[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Oxidation of Unsaturated Compounds. IV. Kinetics of the Reaction of Indene with Oxygen; Evidence of the Identity of Active Intermediates in Thermal and Catalyzed Oxidations

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The reaction of indene and oxygen, which yields a low molecular weight polymeric peroxide, has been investigated at 50° in the presence and absence of α,α'-azodiisobutyronitrile, at atmospheric and reduced pressures, and in the presence and absence of inert diluents. The observed kinetics demonstrate that the reaction in the absence of free radical initiators involves the same active intermediates, alkyl and peroxy radicals, present in the initiated reaction. These kinetics are consistent with a thermal initiation reaction between indene and oxygen molecules to produce two free radicals or a diradical. The thermal initiation reaction that occurs during the oxidation of other olefins is discussed.

The copolymerization of styrene (S) and oxygen in the absence of a catalyst follows closely the rate expression

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k[\mathrm{S}]^{1.5}[\mathrm{O}_2]^{0.5}$$

while in the presence of 0.001–0.1M α,α'-azodiisobutyronitrile (AIBN) the kinetic equation followed is[1]

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k'[\mathrm{S}][\mathrm{AIBN}]^{0.5}$$

These observations suggest an initiation reaction between styrene and oxygen molecules producing two free radicals and that the complete rate expression is

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k''[\mathrm{S}]\mathrm{R}_i^{0.5} = k''[\mathrm{S}](k_i[\mathrm{AIBN}] + k_i'[\mathrm{O}_2][\mathrm{S}])^{0.5} \quad (1)$$

where R_i is the rate of initiation, and k_i and k_i' are the rate constants for the initiation reactions. The fact that a linear relationship between the rate of oxidation and $[\mathrm{AIBN}]^{0.5}$ was observed[1] may mean that (1) is correct and that $k_i[\mathrm{AIBN}] >> k_i'[\mathrm{O}_2][\mathrm{S}]$, or alternatively, that (1) is incorrect and the complete kinetics are

$$-\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k'[\mathrm{S}][\mathrm{AIBN}]^{0.5} + k[\mathrm{S}]^{1.5}[\mathrm{O}_2]^{0.5} \quad (2)$$

Equation 1 is easily derived if both the thermal and catalyzed oxidation reactions involve the same active intermediates (see Discussion). On the other hand, it has been suggested that for oxidations where rate expressions similar to (2) are observed thermal and catalyzed oxidations do not involve common intermediates.[2a]

Mulcahy and Watt have concluded recently that the oxidation of benzaldehyde in the presence of benzoyl peroxide, at constant benzaldehyde and oxygen concentrations, obeys the rate expression

$$-\mathrm{d}[\mathrm{BzH}]/\mathrm{d}t = R_0 + k[\mathrm{Bz}_2\mathrm{O}_2]^{0.5}$$

where R_0 is the thermal rate of oxidation, and that benzoyl and perbenzoate radicals are not involved in the thermal oxidation.[2] Since it was suggested that other thermal oxidations might proceed by a mechanism not involving alkyl or peroxy radicals,[2a] the copolymerization of oxygen with an olefin was investigated under conditions where contributions to the total rate of oxidation by the catalyzed and thermal reactions were about equal. The effect of oxygen pressure, AIBN and indene concentrations were thus investigated in the oxidation of indene at 50°.

Results and Discussion

Rate of Oxidation of Indene.—Indene, when shaken in an oxygen atmosphere in the presence or absence of AIBN at 50°, absorbs oxygen at a constant rate that is independent of the amount of oxygen absorbed up to at least one-fourth mole per cent. oxidation for the thermal reaction and two mole per cent. oxidation for the reaction performed in the presence of 0.01M AIBN. The product of the reactions is essentially a 1:1 copolymer of indene and oxygen.[3] In Table I are summarized the rates of oxidation observed at various indene and AIBN concentrations and at various oxygen pressures. Other experiments demonstrated that an increase or a decrease in the amount of agitation did not affect the rate of oxidation observed. Thus, the rates of oxidation summarized in Table I are not complicated by diffusion controlled processes.

TABLE I

OXIDATION OF INDENE AT 50°

[Indene][a]	[AIBN][a]	Oxygen press., mm.[b]	Rate[c]	Rate/ $[\mathrm{RH}]^{1.5}$-$[\mathrm{O}_2]^{0.5}$ [d]	Rate/ [RH]-$[\mathrm{AIBN}]^{0.5}$ [e]	Calcd. rate[c,f]
8.35	0	750	0.0342	5.17	....	0.035
8.35	0	750	.0339	5.13	....	.035
8.35	0	618	.0301	5.05	....	.032
8.35	0	587	.0296	5.05	....	.031
8.35	0	486	.0277	5.18	....	.028
8.35	0	426	.0261	5.22	....	.027
6.68[g]	0	750	.0229	4.84	....	.025
4.18[g]	0	750	.0115	4.90	....	.012
8.35	0.0005	750	.0398	..	0.0203	.039
8.35	.0025	750	.0500	..	.0126	.052
8.35	.0050	750	.0608	..	.0103	.062
8.35	.0100	750	.0809	..	.0970	.080
8.35	.0150	750	.0950	..	.0928	.095
8.35	.0050	443	.0540	..	.0915	.058
4.18[g]	.0100	750	.0341	..	.0790	.038

[a] Moles liter^{-1}. [b] Corrected for the vapor pressure of indene. [c] Moles liter^{-1} hr.$^{-1}$. [d] Liter$^{0.5}$ moles$^{-0.5}$ mm.$^{-0.5}$ hr.$^{-1}$. [e] Liter$^{0.5}$ moles$^{-0.5}$ hr.$^{-1}$. [f] Calculated from equation 3. [g] Bromobenzene diluent.

From Table I, column 5, it is seen that in the absence of a catalyst the rate law obeyed is similar to the rate law observed in the thermal oxidation of styrene.[1] The data indicate that the rate is proportional to $[\mathrm{RH}]^{1.6}[\mathrm{O}_2]^{0.46}$. However, in the presence of 0.0005–0.015M AIBN the rate of oxidation

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(1) A. A. Miller and F. R. Mayo, THIS JOURNAL, **78**, 1017 (1956).

(2) (a) M. F. R. Mulcahy and I. C. Watt, *Proc. Roy. Soc.* (*London*), **216A**, 10, 30 (1951); *J. Chem. Soc.*, 2971 (1954); (b) see however, T. A. Ingles and H. W. Melville, *Proc. Roy. Soc.* (*London*), **218A**, 175 (1953).

(3) G. A. Russell, THIS JOURNAL, **78**, 1035 (1956).

of indene is not proportional to [RH][AIBN]$^{0.5}$ (column 6).

That (1) correctly summarizes the kinetics of the oxidation of indene and that (2) is incorrect was demonstrated by plotting rate and (rate)^2 as functions of [AIBN]$^{0.5}$ and [AIBN] for the oxidation of indene (8.35 *M*) at 750 mm. oxygen pressure. A definite curvature occurs in the plot of rate *versus* [AIBN]$^{0.5}$ as would be expected from (1) but not from (2). Moreover, a plot of (rate)^2 *versus* [AIBN] gave a straight line in agreement with (1) and not with (2).

The kinetics demanded by (1) are consistent with the following chain reaction wherein *e* represents the efficiency of the radicals from the catalyst (R·′) in initiating oxidation chains containing alkyl or alkenyl radicals (R·) and peroxy radicals (ROO·).[4]

$$\text{AIBN} \xrightarrow{k_i} 2\text{R}\cdot' \xrightarrow[\text{O}_2 + \text{RH}]{\text{RH or}} 2e\text{R}\cdot$$

$$\text{O}_2 + -\text{CH}_2\text{CH}{=}\text{CH}_2- \xrightarrow{k_i'} -\text{CH}_2\underset{\cdot}{\text{C}}\text{HCH}_2\text{OO}\cdot \ (\text{or HOO}\cdot + \text{R}\cdot)$$

$$\text{R}\cdot + \text{O}_2 \xrightarrow{\text{very fast}} \text{ROO}\cdot$$

$$\text{ROO}\cdot + -\text{CH}_2\text{CH}{=}\text{CH}_2- \xrightarrow{k_3} -\text{CH}_2\underset{\cdot}{\text{C}}\text{HCH}_2\text{OOR}$$

$$\phantom{\text{ROO}\cdot + -\text{CH}_2\text{CH}{=}\text{CH}_2-} \xrightarrow{k_3'} \text{ROOH} + -\underset{\cdot}{\text{C}}\text{HCH}{=}\text{CH}_2-$$

$$2\text{ROO}\cdot \xrightarrow{k_6} \text{non-radical products}$$

At steady state conditions the rate of initiation (R_i)

$$R_i = 2ek_i[\text{AIBN}] + 2k_i'[\text{O}_2][\text{RH}]$$

is equal to the rate of removal of radicals by termination (R_t)

$$R_t = 2k_6[\text{ROO}\cdot]^2$$

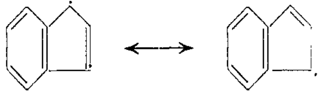
Rate expression 3 is obtained by solving these expressions for [ROO·] and substituting the result into the expression for the rate of disappearance of indene

$$-\text{d}[\text{RH}]/\text{d}t = (k_3 + k_3')k_6^{-0.5}[\text{RH}]\{ek_i[\text{AIBN}] + k_i'[\text{O}_2][\text{RH}]\}^{0.5} \quad (3)$$

From the slope and intercept of the straight line obtained by plotting (rate)^2 as a function of [AIBN] at constant hydrocarbon concentration and oxygen pressure, $ek_i(k_3 + k_3')^2k_6^{-1}$ is calculated to be 7.54×10^{-3} l. mole^{-1} hr.$^{-2}$ and $k_i'(k_3 + k_3')^2k_6^{-1}$ to be 2.86×10^{-9} l. mole^{-1} hr.$^{-2}$ mm.$^{-1}$. The rate constant for the production of free radicals from AIBN, $2k_i$, is known to be 1.9×10^{-4} hr.$^{-1}$ at 50° in benzene solution.[5,6] Provided that the rate of initiation is equivalent to the rate of production of free radicals from AIBN ($e = 1$), it can be calculated that $(k_3 + k_3')/k_6^{-0.5}$ is 8.90 l.$^{0.5}$ mole$^{-0.5}$ hr.$^{-0.5}$ and k_i' is 3.60×10^{-11} mm.$^{-1}$ hr.$^{-1}$.

As shown in Table I, columns 4 and 7, good agreement was found between the experimentally measured rates of oxidation and the rate of oxidation calculated from (3) with the above constants. At lower oxygen pressures the rate expression is probably more complex than (3) because termination can involve interactions of alkyl radicals and peroxy radicals.[4]

Since the ratio of $k_3:k_3'$ is at least 4:1,[3] $k_3k_6^{-0.5}$ is not less than 5.1 and $k_3'k_6^{-0.5}$ is not more than 1.3 l.$^{0.5}$ mole$^{-0.5}$ hr.$^{-0.5}$ at 50°. The values of $k_3k_6^{-0.5}$ determined in the oxidation of styrene, 1,1-diphenylethylene and methyl methacrylate at 50°, are 5.4, 2.3, and 0.5 l.$^{0.5}$ mole$^{-0.5}$ hr.$^{-0.5}$, respectively.[7] Comparable values of $k_3'k_6^{-0.5}$ have been determined at 45° in the presence of benzoyl peroxide for numerous olefins that are oxidized to hydroperoxides.[8] These results indicate that the value of $k_3'k_6^{-0.5}$ for allylbenzene is only 0.06 l.$^{0.5}$ mole$^{-0.5}$ hr.$^{-0.5}$. Thus, cyclization of allylbenzene into indene, a molecule which can give an aralkenyl radical having two equivalent resonance structures,



may increase the reactivity of the α-methylene group considerably.

It is interesting to compare the rate of polymerization of indene with the rate of copolymerization of indene and oxygen. Gutmann has pointed out that in the absence of an added catalyst the latter reaction is about as fast at 40° as the thermal polymerization at 150°.[9] Even in the presence of a free radical initiator the rate of indene disappearance is much greater for the copolymerization with oxygen than for polymerization. Thus, at 50° in the presence of 0.01 *M* AIBN and oxygen at 750 mm., indene is consumed at a rate of 0.4% hr.$^{-1}$ while it can be calculated from the data of Breitenbach and Schindler that the rate of polymerization of indene containing 0.016 *M* AIBN is about 0.06% hr.$^{-1}$ at 50°.[10] These results point out the error of the generality that oxygen inhibits vinyl polymerization since in this particular case oxygen does not act as an inhibitor, but as an active copolymerization agent, and the rate of indene consumption is greater in the presence than in the absence of oxygen. For some other vinyl monomers (*e.g.*, methyl methacrylate) the reverse effect has been noted.[7]

Mechanism of the Thermal Initiation Reaction.—The product and mechanism of the initial reaction of oxygen with non-polymerizable olefins, where the major oxidation product is a hydroperoxide, has been widely discussed.[11] Three distinct reactions

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[4] Analogous reaction sequences have been suggested for the oxidation of olefins (J. L. Bolland, *Quart. Revs.* (*London*), **3**, 1 (1949); L. Bateman, *ibid.*, **8**, 147 (1954)) and aralkyl hydrocarbons (G. A. Russell, THIS JOURNAL, **77**, 4583 (1955)) at "high" oxygen pressures.

[5] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

[6] The rate of production of free radicals from AIBN is not necessarily twice the rate of decomposition of AIBN (G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955)).

[7] A. A. Miller, F. R. Mayo and G. A. Russell, unpublished results.

[8] J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).

[9] V. Gutmann, *J. Polymer Sci.*, **3**, 336 (1948).

[10] J. W. Breitenbach and A. Schindler, *Monatsh.*, **83**, 271 (1952).

[11] (a) E. H. Farmer, G. F. Bloomfield, A. Sundralingam and D. A. Sutton, *Trans. Faraday Soc.*, **38**, 348 (1942); E. H. Farmer, *ibid.*, **42**, 228 (1946); (b) J. L. Bolland and G. Gee, *ibid.*, **42**, 236, 244 (1946); (c) F. D. Gunstone and T. P. Hilditch, *J. Chem. Soc.*, 1022 (1946); T. P. Hilditch, *Nature*, **166**, 558 (1950); (d) N. A. Khan, *Can. J. Chem.*, **32**, 1149 (1954); *J. Chem. Phys.*, **22**, 2090 (1954); (e) R. S. Morrell and S. Marks, *J. Oil and Colour Chemists' Assoc.*, **12**, 183 (1929); T. P. Hilditch, *ibid.*, **30**, 1 (1947); R. S. Morrell and S. Marks, *J. Soc. Chem. Ind.*, **50**, 27T (1931); **55**, 237T (1936); T. R. Bolam and W. S. Sim, *ibid.*, **60**, 50T (1941); (f) L. Bateman, H. Hughes and A. L. Morris, *Disc. Faraday Soc.*, **14**, 190 (1953); L. Bateman, *Quart. Revs.* (*London*), **8**, 147 (1954); *J. Chem. Phys.*, **22**, 2090 (1954).

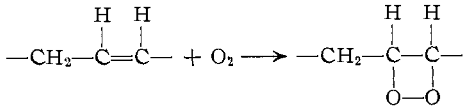
have been proposed. Farmer[11a] and Bolland[11b] have suggested the direct reaction of oxygen with the olefin to yield a diradical or two radicals

$$RCH_2CH{=}CHR + O_2 \longrightarrow RCH_2\underset{\cdot}{C}HCHROO\cdot \text{ (or } HOO\cdot + R\underset{\cdot}{C}HCH{=}CHR)$$

Farmer also considered the possibility of direct formation of hydroperoxide in a one step reaction[11a] and Hilditch[11c] and Khan[11d] have supported this suggestion.

$$RCH_2CH{=}CHR + O_2 \longrightarrow [RCH_2\underset{\cdot}{C}HCHROO\cdot] \longrightarrow RCH{=}CHCHROOH$$

Another proposal has been that the olefin and oxygen react to form a cyclic peroxide.[11c,e]



$$-CH_2-\overset{H}{C}{=}\overset{H}{C}- + O_2 \longrightarrow -CH_2-\underset{O-}{\overset{H}{C}}-\underset{-O}{\overset{H}{C}}-$$

All three of these reactions will explain the autocatalysis observed in the oxidation of olefins since presumably all of these peroxidic products can dissociate into free radicals.

Bateman has concluded that the direct reaction of oxygen and an olefin has never been observed kinetically because of complications arising from the presence of small amounts of peroxidic impurities and autocatalysis of the oxidation.[11f] In the oxidation of indene the hydrocarbon was chromatographically filtered over activated silica gel directly before oxidation and all peroxide tests performed on the hydrocarbon were negative. In Fig. 1 are summarized experimental data which indicate the absence of autocatalysis during the initial stages of the oxidation of indene performed in the absence and presence of AIBN. Therefore, it is believed that the direct reaction of oxygen with indene has been observed. This reaction is probably less complicated than the direct reaction of an olefin like methyl linoleate with oxygen because it occurs more readily and because the polymeric peroxides formed are poor oxidation initiators at 50°.

Of the three suggested initial thermal reactions[11] only the first can give kinetics consistent with (1) at oxygen pressures where alkyl radicals are not involved in the termination reactions.[12] If the thermal reaction involved the direct formation of hydroperoxide, or a cyclic peroxide with an appreciable thermal stability,[12] (2) would be followed. Thus, the kinetics observed in the oxidation of indene not only demonstrate that the thermal and initiated oxidations involve the same active intermediates but that the thermal initiation reaction most likely involves the reaction of indene with oxygen to produce free radicals directly.

Presumably a similar initiation reaction occurs in the thermal oxidation of non-polymerizable olefins such as methyl linoleate or linolenate. In fact, reported kinetic data support this conclusion. The oxidation of methyl linolenate at 50° apparently follows (1) and not (2). The most careful work[13] indicates that a plot of rate *versus* $[AIBN]^{0.5}$ involves a slight curvature, although rate measurements have not been reported at very low AIBN concentrations where this effect would be more easily observed. Similarly, the benzoyl peroxide-catalyzed oxidation of methyl oleate, squalene and ethyl linoleate apparently follow (1) and not (2). Here again, the thermal rate of oxidation cannot be ignored and linear relationships are obtained when $(\text{rate})^2$ is plotted as a function of $[Bz_2O_2]$.[11b]

Experimental

Purification of Indene.—Barrett technical grade indene (1 kg.) was shaken with 6 *N* hydrochloric acid for 24 hours (to remove basic nitrogenous material) and refluxed with 40% sodium hydroxide for two hours (to remove benzonitrile).[14] Rectification of the material thus treated through a Podbielniak column (<50 plates) did not give pure samples of indene. Appropriate fractions obtained in the rectification were combined, and about one-half of the material crystallized. The higher-melting fraction (490 g.) was converted to its sodium salt by sodium amide (126 g.)[15] under a nitrogen atmosphere and the reaction mixture stirred for three hours at 120°. Unreacted organic materials were removed by distillation at 1 mm. and a pot temperature of 120°. The sodium salts were hydrolyzed with water and the organic fraction separated by steam distillation. Upon rectification through the Podbielniak column, 140 g. of pure indene was obtained having a constant b.p., $n^{20}D$ 1.5763; lit.[14,16] 1.5763-1.5764. The freezing point of this material was determined with a calibrated 9-junction copper-constantan thermocouple and a Rubicon portable potentiometer, and found to be −1.22 to −1.59°; lit. m.p. −1.80,[3] −1.50.[14] The indene was further purified before

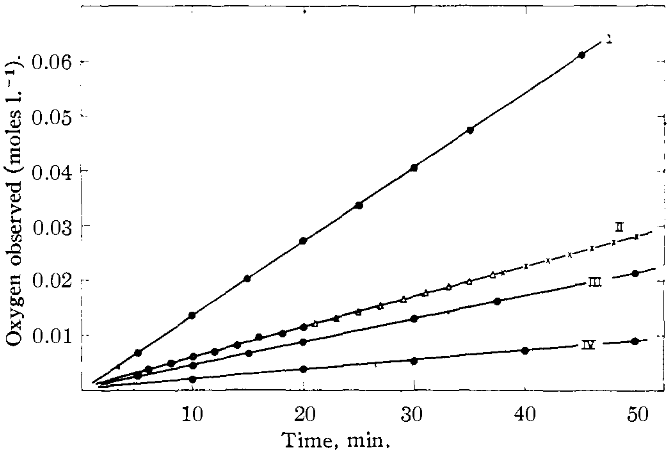


Fig. 1.—Oxidation of indene at 50°: I, 0.01 *M* AIBN, 750 mm. oxygen; II, 750 mm. oxygen, shaking rate 234 (●), 194 (△) and 160 (×) cycles/minute; III, 426 mm. oxygen pressure; IV, 750 mm. oxygen pressure, 50 volume % bromobenzene.

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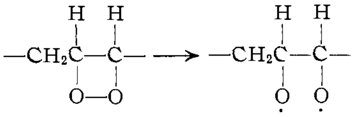
[12] If the cyclic peroxide decomposes to a diradical that can initiate oxidation chains,



$$-CH_2\underset{O-}{\overset{H}{C}}-\underset{-O}{\overset{H}{C}}- \longrightarrow -CH_2\underset{\underset{\cdot}{O}}{\overset{H}{C}}-\underset{\underset{\cdot}{O}}{\overset{H}{C}}-$$

and if the steady state concentration of the cyclic peroxide is established very rapidly, this thermal reaction would also be consistent with (1).

[13] W. Kern and H. Willersinn, *Makromol. Chem.*, **15**, 1, 15, 36 (1955).

[14] E. S. Naidus and M. B. Mueller, THIS JOURNAL, **72**, 1829 (1950).

[15] R. Weissgerber, *Ber.*, **42**, 569 (1909).

[16] E. H. Smoker and P. E. Burchfield, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 128 (1943).

oxidation by passage through a column packed with 60–200 mesh activated silica gel under a nitrogen atmosphere.

Oxidation Procedure.—Oxidations were performed in a closed system using 10 ml. of indene ($d^{50}{}_4$ of indene used, 0.9696). A vigorously shaken modified 25-ml. erlenmeyer flask was used. The oxidation flasks were maintained in a constant temperature bath fairly well shielded from light. The oxygen absorption was followed by a manually controlled gas buret filled with mercury. The oxygen used was of high purity and has been described previously.[1]

The preparation of solutions of indene containing known amounts of AIBN was accomplished by adding the desired amount of a benzene solution of recrystallized AIBN (m.p. 104–105°) to the reaction flask, removing the benzene under reduced pressure and adding the desired amount of freshly chromatographed indene. The flask was cooled by Dry Ice and evacuated and filled with oxygen several times. It was then placed in the water-bath and allowed to come to thermal equilibrium. After a period of about five minutes, shaking was commenced and the oxygen absorption followed by use of the gas buret.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Effect of Oxygen on the Decomposition of α,α'-Azodiisobutyronitrile and Benzoyl Peroxide in Aromatic Solvents

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A method is described whereby the rate of decomposition of certain initiators can be determined from the rate of reaction of appropriate aromatic hydrocarbons with oxygen. The major limitation of this method is that the hydrocarbon must be capable of forming a hydroperoxide of considerable stability at a temperature where the initiator has a half-life of only a few hours. Oxygen was found to have no effect on the rate of decomposition of α,α'-azodiisobutyronitrile in cumene or ethylbenzene solutions at 80° whereas the over-all rate of decomposition of benzoyl peroxide in cumene at 100° was retarded by oxygen. Relative initiation efficiencies can be calculated readily from the data obtained in the oxidations of a hydrocarbon initiated by several free radical sources.

In connection with other work in this Laboratory[1] it was of interest to determine whether oxygen affected the rate of decomposition of α,α'-azodiisobutyronitrile (AIBN). This determination is complicated by the reaction of oxygen with the decomposition products[2] and with many of the conventional free radical traps.[3]

This paper demonstrates how the rate of decomposition of an initiator may be obtained from the rate of oxidation of a hydrocarbon. This procedure has been to measure the rate of decomposition of AIBN in cumene and ethylbenzene at 80° and benzoyl peroxide in cumene at 100°.

The results indicate that the rate of decomposition of AIBN is not affected by the presence of oxygen whereas oxygen retards the over-all rate of decomposition of benzoyl peroxide.

Procedure.—The catalyzed oxidations of aralkyl hydrocarbons, such as cumene, in the presence of oxygen at about 760 mm. and 80–100°, yield hydroperoxides by the following reaction sequence[4]

$$\mathrm{I} \xrightarrow{k_i} 2e\mathrm{R}'\cdot$$

$$\mathrm{R}\cdot + \mathrm{O}_2 \xrightarrow{\text{very fast}} \mathrm{RO}_2\cdot$$

$$\mathrm{RO}_2\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{RO}_2\mathrm{H} + \mathrm{R}\cdot$$

$$2\mathrm{RO}_2\cdot \xrightarrow{k_6} \text{non-radical products}$$

where R· and $\mathrm{RO}_2\cdot$ represent alkyl and peroxy radicals and e is the efficiency, which may vary from 0 to 1, of the initiator (I) in producing radicals (R'·) that start oxidation chains. The rate expression expected from the above reaction sequence is

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = k_3k_6^{-0.5}[\mathrm{RH}](2ek_i[\mathrm{I}])^{0.5} \qquad (1)$$

Since the concentration of I at any time is $[\mathrm{I}]_0 \exp(-k_it)$, (1) can be written

$$-\mathrm{d}[\mathrm{O}]_2/\mathrm{d}t = k_3k_6^{-0.5}[\mathrm{RH}](2ek_i[\mathrm{I}]_0)^{0.5} \exp(-k_it/2) \qquad (2)$$

Provided that [RH] and e remain constant (2) can be integrated but the resulting equation cannot be solved easily for k_i. Therefore (2) was thus solved in the following manner. A plot of the observed rate of oxidation ($\Delta[\mathrm{O}_2]/\Delta t$) as a function of time was made and a smooth curve drawn from which the rate of oxidation at a given time could be read. The log of the rate was then plotted as a function of time since, if e and [RH] remain constant, it follows from (2) that the $\log_{10}$ of the rate as a function of time should give a straight line having a slope of $-k_i/2(2.303)$ and an intercept at zero time equal to $\log A$ where

$$A = k_3k_6^{-0.5}[\mathrm{RH}](2ek_i[\mathrm{I}]_0)^{0.5}$$

Decomposition of AIBN.—In Fig. 1 a plot of oxygen absorption as a function of time is given for the oxidation of cumene, originally 0.0094 M in AIBN, at 80°. The purification of reagents and the technique employed to measure the oxygen absorption have been described previously.[1,4] The reported[2] half-life of AIBN in toluene at 80° in the absence of oxygen is 1.2 hr. and the curve in Fig. 1 for the AIBN concentration has been calculated from this value. In Fig. 1 the rate of oxidation does not approach zero as the initiator concentration diminishes to a very low value, presumably because of autocatalysis of the oxidation by cumene hydroperoxide. Therefore (2) should be followed only during the early stages of the oxidation when the concentration of cumene hydroperoxide is small and the concentration of AIBN large.

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[1] A. A. Miller and F. R. Mayo, THIS JOURNAL, **78**, 1017 (1956); F. R. Mayo and A. A. Miller *ibid.*, **78**, 1023 (1956); G. A. Russell, *ibid.*, **78**, 1035, 1041 (1956).

[2] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

[3] See however, G. S. Hammond, J. N. Sen and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

[4] G. A. Russell, *ibid.*, **77**, 4583 (1955); **78**, 1047 (1956).