E_a for **1** is 14.8 kcal./mole as compared with isobutene[21] 23.4, trimethylethylene[22] 18.9, crotonaldehyde[23] 18.2, and fumaric acid 22 kcal./mole.[24] The hydrolysis of ethoxyethylene has a reported activation energy of 17.9 kcal./mole.[1] Vinyl ether hydrolysis, therefore, is characterized in general by a lower activation energy with **1** having an activation energy even lower than that reported for other compounds of this class.

In attempting to deduce the factors responsible for the rapid enzymatic hydration of olefins it would appear that one should look for ways in which the enzyme can stabilize the incipient carbonium ion.

(21) H. J. Lucas and W. F. Eberz, *J. Am. Chem. Soc.*, **56**, 460 (1934).
(22) H. J. Lucas and Y. P. Liu, *ibid.*, **56**, 2138 (1934).
(23) S. Winstein and H. J. Lucas, *ibid.*, **59**, 1461 (1937).
(24) L. E. Erickson and R. A. Alberty, *J. Phys. Chem.*, **63**, 705 (1959).

Reactions of Peroxy Radicals with Polynuclear Aromatic Compounds. II. Anthracene in Chlorobenzene

L. R. Mahoney

Contribution from the Scientific Laboratory, Ford Motor Company, Dearborn, Michigan. Received July 13, 1964

The products and kinetics of the reactions occurring in the system anthracene–azobis(2-methylpropionitrile)–oxygen in chlorobenzene have been investigated. At anthracene concentrations greater than 0.1 M a chain oxidation of anthracene occurs with radical addition at the meso positions. A study of the rate of oxygen absorption as a function of oxygen pressure shows that the meso carbon radical is significantly less reactive than other carbon radicals toward oxygen. Above 1.0×10^{-4} M, anthracene is capable of scavenging all radicals derived from initiator and oxygen. At lower concentrations of anthracene radicals are destroyed by a competing process. The available evidence indicates that the process consists of an attack on chlorobenzene by radicals derived from the bimolecular reaction of 2-cyanopropylperoxy radicals.

In an earlier paper from this laboratory,[1] it was suggested that anthracene undergoes an apparent free-radical chain reaction with oxygen. Although reactive olefins undergo such reactions[2] and compounds related to anthracene undergo photochemical nonchain additions with oxygen,[3] no chain oxidation of polynuclear aromatic hydrocarbons has been reported previously. The present work was therefore undertaken to examine this chain oxidation in detail. The range of anthracene concentrations was also extended well below that required for chain reaction, and the results suggest that the solvent chlorobenzene is involved in termination reactions of radicals derived from azobis(2-methylpropionitrile), *i.e.*, azobisisobutyronitrile (AIBN) and oxygen.
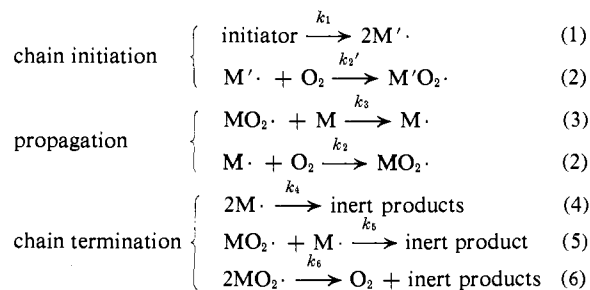
Results and Discussion

The kinetics and products of the reactions of radicals derived from AIBN and oxygen with anthracene in

(1) L. R. Mahoney, *J. Am. Chem. Soc.*, **86**, 44 (1964).
(2) F. R. Mayo, H. H. Miller, and G. A. Russell, *ibid.*, **80**, 2500 (1958).
(3) J. R. Livingston, "Auto-Oxidation and Antioxidants," Vol. I, W. O. Lundberg, Ed., Interscience Publishers, John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 264–287.

chlorobenzene were studied over wide ranges of concentration of anthracene, AIBN, and oxygen. For discussion, the results of this study have been divided into the following two ranges of anthracene concentration: (1) chain-reaction region (greater than 0.1 M in anthracene), and (2) radical-scavenging region (from 2×10^{-6} to 0.1 M in anthracene).

I. Chain Reaction. A. Kinetics. The accepted kinetic mechanism for the low temperature liquid phase oxidation of unsaturated hydrocarbons is[2,4]

$$\text{chain initiation} \begin{cases} \text{initiator} \xrightarrow{k_1} 2M' \cdot & (1) \\ M' \cdot + O_2 \xrightarrow{k_2'} M'O_2 \cdot & (2) \end{cases}$$

$$\text{propagation} \begin{cases} MO_2 \cdot + M \xrightarrow{k_3} M \cdot & (3) \\ M \cdot + O_2 \xrightarrow{k_2} MO_2 \cdot & (2) \end{cases}$$

$$\text{chain termination} \begin{cases} 2M \cdot \xrightarrow{k_4} \text{inert products} & (4) \\ MO_2 \cdot + M \cdot \xrightarrow{k_5} \text{inert product} & (5) \\ 2MO_2 \cdot \xrightarrow{k_6} O_2 + \text{inert products} & (6) \end{cases}$$

where $M' \cdot$ and $M \cdot$ are the initiator radical and substrata radical, and $M'O_2 \cdot$ and $MO_2 \cdot$ are the peroxy radicals derived from the initiator and substrata radicals, respectively. At a steady-state radical concentration, the rate of oxygen absorption, $-dO_2/.dt$, obeys the general expression

$$-\frac{dO_2}{dt} =$$

$$\frac{k_3}{(2k_6)^{1/2}}(R_i)^{1/2}(M)\left[\frac{1}{1 + \dfrac{\phi k_4^{1/2} k_3}{k_2(2k_6)^{1/2}}\dfrac{(M)}{(O_2)} + \dfrac{k_4 k_3^2 (M)^2}{k_2^2 k_6 (O_2)^2}}\right] \quad (7)$$

where $\phi = k_5/(k_4 k_6)^{1/2}$ and R_i is the rate of radical production from the initiator. At sufficiently high concentrations of oxygen, reaction 2 is much faster than reaction 3 so that $(M \cdot) \ll (MO_2 \cdot)$ and termination occurs almost exclusively by reaction 6. The terms

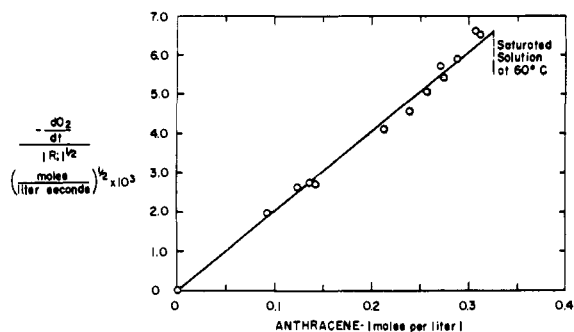(4) L. Bateman, G. Gee, A. L. Morris, and W. F. Watson, *Discussions Faraday Soc.*, **10**, 250 (1951).

Figure 1. Oxidation of anthracene at oxygen pressures greater than 400 mm. (*cf.* eq. 8).

within the brackets of eq. 7 then approach unity and the limiting rate, $-(dO_2/dt)_\infty$, is given by

$$-\left(\frac{dO_2}{dt}\right)_\infty = \frac{k_3}{(2k_6)^{1/2}}(R_i)^{1/2}(M) \tag{8}$$

At concentrations above about 0.1 M, solutions of anthracene in chlorobenzene containing AIBN absorb

Table I. Rates of Oxygen Absorption by Anthracene at 60° in the Presence of AIBN in Chlorobenzene

Anthracene, mole l.$^{-1}$	$-dO_2/dt$ × 10^6,[a] moles l.$^{-1}$ sec.$^{-1}$	R_i × 10^6,[b] moles l.$^{-1}$ sec.$^{-1}$	$\frac{dO_2/dt}{(R_i)^{1/2}(An)}$ × 10^2, l.$^{1/2}$ sec.$^{-1}$ mole$^{-1/2}$
A. Dependence on R_i and Anthracene Concentration at 683 mm. of Oxygen[c]			
0.092	1.38	0.49	2.14
0.124	2.34	0.78	2.12
0.136	1.93	0.49	2.04
0.213	4.71	1.30	1.92
0.239	3.29	0.52	1.91
0.256	2.59	0.26	1.93
0.271	6.37	1.22	2.07
0.273	4.78	0.78	1.99
0.287	4.12	0.49	2.05
0.310	9.65	2.18	2.10
		mean	= 2.03

Anthracene, mole l.$^{-1}$	P_{O_2},[b] mm.	$-dV/dt$ × 10^6, moles l.$^{-1}$ sec.$^{-1}$	R_i × 10^6, mole l.$^{-1}$ sec.$^{-1}$	$\frac{-dV/dt}{(R_i)^{1/2}(An)}$ × 10^2, l.$^{1/2}$ sec.$^{-1}$ mole$^{-1/2}$
B. Dependence on Oxygen Pressure				
0.297	683	3.92	0.42	2.04
0.307	483	4.46	0.49	2.07
0.251	287	2.48	0.49	1.42
0.259	215	2.18	0.49	1.20
0.252	128	1.53	0.49	0.867
0.309	114	1.43	0.49	0.661
0.274	81	1.02	0.49	0.532
0.300	84	0.991	0.42	0.510
0.151	81	0.726	0.42	0.742
0.142	373	1.76	0.49	1.77
0.150	235	1.265	0.42	1.30
0.150	170	1.11	0.42	1.14
0.153	88	0.894	0.42	0.890

[a] Corrected for nitrogen evolution, oxygen absorption by initiator, and oxygen evolution in termination reactions: $|dV/dt + 0.3R_i| = |dO_2/dt|$. [b] The value of R_i, 1.38 × 10^{-6} (AIBN) mole l.$^{-1}$ sec.$^{-1}$, used in this study was adopted by Russell[5] from a compilation of literature values. It corresponds to $(2\epsilon)(1.15 \times 10^{-5})$· (AIBN) where ϵ, the efficiency of radical production, has been determined to be 0.6. [c] Corrected for pressure of solvent vapor (67 mm.).

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

oxygen. The rate of this absorption was followed manometrically using the apparatus previously described.[1] The absorption rates were independent of the stirring rate (varied from 500 to 1300 r.p.m.), were insensitive to the light of the laboratory, and could be inhibited by 2,6-di-*t*-butyl-*p*-cresol. Table I summarizes the results. At oxygen pressures greater than about 400 mm., the rate of oxygen absorption obeys eq. 8 (*cf.* Figure 1). Combining eq. 7 and 8 and rearranging one may write

$$\left\{ \left[\frac{\left(-\frac{dO_2}{dt}\right)_\infty}{\left(-\frac{dO_2}{dt}\right)} \right]^2 - 1 \right\} \frac{(O_2)}{(M)} = \frac{\phi k_4^{1/2} k_3}{k_2(2k_6)^{1/2}} + \frac{k_4 k_3^2(M)}{k_2^2 k_6(O_2)} \tag{9}$$

The value of dO_2/dt when termination is *via* reactions 4, 5, and 6 cannot be calculated from the experimentally determinable quantity dV/dt. It can be shown, however, that

$$\left| -\frac{dO_2}{dt} + 0.2R_i \right| \leq \left| \frac{dV}{dt} \right| \leq \left| -\frac{dO_2}{dt} - 0.3R_i \right|$$

Thus, the true values of dO_2/dt differ by a maximum of 10% from the values of dV/dt in Table IB. Thus, dV/dt has been substituted for dO_2/dt in eq. 9, and Figure 2 shows that this expression is obeyed for the rates at the lower oxygen pressures.
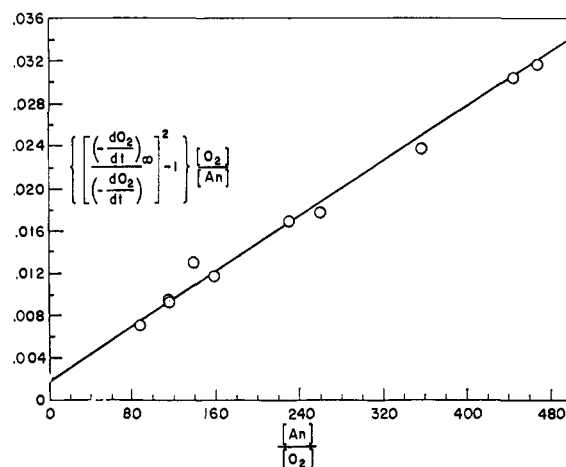

Figure 2. Oxidation of anthracene at oxygen pressures less than 400 mm. (*cf.* eq. 9).

B. Products. Solutions of oxygenated anthracene were examined by several techniques to establish the stoichiometry of the chain reaction. The amount of active oxygen in the product was determined iodometrically and the amount of anthracene consumed was determined spectrophotometrically. Table II summarizes the data which establish that 1 mole of oxygen reacts with 1 mole of anthracene to at least 48% consumption of anthracene.

Repeated attempts to isolate crystalline material from the crude product were fruitless. However, extraction of the reaction mixture with aqueous sodium dithionate–sodium hydroxide produced the water-soluble magenta-colored dianion of anthrahydro-
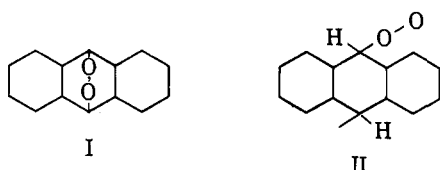
AIBN,[a] mole/l.	Anthracene, mole/l.	Time, sec. × 10³	O₂ absorbed,[b] mole/l.	Anthracene consumed,[c] mole/l.	Active oxygen,[d] mole/l.	Ratio[e]
0.18	0.303	14.22	0.094	0.10	...	0.94
0.18	0.320	28.02	0.154	0.15	...	1.02
0.159	0.318	21.90	0.138	...	0.137	1.01
0.159	0.317	8.82	0.052	...	0.053	0.98

[a] Half-life for AIBN at 60° is 87 × 10³ sec. Efficiency of radical production is 0.6 as determined from induction period using 2,6-di-t-butyl-p-cresol. [b] Corrected value equal to gas absorbed + [0.3 × radicals produced] from AIBN. [c] Determined spectrophotometrically at 3790 Å. [d] Determined by peroxide titration. [e] Ratio = oxygen absorbed/anthracene consumed or oxygen absorbed/active oxygen.

quinone. On exposure to air, the hydroquinone was oxidized to anthraquinone. The mixture was also reduced by the LiAlH₄ method.[6] Figure 3 lists the products and the yields from these reactions as determined by mass spectral and infrared analyses. The results show that more than 96% of the radical attack occurs at the 9,10-positions of anthracene.

Thus, the available evidence indicates that the product resulting from the oxidation contains a peroxide linkage at the meso positions of anthracene. The transannular peroxide I from the photoxidation of anthracene[7] is less soluble than anthracene in chloro-

benzene. However, the primary product is nearly 10 times more soluble (0.385 vs. 0.045 M) than anthracene in chlorobenzene at −5°. Therefore, the product obtained here cannot be the transannular peroxide, and linear peroxides of the type II seem more probable.

C. Interpretation of Rate Constants. In the first paper of this series,[1] the rate constant for the reaction of a cumylperoxy radical with anthracene was determined. If it is assumed that cumylperoxy and anthracenyl peroxy radicals have the same reactivity toward anthracene, the value of 62 mole⁻¹ l. sec.⁻¹ may be substituted for k_3 in eq. 8. The value of k_6 is then calculated to be 5 × 10⁶ mole⁻¹ l. sec.⁻¹, which is of the same order of magnitude as has been reported for secondary peroxy radical termination constants.[8] From the value of $k_3/(2k_6)^{1/2}$ and the slope and intercept of the plot of eq. 2 (Figure 2), $k_2/(2k_4)^{1/2}$ is calculated to be 3.0 mole⁻¹ l. sec.⁻¹. This value is approximately ¹/₅₀₀th as large as the rather constant values of 1 × 10³ to 2 × 10³ mole⁻¹ l. sec.⁻¹ reported for other hydrocarbons.[8] Whether this difference is due to simultaneous changes in the magnitude of both k_2 and k_4 cannot be determined from the present study. However, if the value of k_2 were the same as that reported for other carbon radicals, ca. 10⁷, the value of k_4 would have to be about 10¹¹ mole⁻¹ l. sec.⁻¹. Dimerization rate constants of this magnitude have been observed in diffusion-controlled reactions, but the sterically hindered and resonance stabilized meso carbon radicals should not dimerize at such high rates. Since the difference cannot be attributed solely to an increase in k_4, the

value of k_2 must be lower than those for other carbon radicals. Russell and Bridger[9] have recently suggested that the transition state for the addition of the electrophilic oxygen molecule to hydrocarbon radicals has polar character. The electron-withdrawing inductive effect of the peroxy group at the other meso position may thus decrease the rate for the oxygen reaction compared to that for the dimerization. The low reactivity toward oxygen of the intermediates[10] in the autoxidation of α-methylstyrene may be attributed to the same phenomena.
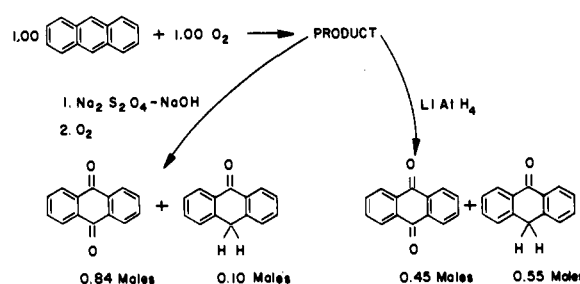

Figure 3. Reduction of products from the oxidation of anthracene.

II. Anthracene as a Radical Scavenger. As the concentration of the oxidizable substrata, M, is decreased, a point will be reached at which the rate of the radical termination reaction 6 will exceed the rate of the propagation reaction 3, i.e.

$$k_6[MO_2\cdot]^2 > k_3[MO_2\cdot][M]$$

A study of the reactions of anthracene at such concentrations (below 1500 × 10⁻⁵ M) with radicals produced from AIBN and oxygen in chlorobenzene has been carried out. The rate of radical production from AIBN has been calculated, and the concentration of anthracene has been followed spectrophotometrically. The results of this study are discussed below in terms of n, the stoichiometric factor, defined as

$$n = \frac{\text{moles of radicals produced from AIBN}}{\text{moles of anthracene consumed}} =$$

$$R_i / -\frac{dAn}{dt}$$

A. Anthracene Concentrations (20 × 10⁻⁵ to 1500 × 10⁻⁵ M). Data for experiments within this range of anthracene concentrations are summarized in Table III. In this region n is small and fairly constant. Thus

(6) G. A. Russell, J. Am. Chem. Soc., 75, 5011 (1953).
(7) C. Dufraisse and M. Gerard, Compt. rend., 201, 428 (1935).
(8) L. Bateman and G. Gee, Trans. Faraday Soc., 47, 155 (1951).

(9) G. A. Russell and R. F. Bridger, J. Am. Chem. Soc., 85, 3765 (1963).
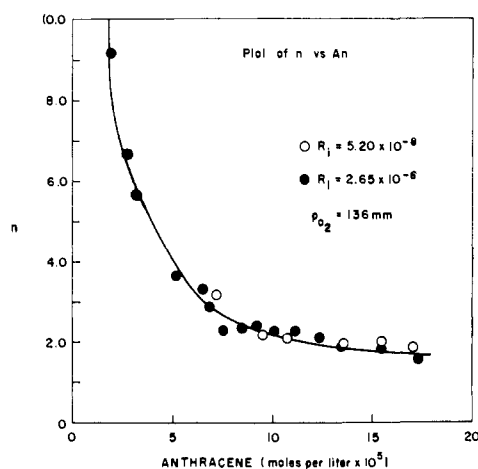(10) F. R. Mayo and A. A. Miller, ibid., 80, 2480 (1958).

Figure 4. Effect of anthracene concentration on the stoichiometric factor n.

the rate of reaction of anthracene is essentially independent of anthracene concentration and is directly proportional to the rate of radical production; all radicals formed from the initiator are scavenged by and terminated by reaction with anthracene.

Table III. Stoichiometric Factor (n) for Reaction of Anthracene with 2-Cyanopropyl Peroxy Radicals

An_0, (moles $l.^{-1}$) $\times 10^6$	An_t, (moles $l.^{-1}$) $\times 10^6$	R_i, (moles $l.^{-1}$ sec.$^{-1}$) $\times 10^8$	P_{O_2}, mm.	n^a
123	37.9	20.5	129	1.53
247	119.5	23.3	129	1.39
717	284	71.8	129	1.40
1530	592	111	683	1.33
1520	123	280	683	1.25

^{a} n was calculated from the expression, $An_0 - An_t = (2\epsilon/n) \cdot (AIBN)_0[1 - e^{-1.15 \times 10^{-6}t}]$, where An_0 is initial concentration of anthracene, An_t is the concentration of anthracene at conclusion of experiment, and An_t is concentration of anthracene at time t.

B. Very Low Concentrations ($<1 \times 10^{-4}$ M). As the anthracene concentration is decreased below 10×10^{-5} M, the factor n increases rapidly (*cf.* Figure 4). This indicates that not enough anthracene is present to scavenge all the radicals and that the radicals are being consumed by a competing reaction.

To ascertain the nature of this competing reaction, the rate of disappearance of anthracene below 2×10^{-5} M was examined in detail. For this study, the chlorobenzene was purified in a variety of ways to remove any impurities (*cf.* column 1 of Table IV). In all cases first-order dependence on anthracene concentration was observed and purification methods B–D had little effect on the pseudo-first-order rate constant at constant R_i. However, pretreatment of the solvent (method E) with AIBN and oxygen followed by distillation increased the rate constant by approximately one-third. Variation in the amount of AIBN (0.006 to 0.300 M) used for this pretreatment does not alter the rate. It appears that an impurity may be present in reagent grade chlorobenzene at a level smaller than 6×10^{-3} M and that this impurity is removed by reaction with radicals generated from AIBN and oxygen.

Table IV. Rate of Disappearance of Anthracene^a

Pretreat-ment of chloro-benzene^b	$R_i \times 10^8$, moles $l.^{-1}$ sec.$^{-1}$	$k' \times 10^4$, sec.$^{-1}$	P_{O_2}, mm.	$k'/R_i \times 10^{-4}$, mole $l.^{-1}$
A	5.12	2.88	136	0.563
A	5.22	3.18	136	0.610
B	5.22	3.07	136	0.588
C_{1800}	5.22	3.29	136	0.630
C_{5400}	5.22	3.03	136	0.580
D	5.06	2.91	683	0.576
D	2.71	1.81	136	0.670
D	2.71	1.73	683	0.638
D	1.07	0.83	683	0.776
D	1.07	0.78	136	0.728
$E_{1.0}$	2.68	1.97	136	0.735
$E_{1.0}$	5.16	4.14	136	0.803
$E_{1.0}$	10.13	7.45	136	0.736
$E_{2.0}$	7.64	5.78	136	0.757
$E_{2.0}$	7.65	5.60	683	0.732
$E_{4.0}$	5.18	4.12	136	0.795
$E_{7.5}$	5.12	3.91	136	0.765
$E_{7.5}$	0.384	0.267	136	0.698
$E_{50.0}$	5.23	3.96	136	0.757
$E_{50.0}$	5.22	3.90	683	0.747

^{a} Initial anthracene concentration, 1.90×10^{-5} mole/l. ^{b} A, reagent grade, no purification; B, reagent grade thru silica gel; C_t, AIBN decomposed for t sec. before anthracene added; D, reagent grade, shaken with H_2SO_4, NaOH, and H_2O, dried with $CaCl_2$, and distilled; E_g, preoxidized with g g./l. of AIBN for 5 days then twice distilled.

The rate of anthracene disappearance is first order with respect to R_i in this pretreated chlorobenzene, *e.g.*

$$-\frac{d(An)}{dt} = k'(An) = a'(R_i)(An) \qquad (10)$$

This rate law implies that the slow step in the destruction of radicals must be of the same order in radicals as the slow step in the consumption of anthracene. If the assumption is made that the rate of anthracene disappearance is first order with respect to radicals as in the case of the cumylperoxy[1] and anthracenylperoxy radicals, then the termination reaction must be first order in radical concentration. Since oxidizable impurities have been removed *via* treatment E, attack by radicals upon the solvent itself must be considered.

C. Radical Attack on Solvent. Chlorobenzene and benzene have been commonly employed as diluents for the study of the autoxidation of hydrocarbons, and the rates of oxidation do not vary from first-order dependence on hydrocarbon concentration. However, such observations do not exclude solvent attack by radicals derived from the initiator in the absence of substrata. There are reports[11,12] that substances are formed in systems containing AIBN, oxygen, and aromatic solvent which inhibit oxidation and polymerization reactions. We have carried out a study of the products to determine if radical attack on the solvent is of importance in the oxidation of AIBN in chlorobenzene and benzene. An amber-colored viscous oil consisting of a mixture of nine components by v.p.c. was obtained on evaporation of a reaction mixture from the air oxidation of a large amount of AIBN in chlorobenzene. This oil had previously been described

(11) J. C. Bevington and H. G. Troth, *Makromol. Chem.*, **53**, 200 (1962).
(12) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **40**, 1851 (1962).

by other workers[13] who reported its infrared spectrum (λ_{max} at 1740, 2240, and 1680 cm.$^{-1}$). The present study revealed that the material contained a large amount of chlorine. After correction for chlorobenzene, 1 g.-atom of chlorine was still present in the oil for each 2.2 moles of AIBN decomposed. On reduction of this oil with LiAlH$_4$, the infrared absorption in the region of 1740 cm.$^{-1}$ disappeared, but the chlorine analysis was essentially unchanged.

The mass spectra of the unreduced and LiAlH$_4$-reduced oils were nearly identical. Ion peaks at masses 222 and 224 occurred in the ratio of 3:2 at both 10 and 70 v. which strongly suggests the presence of dichlorobiphenyls (III). A major fragmentation peak appeared at mass 152 when an ionization potential of 70 v. was used. This fragmentation is consistent with disubstituted biphenyls.[14a] In addition to dichlorobiphenyls,


III   IV
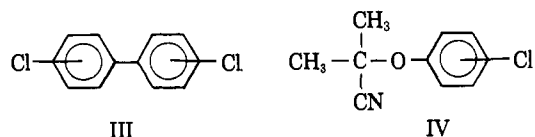
mass spectral peaks at masses 128 and 130 in the ratio of 3:1 and at masses 195 and 197 are consistent with the presence of isomeric ethers IV. Gas chromatography and infrared analysis demonstrated that the oil did not contain free monochlorophenols (masses 128 and 130); however, facile fragmentation *via* reaction 11 of such ethers to phenols is well documented.[14b] For example, at 70 v. the ratio of intensities of mass 94 to mass 150 for *t*-butyl phenol ethers has been reported as 14:1.[15]

(11)
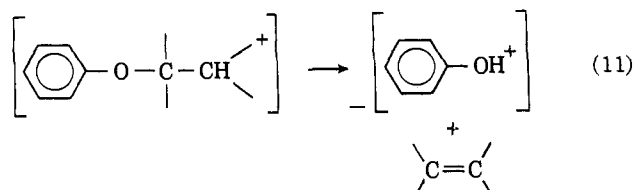
Support for the above interpretation was obtained by the isolation and identification of biphenyl (10% based on AIBN decomposed) from the oxidation of AIBN in benzene. Thus
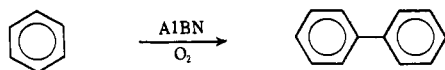
Although other interpretations may be possible, the above results suggest the attack of 2-cyano-2-propyloxy radicals on chlorobenzene. Recently Bartlett and Traylor[16] observed that the primary interaction of the two tertiary peroxy radicals may not be chain terminating. Thus, a possible pathway for production of 2-cyano-2-propyloxy radicals, RO· is

$$2RO_2 \cdot \xrightarrow{k_t} 2\alpha RO \cdot + O_2 + 2(1 - \alpha)ROOR$$
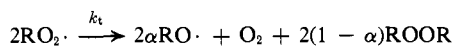
where α is the constant fraction of radicals which

(13) C. E. Boozer, G. K. Hammond, C. E. Hamilton, and C. Peterson, *J. Am. Chem. Soc.*, **77**, 3380 (1955).
(14) F. W. McLafferty, Advances in Chemistry Series, No. 40, American Chemical Society, Washington, D. C., 1963: (a) p. 61; (b) p. 63.
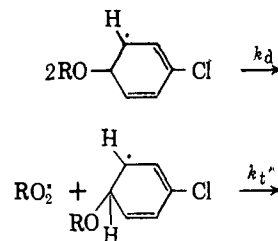(15) "Uncertified Mass Spectra," Chemical Physics Laboratory, Dow Chemical Company, Midland, Mich., Oct. 1963, no. 3092.
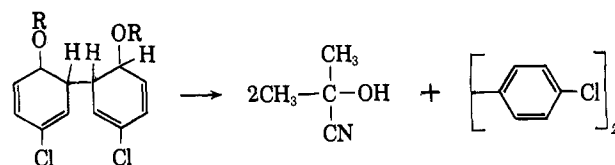(16) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963).

escape recombination in the solvent cage. This reaction is followed by attack on solvent

V
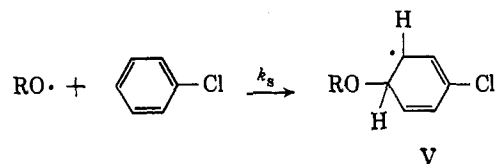
and the fast termination reactions of V.

The HCN and acetone cyanohydrin observed by other workers[11,13] could arise from decompositions such as

These reactions permit rationalization of the kinetic results of the dilute anthracene system since one may write, with the assumption that RO· disappears primarily *via* the addition reaction,

$$\frac{d[RO \cdot]}{dt} = 2\alpha k_t [RO_2 \cdot]^2 - k_s[RO \cdot][S]$$

where [S] is the concentration of solvent, and

$$\frac{d[RO_2 \cdot]}{dt} =$$

$$R_i - 2k_t[RO_2 \cdot]^2 - k_t'[RO_2 \cdot][RO \text{—} \quad \text{—Cl}]$$

If a steady state is assumed for the concentration of radicals in the system

$$[RO \cdot] = \frac{2\alpha k_t [RO_2 \cdot]^2}{k_s[S]} =$$

$$\frac{2\alpha k_t R_i}{k_s[S]\left\{2k_t + \frac{k_t'}{4k_d}[k_t' + \sqrt{(k_t')^2 + 16k_d k_t}]\right\}} =$$

$$\frac{\alpha R_i}{k_s[S]\left\{1 + \frac{k_t'}{8k_d k_t}[k_t' + \sqrt{(k_t')^2 + 16k_d k_t}]\right\}} = \frac{P}{}$$

$$\frac{R_i}{k_s'[S]}$$

and one obtains

$$-\frac{dAn}{dt} = k_{An}[RO \cdot][An] = \frac{k_{An}R_i[An]}{k_s'[S]}$$

which is consistent with experiment in the dilute anthracene region (*cf.* eq. 10). It should be borne in mind that the 2-cyano-2-propyloxy radical may be replaced in the preceding derivation by other radical(s) derived from it in subsequent fast reactions. However, products arising from reactions of methyl or cyano radicals (the most likely candidates) and solvent were not detected.

Although the identity of the radical(s) attacking anthracene is unknown, a value of k_{An}/k_s' has been calculated from Table IV (method E) and the solvent molarity (10 M) to be 0.75 × 10⁵. For comparison, the constants for the chain transfer of growing polystyryl radicals to anthracene and to chlorobenzene[17,18] and of trichloromethyl radicals to anthracene and to benzene[19] lie in the ratio of approximately 10⁵ while methyl affinity of anthracene relative to benzene is 2.5 × 10³ at 85°.[20]

Experimental

1. Materials and Equipment. Anthracene and azobis(2-methylpropionitrile) were purified as previously described.[1] Chlorobenzene (Baker "Analyzed Reagent") was purified by techniques indicated in Table IV. A 40-plate column, 4-ft. length and 25 mm. o.d. packed with ³/₃₂-in. glass helices, was used for all the distillations reported here.

Gas adsorptions were measured using the apparatus previously described.[1] For those measurements where the rate of oxygen absorption was experimentally determined to be dependent upon oxygen pressures, the oxygen concentration in the liquid phase was calculated from solubility measurements assuming that Henry's law was obeyed. The relation used was

$$[O_2] = \frac{683}{760} X_{O_2} (5.8 \times 10^{-3}) \quad (\text{moles/l.})$$

where X_{O_2} is equal to the mole fraction of oxygen in the gas phase. This relation was obtained by equilibrating oxygen and nitrogen in the system with the degassed liquids. The vapor pressure of chlorobenzene used in this calculation was 67 mm.

Infrared analyses were performed on a Perkin-Elmer 237 spectrophotometer utilizing a 2.0-mm. cesium bromide cell and chloroform as solvent. Beer's law was obeyed by anthraquinone at 6.0 mμ with ϵ = 1080 l. mole⁻¹ cm.⁻¹.

Mass spectral analyses were conducted on a Consolidated Electrodynamics Corporation mass spectrometer Model 21-103 (modified C), equipped with an all-glass heated inlet CEC No. 134300. Voltages of 70 and 10 v. were employed with a 7-mil resolving slit and at 1.04- or 0.52-amp. magnetic current. Gas chromatography was performed on an FM 500 equipped with integrator. Columns (60 cm.) of 20% silicon rubber on Chromosorb P and a column of 20% Carbowax 20M-20% polyethylene glycol on Chromosorb P were utilized for analysis.

2. Anthracene Concentrations. Rate measurements in dilute anthracene (less than 0.1 M) were carried out in a three-necked flask equipped with gas dispersion tube and water-cooled condenser in a constant temperature bath (60.00 ± 0.05°). After anthracene–chlorobenzene (200 ml.) attained thermal equilibrium, a solution of AIBN (1–20 ml.) was added and samples were withdrawn and pipetted into an ice-cooled volumetric flask. The spectra of samples were then recorded on a Cary Model 14 from 4500 to 3000 Å. For anthracene concentrations below 2.0 × 10⁻⁵ M, a correction of the absorption due to AIBN at 3790 Å. was necessary: ϵ = 7.2 × 10³ for anthracene and ϵ = 5.5 for AIBN. Table V presents the results of a typical experiment.

Table V. Typical Kinetic Data for Anthracene Disappearance[a]

Time, sec.	Ab[b]	Ab₁/Ab₂	$k' \times 10^4$, sec.⁻¹
78	0.604	1.000	
918	0.431	1.403	4.20
1848	0.304	1.978	3.85
2766	0.220	2.748	3.76
4518	0.108	5.585	3.86
5820	0.064	9.435	3.91
		Mean =	3.91

[a] [Anthracene]₀ = 1.90 × 10⁻⁵ M, [AIBN] = 3.71 × 10⁻³ M; solvent purified by AIBN pretreatment (7.5 g./l.). [b] Absorptions (Ab) were measured in 5.0-cm. cells and were corrected for AIBN absorption (0.100 absorption units).

3. Anthracene Chain Product. For the data in Table II the absorption of gas was quenched by cooling the solution to room temperature, and the sample was quantitatively transferred from the gas absorption cell for the spectrophotometric analysis of anthracene or for the iodometric analysis of peroxide.[21] The transfers required that the solids be rinsed from the cell with chlorobenzene or acetic acid, respectively.

The solubility of the products was determined on large samples (200 ml.) which had been oxidized in the three-necked flask as described in the previous section. The solution was cooled to −5° and rapidly filtered. The filtrate was then analyzed for anthracene and peroxide. This procedure was repeated several times, the volume of the filtrate being reduced before each cooling by removal of one-half of the chlorobenzene *in vacuo* at room temperature. Constant values of 0.385 M peroxide and 0.045 M anthracene were obtained in the filtrate after each evaporation and removal of solids.

Complete evaporation of the solvent at room temperatures yielded a dark yellow residue, the infrared spectrum of which indicated carbonyl materials (5.95 to 6.04 μ) present in small amounts (less than 10%) by comparison with anthraquinone, anthrone, oxanthrone, and bromanthrone. Repeated attempts were made to purify this yellow residue by recrystallization from various solvents such as carbon disulfide, benzene, chloroform, pentane, and methanol or the mixtures of these solvents. However, no crystalline material was obtained.

(17) R. G. W. Norrish and S. P. Simmons, *Proc. Roy. Soc.* (London), **A250**, 4, (1959), report a value of 3 for the chain-transfer constant of polystyryl radical with anthracene at 50°.

(18) F. R. Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943), reports a value of 5 × 10⁻⁵ for the constant for chlorobenzene at 100°. This constant should be one-fifth to one-tenth as large at 60° in analogy with data for benzene at 50 and 100°.

(19) E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

(20) M. Szwarc and J. H. Binks, Special Publication No. 12, The Chemical Society, London, 1959, p. 262.

(21) J. S. Fritz and G. S. Hammond, "Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 278.

Since isolation of the products was not successful, the following two reductive techniques were used on the reaction mixture.

(a) *Reaction with Sodium Hydroxide–Sodium Dithionate.* A reaction mixture originally containing 3.03 mmoles of anthracene and 1.8 mmoles of AIBN absorbed 0.94 mmole of oxygen in 237 min. Ultraviolet analysis indicated that 1.0 mmole of anthracene had been consumed. This mixture was shaken with a 5% sodium hydroxide–5% sodium dithionate solution. The red-colored aqueous layer (A) was separated from the chlorobenzene layer (B) and was then air blown; a yellow solid separated as the solution discolored. The yellow solid was then dissolved in benzene and transferred to a tared flask, and the solvent was evaporated to yield 132 mg. of a yellow solid. This solid contained 61% anthraquinone (0.39 mmole) by infrared analysis at 6.02 mμ, and 10.6% (0.08 mmole) anthracene by the absorption at 3790 Å. Mass spectral analysis (Table VI) indicated 62% (0.394 mmole)

Table VI. Mass Spectral Data on Product from Autoxidation of Anthracene

Sample	Wt., mg.	Mass	Counts	Counts/ mg.	Temp., °C.
Reference Spectra					
Anthraquinone	3.5	208	12,240	3,500	310
	1.2	208	4,270	3,550	310
Anthrone	3.45	194	20,790	6,025	320
Anthracene	3.5	178	41,700	11,920	320
	2.5	178	29,400	11,750	315
	1.45	178	18,870	12,950	316

Wt., mg.	Mass	Counts	Total mmoles in sample	Temp., °C.
NaOH–Na$_2$SO$_4$ Reduction				
Chlorobenzene layer (B) (708.1 mg.)				
1.6	178	11,400	2.280	317
	194	155	0.069	
	208	563	0.374	
			2.723	
Aqueous layer (A) (132.1 mg.)				
2.6	178	4,000	0.091	318
	194	681	0.028	
	208	5,800	0.394	
			0.513	
LiAlH$_4$ Reduction (896.3 mg.)				
3.3	178	18,000	2.22	318
	194	2,343	0.55	
	208	1,242	0.45	
			3.22	

anthraquinone mass 208, 12.3% (0.091 mmole) anthracene mass 178, and 4.2% (0.028 mmole) anthrone mass 194.

Evaporation of the chlorobenzene layer (B) yielded 708.1 mg. of a pale yellow solid. Ultraviolet analysis indicated 45.4% (0.180 mmole) anthracene. Mass spectral analysis at 315° indicated 57.0% (2.28 mmoles) anthracene, 1.9% (0.069 mmole) anthrone, and 10% (0.374 mmole) of anthraquinone.

(b) *Reaction with Lithium Aluminum Hydride.* A reaction mixture originally containing 3.14 mmoles of

anthracene and 1.81 mmoles of AIBN which had adsorbed 1.0 mmole of oxygen in 230 min. was added to 250 mg. of LiAlH$_4$ in 500 ml. of ether. The solution was stirred for 1 hr., a slurry of H$_2$O–Na$_2$SO$_4$ was added, the solution was filtered, and the filtrate was evaporated in a tared flask. The weight of the residue was 896.3 mg. and ultraviolet analysis indicated 41.2% anthracene (2.08 mmoles). Mass spectral analysis at 315° indicated 44.3% (2.22 mmoles) anthracene, 11.8% (0.55 mmole) anthrone, and 10.6% (0.45 mmole) anthraquinone.

4. Oxidation of AIBN in Chlorobenzene. Air was bubbled through a solution of 42.0 g. of AIBN in 2000 ml. of chlorobenzene for 5 days at 65–70°. The solution was filtered and evaporated *in vacuo* at room temperature to leave 45.2 g. of an amber-colored viscous oil. Vapor phase chromatography of the oil on silicone rubber programmed from 60 to 250° at 11°/min. revealed a minimum of nine components. One component had the same retention temperature as chlorobenzene (100°). The oil contained 10.74 ± 0.06% chlorine by weight as determined by the sealed-tube sodium peroxide method; less than one-sixth of this amount (1.73 ± 0.07%) was found to be in the form of chlorobenzene, as determined by v.p.c.

On subjection of the oil to mass spectral analysis at 10 and 70 e.v., the results in Table VII were obtained.

Table VII. Mass Spectral Data

Mass	Unreduced (1.28 mg.) run		LiAlH$_4$-reduced (1.24 mg.) run	
	Counts (10 v.)	Counts (70 v.)	Counts (10 v.)	Counts (70 v.)
Products from Oxidation of AIBN in Chlorobenzene				
224	707	1740	1299	2769
222	1110	2580	1992	4400
197	60	100	45	75
195	177	288	74	122
152	..	2055	34	3600
130	154	980	189	735
128	480	3140	529	2184
114	140	536	62	337
112	425	1707	79	654
69	316	7270	248	1580
58	279	1500	175	3060

Mass	o-Cl (1.40 mg.)	m-Cl (1.43 mg.)	p-Cl (1.40 mg.)
Monochlorophenol Reference Spectrum, 70 v.			
130	10,500	1,215	4,470
128	32,500	3.800	13,800

A portion of the oil, 742.2 mg., was treated with 250 mg. of LiAlH$_4$ in 150 ml. of ether for 1 hr. A slurry of H$_2$O–Na$_2$SO$_4$ was added. The ether was then dried over Na$_2$SO$_4$ and evaporated at room temperature in a tared flask. A viscous oil, 462.7 mg., was obtained. Analysis by v.p.c. revealed less than 0.2% chlorobenzene. Total chlorine analysis gave a value of 12.00%. The mass spectral analysis is listed in Table VII.

5. Oxidation of AIBN in Benzene. A solution of 20.0 g. of AIBN (0.1215 mole) in 400 ml. of benzene was air blown for 4 days at 65–70°. The solution was filtered and evaporated at room temperature to

yield 22.2 g. of an amber-colored oil. Gas chromatography on 20% Carbowax 20M-20% polyethylene glycol programmed from 100 to 250° at 11°/min. indicated a complex mixture with one of the peaks having the same retention temperature (150°) as biphenyl. Comparison with standard biphenyl solutions gave a value of 2.0 g. (0.0130 mole) of biphenyl.

A portion (13.5 g.) of the oil was chromatographed on acid-treated alumina with hexane and thirty-two 30-ml. fractions were collected. Fractions 3 to 7 were combined to yield 809.5 mg. of a white solid, m.p. 68.5–69.5°, with the characteristic odor of biphenyl. Admixture did not lower the melting point (69–70°) of pure biphenyl. The remaining fractions, consisting of oils containing small amounts of biphenyl (v.p.c.), were not further examined.

Metal Ion Decomposition of Hydroperoxides.
II. Kinetics and Mechanism of Cobalt Salt Catalyzed Decomposition of t-Butyl Hydroperoxide[1]

William H. Richardson

Contribution from the California Research Corporation, Richmond, California, and the Department of Chemistry, San Diego State College, San Diego, California. Received September 22, 1964

A thorough kinetic and product investigation of cobalt acetate tetrahydrate catalyzed decomposition of t-butyl hydroperoxide in acetic acid is reported. The order in cobalt salt varies with temperature. At 50, 60, and 70° the orders are 1.28, 1.52, and 1.39, respectively. The order in t-butyl hydroperoxide increases from 1.086 ± 0.007 to 1.17 ± 0.01 between 50 and 70°. Reaction products are acetone, methanol, methyl acetate, t-butyl alcohol, di-t-butyl peroxide, and oxygen. The effect of reactant concentrations on the yield of products was investigated. A mechanism, based on cobalt–hydroperoxide complexes, is proposed to explain the data. To determine the generality of this mechanism where the solvent does not complex strongly with the cobalt salt, the kinetics and products of cobalt 2-ethylhexanoate catalyzed decomposition of the t-butyl hydroperoxide in chlorobenzene were studied. The order in cobalt, at low concentrations, varies from 1.0 to 1.56 at 20°. With higher cobalt concentrations at 0°, the order varies from 1.5 to 0.05. First-order dependence on hydroperoxide is observed throughout. t-Butyl alcohol and oxygen are the major products and di-t-butyl peroxide and acetone are the minor products. These results are accommodated by the mechanism proposed for cobalt acetate catalysis in acetic acid.

Introduction

Some kinetic studies of cobalt ion-catalyzed decomposition of hydroperoxides have been reported[2]; however, all the data are not in agreement. Although there has been a considerable interest in reactions of hydroperoxides with metal ions, an adequate mechanism has been lacking.[3]

The first paper in this series reported a study of the irreversible Co(II) to Co(III) change by *t*-butyl hydroperoxide.[1] A kinetic and product study of cobalt-catalyzed hydroperoxide decomposition is now reported where both valence states are reactive. As an aid to formulating a general mechanism, we have studied the reaction in acetic acid and chlorobenzene, which differ widely in their complexing ability with cobalt. Decomposition of *t*-butyl hydroperoxide was studied primarily because complicating reactions such as hydration and rearrangement may be avoided with a tertiary alkyl hydroperoxide. Also, a direct comparison may be made with other investigations where *t*-butyl hydroperoxide was used.

Experimental

Materials. Reagent grade chemicals were used when available without further purification unless specified. Reagent grade acetic acid was further purified by distillation from chromic acid. Cobalt acetate tetrahydrate (Baker's reagent grade) was used throughout this investigation. We have found that anhydrous cobalt acetate is insoluble in glacial acetic acid in contrast to a previous report.[2] Also, *in situ* dehydration of the tetrahydrate by acetic anhydride caused precipitation from acetic acid solvent.[4] Ninety per cent *t*-butyl hydroperoxide (Lucidol Division, Wallace and Tiernan, Inc.) was purified by azeotropic distillation.[5] The purified hydroperoxide was shown to be 99.3% pure by iodometric titration.[1] Chlorobenzene was first dried over Drierite and the residual water

(1) Part I: W. H. Richardson, *J. Am. Chem. Soc.*, 87, 247 (1965).

(2) (a) H. Tomišha, *Collection Czech. Chem. Commun.*, 27, 1549 (1962); (b) H. Kropf, *Ann.*, 637, 111 (1960); (c) E. Dyer, K. R. Carle, and D. E. Weiman, *J. Org. Chem.*, 23, 1464 (1958); (d) M. H. Dean and G. Skirrow, *Trans. Faraday Soc.*, 54, 849 (1958); (e) A. E. Woodward and R. B. Mesorbian, *J. Am. Chem. Soc.*, 75, 6189 (1953); (f) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948).

(3) For a review see A. G. Davies, "Organic Peroxides," Butterworth and Co. (Publishers), Ltd., London, 1961, Chapter 12.

(4) J. Z. Pasky, unpublished results.

(5) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, 80, 1398 (1958).