.9	18.7	0.889
		6.08×10^{-4}	3.89×10^{-2}	449.8	21.5	0.985
		2.35	4.42	190.4	20.2	0.994
2-Aminochrysene		1.23	4.63	106.4	19.7	0.999
		4.59×10^{-5}	2.32×10^{-2}	70.0	27.8
		6.42	2.32	89.3	27.8
2-Aminofluorene		9.17	2.32	116.3	27.8
		3.31×10^{-4}	1.87×10^{-2}	371.5	31.0
		1.65	1.87	237.3	31.0
		8.26×10^{-5}	1.87	143.5	31.0
4-Nitro-1-naphthylamine		4.13	1.87	85.5	31.0
		1.35×10^{-3}	1.95×10^{-2}	72.7	30.4
		7.50×10^{-4}	2.16	47.3	28.8
		4.71	2.26	39.5	28.2
		3.22	2.32	35.5	27.8
	1.14	1.78	34.8	31.8	

Table II. Summary of the Observed Relative Reactivities of Aromatic Amines toward Methyl Methacrylate Peroxy Free Radicals

	E		E
N,N-Dimethylaniline	<1	N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine	121.
2,3,4,5-Tetraphenylpyrrole	<1	2-Aminoanthracene	132.
4-Nitro-1-naphthylamine	1.8	2,3-Diaminonaphthalene	139.
2-Aminobiphenyl	9.5	1-Naphthylamine	143.
Aniline	10.4	1,2-Diaminonaphthalene	150.
2-Naphthylamine	29.9	Diphenylamine	151.
4-Aminobiphenyl	38.6	<i>p</i> -Hydroxydiphenylamine	154.
N-Methylaniline	~50	N,N'-Diphenyl- <i>p</i> -phenylenediamine	162.
<i>m</i> -Phenylenediamine	52.3	N,N'-Dimethyl- <i>p</i> -phenylenediamine	194.
2,7-Diaminonaphthalene	67.5	N,N-Dimethyl- <i>p</i> -phenylenediamine	~200
2-Aminochrysene	115.	<i>o</i> -Phenylenediamine	220.

available to explain why some amines are more prone to exhibit this phenomenon than others. Nor is it clear why a few terminators, which produced satisfactory plots for both eq. 8 and 14, yielded N values in excess of 2. The most dramatic example of this behavior was found for *o*-phenylenediamine for which $N = 3.3$.

It was assumed in the derivation of the kinetic equations that the terminator molecules do not react directly with dissolved molecular oxygen, and this assumption has been justified by its success in the treatment of the amines of Table II. There must, however, be an upper limit to the range of reactivity over which the assumption is applicable, and above which an amine is reactive enough toward molecular oxygen so that direct interaction between these species constitutes an important source of terminator depletion. It seems likely that the diaminonaphthalenes and *p*-phenylenediamine mentioned in the previous section were reacting, in part, this way. The borderline cases are probably those amines showing N values significantly greater than 2. In this connection it is noteworthy that *o*-phenylenediamine was the most reactive of those tested which could still be included

in Table II. Clearly, the application of the stoichiometric equation must be more cautious with amine terminators than for phenols.

In support of the tentative conclusions advanced in the preceding paragraphs are the results of MO calculations of molecular energies and reactivities of amines toward methyl methacrylate peroxy radicals.¹⁹ In brief, the diaminonaphthalenes with an NH₂ group in the 1-position rate highest on a relative molecular energy scale followed closely by *p*- and *o*-phenylenediamines.

In summary, the results of this study appear to confirm and extend the conclusion of part I that phenols and amines in this polymerizing system act as antioxidants by conserving the supply of oxygen inhibitor present. The reactivities of the amines do seem somewhat greater as a group, and the observation of these reactivities defines more clearly the boundaries of the kinetic treatment devised earlier, especially the applicability of eq. 8 and 14. Any further extension to more reactive terminators or monomer-peroxy radicals will have to take into account the strongly competitive direct reaction with oxygen, a reaction which is itself productive of retarding species.