

served value of 2.47×10^{-3} . We therefore conclude that the charges are much closer in Salt I-6 than in the extended configuration, and hence present a more powerful attractive field to an anion. In fact, the identity of the k_2 's for Salts I-0 and I-6 suggests that they have the same value of R . A configuration is readily obtained in which this identity appears: as shown in Fig. 4, the suberamide can contract to form a compact central ring structure stabilized by hydrogen bonds between the two amide groups. (The hexamethylene chain joining the latter is curled up behind the central ring.) In Salts I-2 and I-4, ring formation is also possible, according to the models, although a little strain and steric hindrance interfere somewhat. Since k_2 is somewhat smaller (*i.e.*, more association) for I-2 and I-4 than for I-0 and I-6, the former probably exist partly as bent configurations in which the externally positive NH dipoles also contribute to the electrostatic binding of an associated anion. Further data on salts of related structure are needed to clarify these speculations: we feel reasonably certain, however, that the cation of Salt I-6 must be intramolecularly bonded to a compact structure, in view of the identity of its k_2 with that of Salt I-0.

The physiological behavior of the amide derivatives also appears to support the conclusion that they are not extended chains in solution. In the series $\text{Me}_3\text{N}^+(\text{CH}_2)_m\text{N}^+\text{Me}_3$, curarimimetic activity reaches a peak when approximately ten atoms are between the quaternary nitrogen atoms.²⁰

(20) "Curare and Anti-curare Agents," *Ann. N. Y. Acad. Sci.*, **54**, 297 (1951).

In the amide series, a chain of ten atoms appears in Salt I-2. Nevertheless, it shows no curare activity (at least in the conventional dose levels); instead, it and its homologs prolong the neuromuscular block induced by diacetylcholine. Phillips³ emphasized that "this latter activity persisted in all members of the group above oxalic regardless of chain length." If, therefore, we are to assume any correlation between configuration and activity, we must conclude that the Salts I-2, I-4 and I-6 have essentially the same configuration, and this is precisely the conclusion reached on the basis of the conductance measurements. In effect, the formation of a hydrogen bonded central ring wastes the chain atoms between the amide nitrogens in Salts I-*n*; lengthening the external methylene chains joining the quaternary nitrogen to the amide nitrogen should then produce curare activity (unless the amide groups *per se* are anticurare). Also, the malonamide should behave differently from the other members of the series, because the presence of a single methylene between amides makes ring closure by hydrogen bonds sterically impossible.

Acknowledgments.—We are indebted to the Wellcome Research Laboratories for samples of salts, and to Drs. E. J. de Beer, R. Baltzly and A. P. Phillips for helpful discussions. A grant from the Eugene Higgins Trust for a post-doctoral fellowship is most gratefully acknowledged. Part of the electrical apparatus was purchased with funds made available by a contract with the Office of Naval Research.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A Magnetic Study of Polymerization Retardation

BY JUDSON L. IHRIG¹ AND HUBERT N. ALYEA

RECEIVED JANUARY 14, 1953

In the retardation of vinyl polymerization by quinones and aromatic nitro compounds, the primary step is considered to be the formation of a resonance-stabilized radical too inactive to continue the chain. The experimental confirmation of this idea was the purpose of the present investigation. The diamagnetic susceptibility of a polymerizing methyl methacrylate mixture initiated by benzoyl peroxide and retarded by a quinone was found to be initially lower than the same mixture without retarder present. As the polymerization proceeded, the difference in susceptibilities decreased. The same polymerizing mixture retarded by aromatic nitro compounds, aromatic amines, or hydroquinone showed no initial susceptibility difference between the retarded and non-retarded systems. Conclusions drawn from the experimental results give evidence for: (a) the formation of stabilized radicals in quinone-retarded polymerizations in concentrations much above that of the chain carriers; (b) the formation of these radicals before the polymer chain has grown to a length of more than five monomer units; (c) the absence of appreciable concentration of stabilized radicals formed by direct interaction of quinone molecules and initiator fragments; (d) the operation of a different retarding mechanism in systems containing an amine, nitro compound, or hydroquinone.

It has long been known that the addition of certain classes of organic molecules to vinyl monomers may retard or even inhibit their polymerization to long-chain products.^{2,3} These substances include quinones, aromatic nitro compounds, aromatic, primary and secondary amines, and some polyhydric phenols. Only very small quantities are necessary to bring about a decrease in polymeri-

zation rate and often a marked change in the character of the final polymer. With quinones and nitro compounds the primary step in the retardation process is usually considered to be the addition of the neutral molecule to a growing radical chain resulting in the formation of a new resonance-stabilized radical which is not sufficiently reactive to propagate the chain further without difficulty, if at all.⁴⁻⁶ The locus of attack upon the retarder

(1) This article is based upon a thesis submitted by Judson L. Ihrig in partial fulfillment of the requirements for the degree of Ph.D. at Princeton University. Now at University of Hawaii, Honolulu, Hawaii.

(2) K. K. Jau and H. N. Alyea, *THIS JOURNAL*, **55**, 575 (1933).

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

(4) P. D. Bartlett, G. S. Hammond and H. Kwart, *Discussions of the Faraday Soc.*, **2**, 342 (1947).

(5) S. G. Cohen, *THIS JOURNAL*, **69**, 1057 (1947).

(6) H. W. Melville and W. F. Watson, *Trans. Faraday Soc.*, **44**, 886 (1948).

molecule and the subsequent fate of the new radical so formed are still in doubt. Nevertheless, the first part of the retardation mechanism involving the conversion of highly labile aliphatic chain carriers into relatively stable aromatic radicals appears now to be as universally accepted as the free radical theory of polymerization itself.

Although the well-established primary act is entirely reasonable, it has never been confirmed by direct experiment. The present research was initiated in an effort to confirm experimentally the presence of free radicals in a polymerizing system in concentrations well above that of the chain carriers. It was felt that if the radicals formed were so stable as to be unable further to propagate chains, they might well be stable enough to remain in the solution some time before disappearing in other ways. In this event, a reasonable concentration of these radicals could build up and be detected magnetically. The result would be an independent confirmation of the present theory of retarder action. Earlier studies on magnetic susceptibility changes in polymerizing systems⁷⁻¹⁰ have not included any data on polymerizations retarded by neutral organic molecules. The only exception is the work of Boardman and Selwood.¹¹ They investigated the susceptibility change of styrene in the presence of *t*-butyl catechol and hydroquinone. However, an excess of oxygen was present, and these two substances apparently acted as antioxidants. In this study oxygen was excluded since its presence modifies considerably the polymerization characteristics of vinyl monomers.¹²

Experimental

Materials.—Methyl methacrylate monomer stabilized with 0.006% hydroquinone was supplied by Rohm and Haas Co. The hydroquinone was removed by four washings with 3 *N* sodium hydroxide solution followed by four washings with distilled water. The monomer was then dried over calcium chloride, and twice fractionally distilled under reduced pressure in a stream of nitrogen. For this and other distillations, an all-glass apparatus was employed using a 40-cm. vacuum-jacketed column packed with glass helices. The monomer was stored in all-glass containers at 0° in a refrigerator.

Commercial "thiophene-free" benzene from Union Carbide and Carbon Chemicals, Inc., was mechanically stirred with portions of concentrated sulfuric acid until there was no thiophene coloration in the acid layer. It was then washed with 10% sodium bicarbonate solution and with distilled water, dried over calcium chloride, and fractionally distilled.

C.P. grade acetone from the same supplier was treated twice with solid potassium permanganate, filtered, dried with anhydrous potassium carbonate, and fractionally distilled.

C.P. grade ethyl acetate from U. S. Industrial Chemicals Co. was shaken with anhydrous potassium carbonate, filtered and fractionally distilled.

Benzoyl peroxide supplied by the Matheson Co., Inc., was purified by reprecipitating twice from chloroform-methanol and drying *in vacuo* according to the procedure of Nozaki and Bartlett.¹³

(7) J. Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1936).

(8) S. S. Bhatnagar, P. L. Kapur and G. Kaur, *J. Indian Chem. Soc.*, **17**, 177 (1940).

(9) M. E. Bedwell, *J. Chem. Soc.*, 1350 (1947).

(10) J. Hoarau, *Bull. soc. chim. (France)*, [5] **17**, 1153 (1950).

(11) H. Boardman and P. W. Selwood, *THIS JOURNAL*, **72**, 1372 (1950).

(12) H. Mark and A. V. Tobolsky, "The Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York, N. Y., 1950, pp. 447-449.

(13) K. Nozaki and P. D. Bartlett, *THIS JOURNAL*, **68**, 1688 (1946).

The retarders used were the best commercial grades available, and were recrystallized or vacuum-sublimed (in the case of the quinones) before use. Hydroquinone from General Chemical Co. was used as received. Duroquinone was prepared from Eastman White Label durene by the method of Smith.¹⁴

Apparatus.—The magnetic susceptibility balance utilizing a bifilar suspension was patterned after that of Boardman and Selwood.¹¹ Figure 1 shows the main features of construction. The sample tube was suspended from A, a converted microscope stage, by two fine copper wires about 6 feet in length which displayed no detectable ferromagnetic impurities. The stage was affixed to a steel plate, B, which with the suspension housing, C, E and F, was supported by a framework of 2" pipe. The sample tube was suspended in a cavity, F, made of Plexiglas and its deflections observed with a micrometer microscope, K. The suspension housing was generously proportioned to avoid spurious displacements due to convection currents. A permanent magnet supplied by Indiana Steel Products Corp., G, was moved back and forth over stainless steel tracks, H, by means of a low-pressure-double-acting water cylinder, I, connected to the water supply and drain at J. The Alnico magnet with 2-inch pole faces and 1-inch pole gap produced a field strength of approximately 9100 gauss. The balance was calibrated in the usual fashion by using two substances of known susceptibility. Benzene, $\chi = -0.7020$, and acetone, $\chi = -0.5866$, were the standards employed.¹⁵ Each micrometer scale unit corresponded to a change in κ , the volume susceptibility, of 0.00050×10^{-6} c.g.s.

The sample tube itself was made of 11-mm. Pyrex tubing with an over-all length of about 11.5 in. At the end distant from the field it was provided with an expansion bubble and a ground glass stopper.

For each run the retarder and the initiator (benzoyl peroxide) were weighed directly into a 25-ml. volumetric flask. Pure methyl methacrylate monomer was added to the mark and the whole well mixed. The magnetic sample tube was filled and air carefully removed by four cycles of a three-stage operation comprising freezing, evacuating and thawing.¹⁶ The sample tube was then warmed to room temperature and placed in the magnetic balance. About 40-45 minutes later the tube had stopped swinging, and the first readings were made. The rest position was noted, and then the magnet was brought up into position so that the closed end of the tube was in a position of homogeneous field. The micrometer scale reading was again recorded, and the difference in the two readings was the displacement due to the influence of the field. Further readings were taken at convenient intervals, never less than 30 minutes apart, for it required about this length of time for the tube to return to an equilibrium rest position after removal of the field. Readings taken more frequently tended to give displacement values which were too small.

All experiments were conducted in a small room whose temperature could be controlled to within rather narrow limits. The temperature of the runs ranged from about 22 to 25° and was held to within $\pm 0.5^\circ$ (usually less) during any given run.

Results

In all runs methyl methacrylate was the monomer of choice because of its relatively low polymerization temperature. The peroxide concentration was kept fixed at $7.03 \times 10^{-2} M$; this amount ensured a reasonable rate of chain starting even at room temperature. Smaller concentrations of the various retarders were used.

Figure 2 shows a typical plot of displacement vs. time. The greater the deflection the greater was the diamagnetic susceptibility. The upper curve represents the change in susceptibility of monomer-peroxide solution as polymerization proceeds. The shape of the curve is in agreement with other inves-

(14) L. I. Smith, "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 254.

(15) C. M. French and V. C. G. Trew, *Trans. Faraday Soc.*, **41**, 439 (1945).

(16) L. M. Arnett, *THIS JOURNAL*, **74**, 2027 (1952).

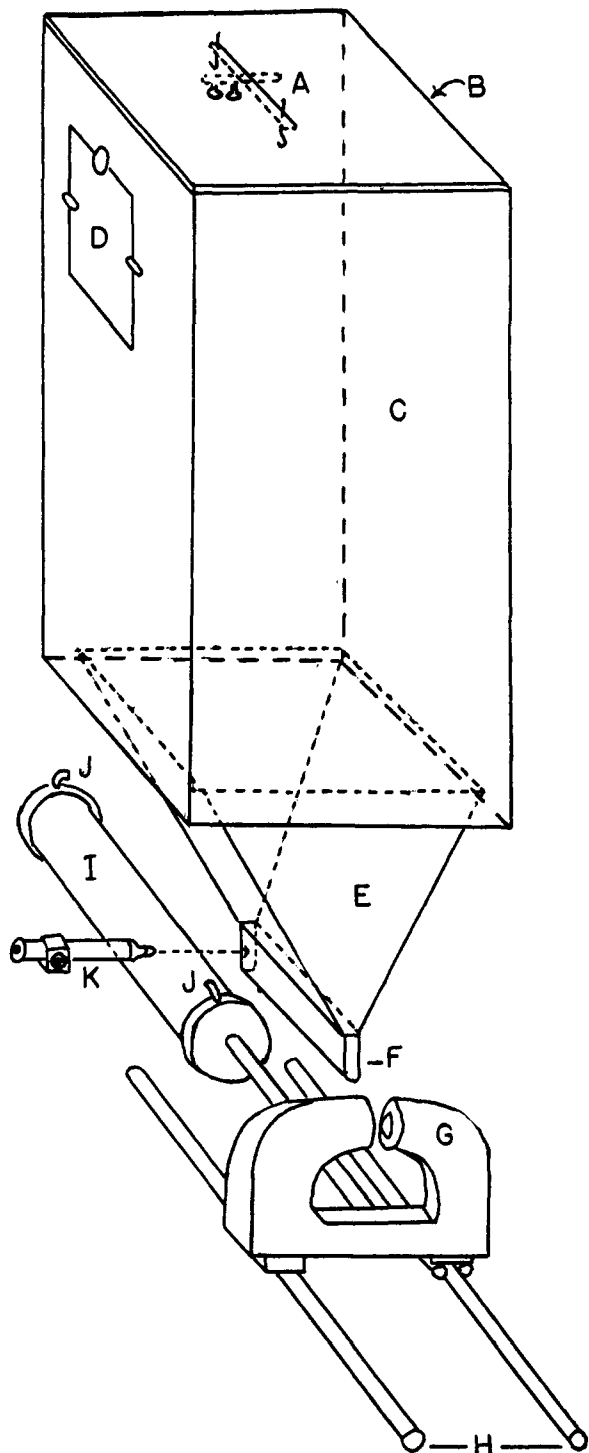


Fig. 1.

tigators.⁷⁻¹⁰ This increase in diamagnetism may be attributed to the loss of double bonds from the system. The lower curve shows susceptibility changes in the same mixture which has also been made $1.9 \times 10^{-2} M$ in anthraquinone, a weak retarder. Initially, the diamagnetic susceptibility is lower and then rises rapidly for a time after which the approach to the non-retarded curve becomes more gradual. The same type of plots was obtained for other quinones which acted as weak retarders. Duroquinone, Fig. 3, gave the greatest spread between the

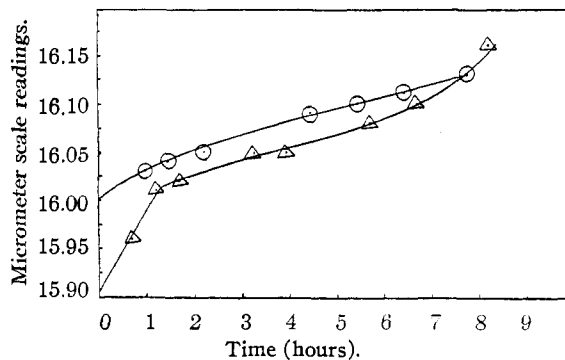


Fig. 2.

curves of all the quinones tested. Chloranil and benzoquinone were found to be very efficient retarders. The susceptibility curves for polymerizing systems retarded by these substances show the initial diamagnetic decrease but not the sharp rise in the early stages of the polymerization.

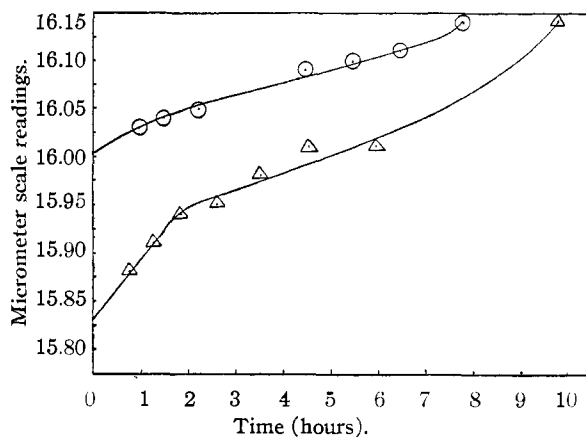


Fig. 3.

Although the same lowering effect was obtained when using complex quinoid dyes as retarders, none of the non-quinoid retarders gave curves displaying an initial decrease in diamagnetic susceptibility. The differences in magnetic behavior between quinone-retarded polymerizations and those retarded by other types may be seen by comparing Fig. 4, the curves of non-retarded and trinitrobenzene-retarded methacrylate, with the previous figures.

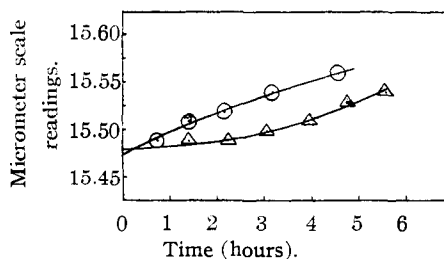


Fig. 4.

Because the spread was greatest in the case of duroquinone, it was decided to use this retarder in a series of runs to test the effect of retarder concentration upon the initial fall in diamagnetism.

It was found that the diamagnetic susceptibility lowering increased with increasing concentration of quinone. The effect was greatest at a duroquinone concentration of about $2.0 \times 10^{-3} M$. More than this tended to decrease the differences between the retarded and non-retarded curves.

Runs were also made with a quinoid and non-quinoid present together. No initial susceptibility difference from the non-retarded run was noted. The results of the whole study are summarized in Table I.

TABLE I

Retarder	Concn., <i>M</i>	$10^5 \times \Delta\kappa$ at 45 min.	$10^5 \times \Delta\kappa$ at 0 time (extra- polated)
9,10-Anthraquinone	1.9×10^{-3}	0.003	0.005
1-Aminoanthraquinone	2.2×10^{-3}	.003	.004-
1,4-Naphthoquinone	2.5×10^{-3}	.003	.004
Phenanthrenequinone	2.2×10^{-3}	.003	.004
1,4-Benzoquinone	1.9×10^{-3}	.007	.005
Chloranil	1.8×10^{-3}	.004-	.003-
Duroquinone	2.0×10^{-3}	.007	.009-
Aurin tricarboxylic acid	7×10^{-2}	.004	.003
Indanthrene	1×10^{-3}	.005	.006
1,3,5-Trinitrobenzene	2.6×10^{-3}	0	0
Hydroquinone	2.9×10^{-3}	0	0
	4.0×10^{-3}	0	0
<i>p</i> -Phenylenediamine	4.4×10^{-2}	0	0
<i>N,N</i> -Di- β -naphthyl- <i>p</i> - phenylenediamine	7.6×10^{-4}	0	0
	2.0×10^{-3}	0	0
<i>p</i> -Nitroaniline	2.6×10^{-3}	0	0
{ Duroquinone + }	2.2×10^{-3}	0	0
{ hydroquinone }	4.0×10^{-3}		
{ Duroquinone + }	2.2×10^{-3}	0	0
{ 1,3,5-trinitrobenzene }	2.4×10^{-3}		

Discussion

The results indicate the formation of a paramagnetic component in the quinone-retarded polymerizations with the resultant effect of lowering the over-all diamagnetic susceptibility. A number of reasons may be advanced to explain the phenomenon. The experimental evidence indicates the formation of stabilized free radicals in appreciable amounts. However, some alternate possibilities may be considered.

First, it might be thought that the steep slope of the quinone-retarded curve is due to faulty degassing of the sample or air leakage at some early stage. If this were true, then the same effect should be noted with non-retarded runs as well, since the sample preparation procedure was the same in all cases. Repeated experiments with samples of monomer plus peroxide and with monomer alone gave reproducible results and no indication of a steep-slope section on the curve. Whenever a quinone was added to the solution, the steep slope resulted.

Second, it might be said that the steep-slope portion of the quinone-retarded curve represents the consumption of elementary oxygen formed in a direct reaction between the peroxide and a quinone. Our knowledge of peroxide decomposition shows that the process is a complex one. If such were the case the phenomenon ought to be observed in a solvent other than methyl methacrylate. Experiments were, therefore, performed using ethyl ace-

tate solutions of peroxide and duroquinone in concentrations equal to those of the polymerization runs. Ethyl acetate is chemically quite similar to the monomer and also stands high on the lists of Nozaki and Bartlett¹⁵ and Cass¹⁷ as a good medium for peroxide decomposition. Within experimental error, there was no susceptibility difference between a solution of ethyl acetate containing only benzoyl peroxide and one containing both the peroxide and the quinone. Furthermore, the release of oxygen in a quinone-peroxide reaction should be greater, the greater the amount of quinone present. The results of varying duroquinone concentrations do not support this prediction.

Third, even granted the presence of stabilized free radicals, it is barely possible that their formation might come about independently of the polymerization process. From the above results using ethyl acetate instead of monomer, it is apparent that no stabilized radicals are formed. Not only do oxygen "radicals" fail to manifest themselves but the results also preclude a high concentration of species formed by direct reaction of a benzoyl (or phenyl) fragment with a quinone molecule. Also, it will be recalled that no evidence of stabilized radicals was found when monomer was polymerized with a quinone and a non-quinoid retarder both present. Thus, it becomes even less likely that we have stabilized radical formation independent of the polymerization process.

The results of these last experiments eliminate the possibility of duroquinone semi-quinone radical formation during the polymerization. Moreover, the conclusion from kinetic data¹⁸ that duroquinone terminates but one chain per molecule appears very convincing. If the semi-quinone were formed, presumably by hydrogen transfer, then duroquinone might well stop up to two chains per molecule, the exact number depending upon the rate of the competing semi-quinone dimerization reaction.

Thus, it appears as if radicals are formed by interaction of growing chains with the quinone retarder. As the reaction proceeds these radicals are consumed and the susceptibility curve approaches that of the non-retarded sample. The question now arises as to the nature of the radicals produced in these polymerizations. An estimate of their concentration is of interest in this connection. Because of the slight depression in susceptibility caused by the radicals (about 1%), it is possible only to obtain a very rough value for their concentration. These figures are listed in Table II. Using the benzoquinone system as an example, the method of calculation is outlined below:

From the "spin-only" formula we obtain the value for the susceptibility of one mole of any free radical.

$$\chi_M = \chi \times \text{mol. wt.} = 1257 \times 10^{-6} \text{ c.g.s. units at } 23^\circ$$

For benzoquinone the depression in diamagnetic susceptibility $\equiv 0.10$ scale unit $\equiv 0.005 \times 10^{-6}$ unit of volume susceptibility, κ . The density of the mixture is approximately unity; therefore, the mass susceptibility due to radicals is

$$\chi = \kappa/\rho = 0.005 \times 10^{-6}/1. = 0.005 \times 10^{-6}$$

(17) W. E. Cass, *This Journal*, **68**, 1976 (1946).

(18) P. D. Bartlett and H. Kwart, *ibid.*, **72**, 1051 (1950).

TABLE II

Quinone	Initial retarder concn. (M)	Radical concn. if only one monomer unit present	Radical concn. if five monomer units present
Anthraquinone	1.9×10^{-3}	2×10^{-3}	3×10^{-3}
Aminoanthraquinone	2.2×10^{-3}	1×10^{-3}	3×10^{-3}
Phenanthrenequinone	2.2×10^{-3}	1×10^{-3}	3×10^{-3}
Benzoquinone	1.9×10^{-3}	1×10^{-3}	3×10^{-3}
Naphthoquinone	2.5×10^{-3}	1×10^{-3}	2×10^{-3}
Chloranil	1.8×10^{-3}	1×10^{-3}	2×10^{-3}
Duroquinone	2.0×10^{-3}	3×10^{-3}	6×10^{-3}
Aurin tricarboxylic acid	7×10^{-2}	1×10^{-3}	2×10^{-3}
Indanthrene	1×10^{-3}	3×10^{-3}	5×10^{-3}

Assuming the simplest composition of the radical, that is, a benzoyl (or phenyl) fragment linked through only one monomer unit to a quinone residue, we obtain a molecular weight of about 300. In this case the apparent molar susceptibility would be

$$\chi_M = 0.005 \times 10^{-6} \times 300 = 1.5 \times 10^{-6}$$

But if *one* mole has a susceptibility of 1257×10^{-6} , then a "molar" susceptibility value of 1.5×10^{-6} will be exhibited by $1.5/1257$ or 1×10^{-3} mole of radicals. Let us now assume that the radical has five monomer units. In this case its molecular weight will be 700 giving an apparent χ_M of 3.5×10^{-6} which is equivalent to a molar concentration of stabilized radicals of $3 \times 10^{-3} M$. Inasmuch as the original quinone concentration was $1.9 \times 10^{-3} M$, it would appear that the stabilized radicals are formed before the chain making up this stabilized radical has grown to more than five monomer units long (plus, of course, an initiator fragment) even if every molecule of quinone is used up in the formation of such radicals.

The idea that the stabilized radicals formed in quinone-retarded polymerizations are constituted from few monomer units has received support from the purely chemical study of Cohen.¹⁹ He con-

(19) S. G. Cohen, *J. Polymer Sci.*, **2**, 511 (1947).

cludes that at low quinone concentrations ($4.5 \times 10^{-3} M$, in his work) the chain growth process may be interrupted before the addition of a second monomer molecule.

It is, perhaps, not surprising that the amines and hydroquinone did not behave in the same fashion as did the quinones. Here the primary retarding step may be the abstraction of a hydrogen atom as postulated by Price²⁰ instead of direct addition to the retarder molecule. With aromatic nitro compounds, however, the reaction with aliphatic radicals has been considered to be nuclear addition resulting in a resonance stabilized species much like that visualized for quinone retardation. The evidence from the present work tends to cast some doubt upon close similarity of the two reactions. A possible alternative mechanism for the nitro compound retardation is that put forth by Bartlett^{21,22} on kinetic grounds involving a radical which appears much less stable.

It is interesting to note that while an aromatic amine does not produce highly stabilized radicals, the amine group attached to a quinone, as in aminoanthraquinone and indanthrene, has no effect in preventing their formation. In each of these cases, however, the ring to which the amine group is linked has lost much of its aromatic character.

These results do not by any means disprove the theory of free radical intermediates in non-quinoid retardation. However, any radicals formed must be of an entirely different order of stability, the limits of detection of the present method being 10^{-4} to $10^{-5} M$ concentration of free radicals.

Acknowledgment.—We wish to thank Prof. P. W. Selwood of Northwestern University for helpful discussions during the early phases of this work.

(20) C. C. Price, *Ann. N. Y. Acad. Sci.*, **44**, 351 (1943).

(21) G. S. Hammond and P. D. Bartlett, *J. Polymer Sci.*, **6**, 617 (1951).

(22) P. D. Bartlett and H. Kwart, *THIS JOURNAL*, **74**, 3969 (1952).

PRINCETON, N. J.

[CONTRIBUTION NO. 53 FROM THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING COMPANY]

The Effects of Structure on the Viscosities of Perfluoroalkyl Ethers and Amines

BY T. J. BRICE AND R. I. COON

RECEIVED DECEMBER 1, 1952

The viscosities of a number of fluorocarbons, cyclic and straight chain fluorocarbon ethers, and perfluoroalkyl tertiary amines have been measured over a range of temperatures. The oxygen and nitrogen-containing compounds have lower viscosities than fluorocarbons of the same type (cyclic or straight chain) and the same number of carbon atoms. Thermodynamic quantities related to viscous flow were calculated. Possible reasons for the viscosity effects observed are discussed.

The viscosities of a number of fluorocarbons have previously been measured, and in particular an extensive study of three perfluoropentanes has been made by Burger and Cady.¹

The absolute viscosities and the temperature coefficients of viscosity of fluorocarbons are high compared to those of analogous hydrocarbons, hydrocarbon ethers (polyalkylene oxides) and

(1) L. L. Burger and G. H. Cady, *THIS JOURNAL*, **78**, 4248 (1951).

siloxanes. The low viscosities and temperature coefficients of viscosity of the latter compounds have been attributed to high internal flexibility. This in turn has been attributed to progressively greater ease of rotation about the C-C, C-O, and Si-O bonds.^{2,3} In siloxanes an additional factor is believed to be the ease of rocking of the $(CH_3)_2-$

(2) A. Bondi, *J. Phys. Colloid Chem.*, **55**, 1355 (1951).

(3) C. M. Murphy and W. A. Zisman, *Ind. Eng. Chem.*, **48**, 2415 (1950).