

oxide by the procedure of Barnard and Hargrave.¹⁹ In this analysis nitromethane interfered slightly and a blank correction obtained using the same amount and concentration of nitromethane was applied. Table V summarizes typical hydroperoxide yields. It is not believed that the solvents employed (Table I) were involved in a cooxidation sequence. In the absence of cyclohexene or cumene the solvents themselves did not undergo oxidation at a significant rate. Moreover, many of the solvents would be inert to peroxy radical attack because of the polar effect of electron-withdrawing functional groups such as nitro, cyano, sulfoxide, carbonyl, and carboxyl substituents. Substituents such as ethers, sulfides, amines, or amides were not employed because of the possible complications from cooxidation.

TABLE V
HYDROPEROXIDE YIELDS IN AUTOXIDATION OF CYCLOHEXENE^a

Hydrocarbon	Solvent	% of absorbed O ₂ found as ROOH
Cyclohexene	CH ₃ NO ₂	101
Cyclohexene	(CH ₃) ₂ CHOH	104
Tetralin	CH ₃ NO ₂	93
Cycloocta-1,5-diene	CH ₃ NO ₂	90
Cycloheptene	CH ₃ NO ₂	65
Cycloheptatriene	CH ₃ NO ₂	47
Cycloheptatriene	C ₆ H ₅ Cl	36
Cyclooctene	C ₆ H ₅ Cl	62
Cyclopentene ^b	CH ₃ NO ₂	70
Norbornadiene	CH ₃ NO ₂	9

^a 2.0 M hydrocarbon at 60° in presence of 0.0504 M AIBN.

^b 1.0 M hydrocarbon.

(19) D. Barnard and K. Hargrave, *Anal. Chem. Acta*, **5**, 476 (1951).

Reagents.—Research grade cyclopentene (99.89 mole %), cyclohexene (99.98 mole %), and cumene (100.0 mole %) were obtained from Phillips Petroleum Co. Cycloheptene was prepared by the reduction of cycloheptanone by lithium aluminum hydride followed by elimination of water catalyzed by naphthalenesulfonic acid. Cyclooctene and cycloocta-1,5-diene were gifts from Cities Service Research and Development Co., while cycloheptatriene and norbornadiene were gifts from Shell Chemical Co. Indan (Aldrich Chemical Co.) and tetralin (Matheson, Coleman and Bell) were shaken with sulfuric acid, washed, and dried. Cyclohexa-1,3-diene was prepared by bromination of cyclohexene with N-bromosuccinimide followed by quinoline-catalyzed dehydrobromination.²⁰ The preparation of *p*-nitro-cumene has already been described.¹¹

The hydrocarbons other than those of research grade were rectified in a Todd column with a monel spiral and center fractions selected having constant boiling points and having no impurities detectable by gas chromatography. The purified hydrocarbons were passed through silica gel under a dry nitrogen atmosphere and stored under nitrogen prior to use. Cyclohexenyl hydroperoxide was prepared by oxidizing a large volume of cyclohexene to the extent of a few per cent with AIBN and oxygen. The excess cyclohexene was removed at reduced pressure and the hydroperoxide fractionated *in vacuo*. Purity by hydroperoxide analysis was 82.5%.

Solvents.—Commercial solvents were distilled prior to use and where possible passed through a silica gel column prior to use. *t*-Butylnaphthalene was prepared by the reaction of *t*-butyl alcohol with naphthalene in the presence of boron trifluoride and phosphoric anhydride. Distillation gave material, b.p. 84–89° (1 mm.), *n*_D²⁰ 1.5694, which was passed through silica gel before use.

(20) G. S. Hammond and J. Warkentin, *J. Am. Chem. Soc.*, **83**, 2554 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Retarding Effects of Polyarylmethanes in Autoxidation Reactions^{1,2}

BY DALE G. HENDRY^{3a} AND GLEN A. RUSSELL^{3b}

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The retarding effect of polyarylmethanes or polyarylalkenes on the autoxidation of cyclohexene or cumene has been established to be due to the low reactivity of the polyarylmethyl radicals formed by attack of peroxy radicals. The polyarylmethyl radicals can persist in the presence of oxygen and retard the reaction by trapping peroxy radicals to give nonradical products. Abilities of polyarylmethanes to inhibit autoxidation reactions parallel and are a measure of the resonance stabilization of the polyarylmethyl radicals. Inhibition of this type becomes more pronounced as the temperature is raised.

The rate of autoxidation is generally retarded by materials which destroy the chain-propagating free radical intermediates. The effectiveness of phenols and anilines as inhibitors depends on the reactivity of these substances with peroxy radicals and the inability of the resulting phenoxy or anilino radicals to carry on effectively the chain oxidation.⁴

The presence of substances which give rise to peroxy radicals which readily terminate can bring about a retardation of the autoxidation of substances which yield peroxy radicals that terminate at a slower rate.⁵ Thus small amounts of tetralin drastically retard the oxidation of cumene even though tetralin is more reactive than cumene toward peroxy radicals.^{5,6} In this competitive oxidation it can be proved that only peroxy radicals are involved in the termination process.⁵

(1) Directive Effects in Aliphatic Substitutions. XXVII.

(2) This work was supported by a grant from the Petroleum Research Foundation administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

(3) (a) Ethyl Corporation Predoctoral Research Fellow, 1960–1961;

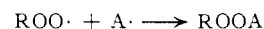
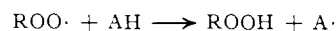
(b) Alfred P. Sloan Foundation Fellow, 1959–1963.

(4) For an extensive review see K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).

(5) G. A. Russell, *J. Am. Chem. Soc.*, **77**, 4583 (1955); **78**, 1047 (1956).

(6) G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2364 (1964).

We herein describe another type of retardation in the cooxidation of hydrocarbons (RH and AH). When one of the hydrocarbons (AH) forms an alkyl radical which reacts only slowly with oxygen, retardation can result from the sequence of reactions



Such retardation is apparently widespread in high temperature vapor phase autoxidations. Thus, toluene, ethylbenzene, or cumene retard the oxidation of alkanes in the vapor phase at 250° with the formation of dimers and disproportionation products derived from the resulting benzyl radicals.⁷ Propylene retards the oxidation of propane presumably through the formation of the relatively stable allyl radical,⁸ and diisobutylene inhibits the high temperature oxidation of heptane.⁹

(7) J. Giammaria and H. Norris, *Ind. Eng. Chem., Prod. Res. Dev.*, **1**, 16 (1962).

(8) J. W. Falconer and J. H. Knox, *Proc. Roy. Soc. (London)*, **A250**, 493 (1959); C. N. Satterfield and R. C. Reid, "5th Symposium on Combustion," Reinhold Publishing Corp., New York, N. Y., 1955, p. 511.

(9) F. H. Garner, R. Long, and G. A. Webster, *ibid.*, p. 541.

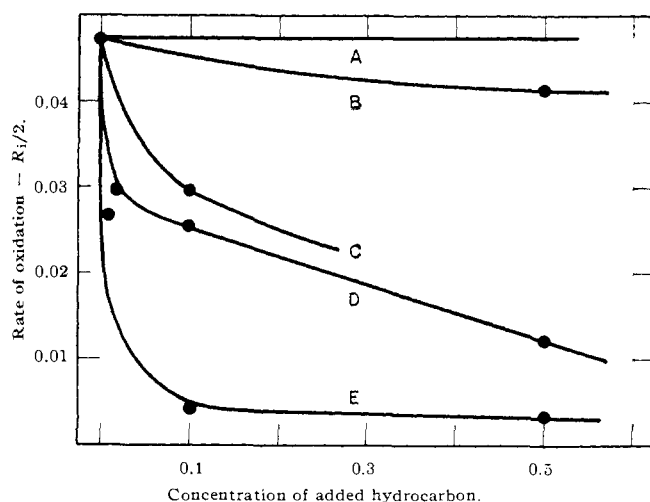


Fig. 1.—Effect of polyarylmethanes on the oxidation of 2.0 *M* cyclohexene in chlorobenzene containing 0.0504 *M* AIBN at 60°: A, inert hydrocarbon; B, 1,1-diphenylethylene; C, 1-naphthyldiphenylmethane; D, triphenylmethane; E, 9-phenylfluorene.

Retardations were observed in the present work in liquid phase autoxidation of cumene or cyclohexene at 60–90° by the presence of polyarylmethanes capable of forming di- or triarylmethyl radicals. This retardation is distinct from the reported inhibitions by polynuclear aromatics¹⁰ whose high radical affinities¹¹ result in the addition of a peroxy radical to the aromatic nucleus to form a radical incapable of chain propagation.

The observed retardations are connected with the fact that the polyarylmethanes are themselves rather inert in autoxidation reactions⁵ although they are known to be quite reactive toward free radicals.

Results

Kinetics of Cyclohexene Oxidation.—The effects of catalyst concentration (azobisisobutyronitrile = AIBN), hydrocarbon concentration, and oxygen pressure on the oxidation of cyclohexene at 60° are given in Table I.

TABLE I
OXIDATION OF CYCLOHEXENE IN PRESENCE OF AIBN AT 60°

Cyclohexene concentration ^a	Solvent	AIBN concentration ^a	Oxygen pressure ^b	Rate - $R_i/2^c$	$\frac{\text{Rate} - R_i/2}{[\text{C}_6\text{H}_{12}] \times [\text{AIBN}]^{1/2}}$
9.4	None	0.0933	710	0.199	0.00706
9.4	None	.0504	710	.145	.00687
9.4	None	.0332	710	.123	.00718
7.34	Cyclohexane	.0504	710	.107	.00648
5.99	Cyclohexane	.0504	710	.0885	.00657
3.93	Cyclohexane	.0504	710	.0532	.00603
1.99	Cyclohexane	.0504	710	.0306	.00684
2.00	Chlorobenzene	.0504	710	.0472	.0105
2.00	Chlorobenzene	.0504	300	.0476	.0106

^a Concentration in moles/l. ^b Oxygen pressure in mm., uncorrected for vapor pressure of solvent and hydrocarbon. ^c Rate in moles of oxygen absorbed/l.-hr.

The rate followed the kinetic equation

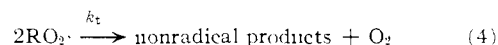
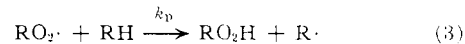
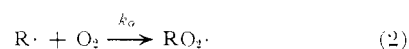
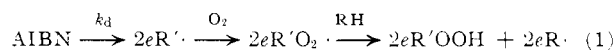
$$-d[\text{O}_2]/dt = k[\text{RH}][\text{AIBN}]^{1/2} + R_i/2$$

(10) J. R. Dunn, W. A. Waters, and I. M. Roitt, *J. Chem. Soc.*, 580 (1954).

(11) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 1949 (1955).

where R_i = rate of initiation, between 300 and 710 mm. saturation pressures of molecular oxygen. Titration of hydroperoxide by the method of Barnard and Hargrave¹² demonstrated that 95–100% of the absorbed oxygen was present as titratable hydroperoxide.

The oxidation of cyclohexene (RH) is recognized¹³ to follow the mechanism



Under steady-state conditions where $k_o \gg k_p$

$$-d[\text{R}_1\text{H}]/dt = -d[\text{O}_2]/dt - R_i/2 =$$

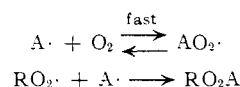
$$\frac{k_p}{(2k_t)^{1/2}} [\text{RH}](R_i)^{1/2}$$

where $R_i = 2ek_d[\text{AIBN}]$.¹⁴

The value of ek_d was evaluated by the method of Hammond, Sen, and Boozer¹⁵ using di-*t*-butyl-*p*-cresol for the inhibitor for the AIBN-initiated oxidation of cumene and found to be 6.74 and 6.54 $\times 10^{-6}$ sec.⁻¹ in cyclohexane and chlorobenzene. Assuming k_d to be 9.60 $\times 10^{-6}$ sec.⁻¹ at 60°¹⁶ gives rise to values of e of 0.70 and 0.68 in cyclohexane and chlorobenzene. The above values of ek_d lead to values of $k_p/k_t^{1/2}$ of 0.48 and 0.67 (l./mole-hr.)^{1/2} at 60° in cyclohexane and chlorobenzene solutions.

Rates of Cooxidations.—Cyclohexene was cooxidized with triphenylmethane, α -naphthyldiphenylmethane, fluorene, 9-phenylfluorene, triphenylethylene, and 1,1-diphenylethylene in chlorobenzene solution. The data of Table II show a drastic reduction in rate of oxidation of 2 *M* cyclohexene, particularly by 9-phenylfluorene. Figure 1 shows that the ability of the hydrocarbons to retard the oxidation of cyclohexene is 9-phenylfluorene > triphenylmethane > α -naphthyldiphenylmethane > 1,1-diphenylethylene > triphenylethylene. Table II also shows that the retarded rate of oxidation is dependent on oxygen pressure and is lower at a lower oxygen pressure.

Temperature Dependence of Retardation.—The results of cooxidations of cumene and triphenylmethane performed at 60 and 90° are summarized in Fig. 2. The retardation is more pronounced at 90 than at 60°. This is somewhat surprising since one would expect that triphenylmethane would be attacked more selectively at the lower temperature. The effect of temperature on retardation suggested that possible oxygen reacted with the polyarylmethyl radicals rapidly but that the reaction was reversible. To test for this possi-



bility we searched for a reagent stable in the presence of oxygen which would react readily with $\text{AO}_2 \cdot$ and which would propagate the chain reaction by regenerating $R \cdot$ and $A \cdot$.

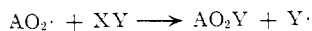
(12) D. Barnard and K. R. Hargrave, *Anal. Chim. Acta*, **5**, 476 (1951).

(13) L. Bateman, *Quart. Rev. (London)*, **8**, 147 (1954).

(14) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

(15) G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

(16) J. P. Van Hook and A. V. Tobolsky, *ibid.*, **80**, 779 (1958).



The only reagent we know of that can perform the requirements demanded of X-Y is hydrogen bromide.¹⁷ The oxidation of cumene in the liquid phase containing traces of hydrogen bromide proceeds extremely rapidly initially but soon inhibits itself presumably due to the

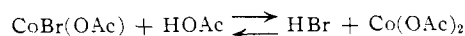
TABLE II
COOXIDATION OF CYCLOHEXENE AND POLYARYLMETHANES^a

Added hydrocarbon	Cyclohexene concentration ^b	Hydrocarbon concentration ^b	Oxygen pressure ^c	(Rate - $R_1/2$) ^d
None	2.0	..	710	0.0472
None	2.0	..	300	.0476
Triphenylmethane	2.0	0.02	710	.0394
Triphenylmethane	2.0	.10	710	.0254
Triphenylmethane	2.0	.50	710	.0123
Triphenylmethane	1.9	.10	710	.0252
Triphenylmethane	1.9	.10	300	.0194
Triphenylmethane	1.5	.50	710	.0100
Triphenylmethane	1.5	.50	300	.0071
Triphenylmethane	0.0	2.0	710	.0022
9-Phenylfluorene	2.0	0.01	710	.0266
9-Phenylfluorene	2.0	.01	300	.0202
9-Phenylfluorene	2.0	.10	710	.0043
9-Phenylfluorene	2.0	.50	710	.0034
α -Naphthyl-diphenylmethane	2.0	.10	710	.0295
	2.0	.10	300	.0271
Triphenylethylene	2.0	.50	710	.0462
1,1-Diphenylethylene	2.0	.50	710	.0415
Fluorene	1.9	.10	710	.0429
Fluorene	1.9	.10	500	.0409
Fluorene	1.9	.10	400	.0380
Fluorene	1.9	.10	300	.0340
Fluorene	1.5	.50	710	.0376
Fluorene	1.5	.50	500	.0354
Fluorene	1.5	.50	400	.0309
Fluorene	1.5	.50	300	.0246
Fluorene	0.0	2.00	710	.0220
Fluorene	0.0	2.00	300	.0178

^a In chlorobenzene at 60° in the presence of 0.0504 M AIBN.

^b Concentration in moles/l. ^c Pressure in mm. and uncorrected for vapor pressure of reaction mixtures. ^d Rate in mole/l.-hr.

formation of phenol by an acid-catalyzed decomposition of cumene hydroperoxide. Cobalt bromoacetate in acetic acid appears to generate a low and constant concentration of covalent¹⁸ hydrogen bromide.¹⁹ Dr. H.



S. Blanchard has found that cobalt bromoacetate has no effect on the rate of initiation of the AIBN-catalyzed autoxidation of cumene using the Hammond, Sen, and Boozer technique. Pronounced accelerations on the rate of oxidation of cumene (AIBN catalyst) can be duplicated by cobalt(II) bromide in acetic acid, but in this case the initial high rate rapidly decreases due to the formation of an inhibitor, presumably phenol.²⁰ Cobalt(II) acetate accelerates the AIBN-catalyzed oxidation of cumene but to a lesser extent than the bromoacetate. The effect of cobalt(II) ion in acetic

(17) F. F. Rust and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 2595 (1949).

(18) I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, **56**, 1007 (1934).

(19) D. A. S. Ravens, *Trans. Faraday Soc.*, **55**, 1768 (1959).

(20) Private communication, Dr. H. S. Blanchard, General Electric Research Laboratory.

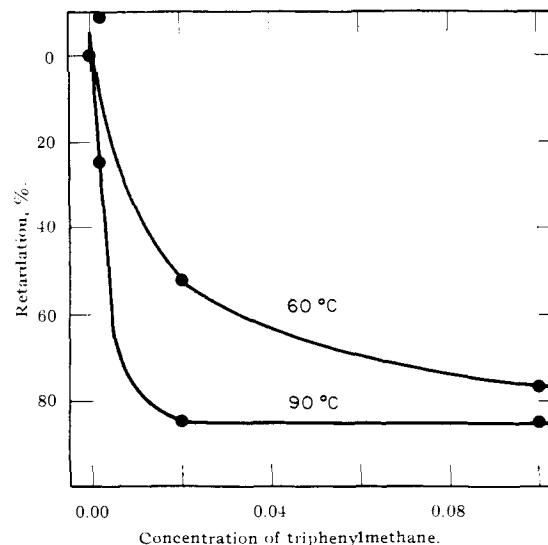
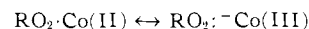


Fig. 2.—Effect of concentration of triphenylmethane on the oxidation of 2.0 M cumene in bromobenzene solution at 60° and 90°. In the absence of triphenylmethane at 60° and in the presence of 0.0504 M AIBN, rate - $R_1/2$ = 0.0144 mole/l.-hr. while at 90° in the presence of 0.040 M *t*-butyl perbenzoate, rate - $R_1/2$ = 0.00954 mole/l.-hr.

acid may simply be the effect of the cobalt(II) ion complexing with the peroxy radical



and affecting the relative values of k_p and k_t .²¹ The initial rates of oxidation of cumene and cumene-triphenylmethane mixtures in acetic acid in the presence or absence of cobalt(II) acetate and the bromoacetate are given in Table III.

TABLE III
RATES OF OXIDATION OF CUMENE IN ACETIC ACID^a

Concn. of (C ₆ H ₅) ₃ CH ^b	Accelerator ^c	Initial rate - $R_1/2$ ^d	Inhibition, %
0	None	0.0151	0
0.1	None	0.0028	80
0.5	None	Too slow to measure	100
0	CoBr(OAc)	0.160	0
0.1	CoBr(OAc)	.0424	75
0.5	CoBr(OAc)	.0014	99
0	Co(OAc) ₂	.0581	0
0.5	Co(OAc) ₂	.0027	96

^a 2.0 M cumene at 60°, 0.0504 M AIBN. ^b Moles/l. ^c 0.02 M. ^d Moles/l.-hr.

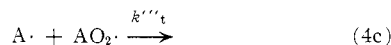
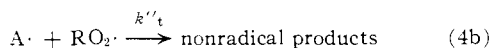
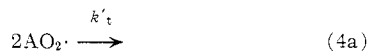
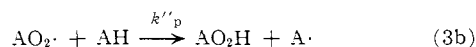
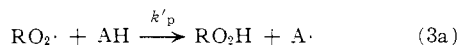
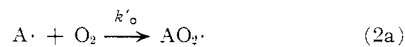
The data of Table III show that triphenylmethane inhibits the oxidation of cumene to the same degree in the presence or absence of cobalt(II) acetate and cobalt bromoacetate. We believe this evidence excludes the possibility that a fast equilibrium between the triphenylmethyl radical and the triphenylmethylperoxy radical is involved.

Discussion

The dependence of rate of oxidation of cyclohexene inhibited by polyarylmethanes or polyarylethylenes upon the oxygen pressure clearly indicates that the retardation involves a termination reaction involving a radical other than a peroxy radical. The most reasonable interpretation is that this is the polyarylmethyl radical which because of resonance stabilization is able to persist in the presence of oxygen.

(21) H. S. Blanchard, *J. Am. Chem. Soc.*, **82**, 2014 (1960).

Bateman has observed that there appears to be an inverse relationship between the relative reactivity of various hydrocarbons toward peroxy radicals and the relative reactivity of the corresponding alkyl radicals toward oxygen.¹³ The cooxidations of cyclohexene or cumene (RH) with polyarylmethanes (AH) apparently involves the following steps in addition to reactions 1-4.



In the event that the retarder is an olefin (A) such as 1,1-diphenylethylene, step 3a would be replaced by 3a'; $RO_2\cdot + A \rightarrow RO_2A\cdot$.

The retardation in rate is thought to result from the fact that k'_p , $k''_p > k_p$ and $k_o \gg k'_o$. This leads to a situation wherein the rate is reduced ($-d[RH]/dt = \Sigma k_p [RO_2\cdot][RH]$) because of the reduced concentration of peroxy radicals due to the fact that an appreciable fraction of the total radical concentration is the unreactive $A\cdot$. In addition, termination by processes 4a-4d may well occur more readily than reaction 4.

The rate expression predicted for steps 1-4d is complicated. However, it is apparent that if termination between a nonoxygenated radical and a peroxy radical is important, the observed retardation should depend on: (1) polyarylmethane concentration, (2) the rate constant for attack of peroxy radicals on the polyarylmethane, and (3) the oxygen concentration. In reference to item (2) it has been mentioned that the ability of a hydrocarbon to retard the oxidation of cyclohexene is qualitatively proportional to the expected stability of the resulting polyarylmethyl radical. Table IV demonstrates that this prediction is fulfilled, but that α -naphthyldiphenylmethane is not as efficient an inhibitor as the calculated delocalization energy of the radical predicts. This is presumably due to steric inhibition of resonance which is well recognized for the corresponding carbonium ion.²²

The present results suggest that the higher degree of dissociation of 1,2-di- α -naphthyl-1,1,2,2-tetraphenyl-

(22) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **74**, 5288 (1952).

TABLE IV
CORRELATION BETWEEN INHIBITING ABILITY OF AH AND THE STABILITY OF $A\cdot$

Retarder (AH)	Retardation, ^a %	Calculated delocalization energy of $A\cdot$, ^b
Fluorene	4.5	1.343
α -Naphthyldiphenylmethane	38	1.856
Triphenylmethane	47	1.794
9-Phenylfluorene	91	1.835

^a From Table II, $AH = 0.1 M$. ^b In units of β ; ref. 23.

ethane compared to hexaphenylethane²⁴ is due to steric interaction between the substituents rather than due to a greater resonance stabilization of the α -naphthyldiphenylmethyl radical.

The greater ability of triphenylmethane to retard the oxidation of cumene at 90° than at 60° suggests that at the higher temperature a relatively greater proportion of triphenylmethyl radicals are present. This may be due to the fact that the reactions in which the nonoxygenated radical disappears have a smaller E_a and thus show less temperature dependence than the reaction whereby the triphenylmethyl radical is formed, *i.e.*, hydrogen abstraction by peroxy radicals. A similar phenomenon has been observed in a study of the influence of temperature in the effect of oxygen pressure on the oxidation of unsaturated hydrocarbons.¹³

The retardations observed in the present study are analogous to the inhibiting action of arylethylenes on the oxidation of benzaldehydes. In particular the retardation of the oxidation of benzaldehyde by $\Delta^{9,9}$ -bifluorene²⁵ is readily explained by the retardation mechanism demanded by the present results.

Experimental

Apparatus and Procedure.—Autooxidations were performed using the apparatus and technique described previously.⁶

Solvents.—Acetic acid was from freshly opened bottles. Cyclohexane, chlorobenzene, and bromobenzene were distilled, chromatographically filtered over silica gel and stored under nitrogen.

Reagents.—Cyclohexene (99.98 minimum mole %) and cumene (100.0 minimum mole %) were obtained from Phillips Petroleum Co. The AIBN used was described previously.⁶ Triphenylmethane and fluorene were obtained from Matheson Coleman and Bell while triphenylethylene and 1,1-diphenylethylene were from Aldrich Chemical Co. 9-Phenylfluorene from an unknown source was recrystallized; m.p. 145-147°. α -Naphthyldiphenylmethane was prepared by reduction of the carbinol obtained by the addition of α -naphthylmagnesium bromide to benzophenone.²⁶ Cobalt bromoacetate was prepared by the addition of 1 equivalent of anhydrous hydrogen bromide to anhydrous cobalt(II) acetate in acetic acid solution. The hydrogen bromide was measured in a calibrated standard bulb of a Stock-type high vacuum apparatus.

(23) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(24) G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 774.

(25) G. Wittig and W. Lange, *Ann.*, **536**, 266 (1938); G. Wittig and G. Pieper, *ibid.*, **546**, 142, 172 (1941); **558**, 207, 218 (1947); G. Wittig, *ibid.*, **558**, 201 (1947).

(26) S. F. Acree, *Ber.*, **37**, 616, 625 (1904).