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]

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

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{\text{very fast}} \mathrm{RO_2}\cdot$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_3} \mathrm{RO_2H} + \mathrm{R}\cdot$$

$$2\mathrm{RO_2}\cdot \xrightarrow{k_6} \text{non-radical products}$$

where R· and RO$_2$· 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).

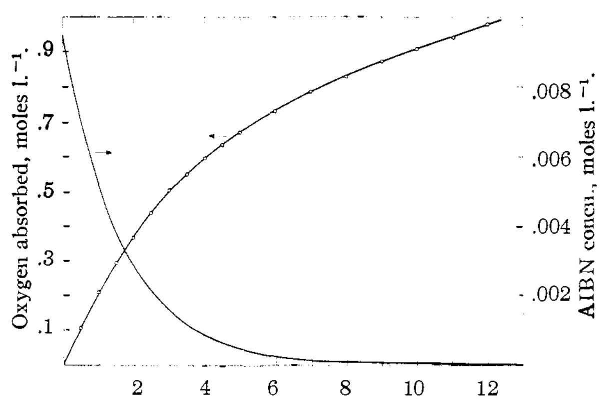

Fig. 1.—Oxidation of cumene catalyzed by AIBN at 80°.

A plot of the log of the rate of oxidation of cumene as a function of time (Fig. 2) gave a straight line over the first half-life of AIBN. From the slope of this line, −0.128 hr.$^{-1}$, a value for k_i of 0.59 hr.$^{-1}$ is calculated. Values of k_i between 0.59 and 0.61 were observed at other initial AIBN concentrations and other cumene concentrations (Table I). The reported rate constants for the decomposition of AIBN in the absence of oxygen are 0.60 hr.$^{-1}$ in toluene at 80.2[2] and 0.55 hr.$^{-1}$ in xylene at 80°.[5]

TABLE I

OXIDATION OF CUMENE, ETHYLBENZENE AND TOLUENE AT 80°

Hydrocarbon	$[RH]^a$	$[AIBN]_0{}^a$	$k_i{}^b$	A^c	$k_3(e/k_6)^{0.5d}$
Cumene	6.76	0.0094	0.59	0.241	0.34
Cumene	6.76	.0047	.59	.169	.35
Cumene	3.72^e	.0094	.60	.134	.34
Cumene	3.72^e	.0047	.61	.098	.36
Cumene^f	6.60	$.01025^g$	.90	.228	.25
Ethylbenzene	7.66	.0094	.63	.050	.062
Toluene	8.80	.0093	.72	.012	.012

[a] Mole l.$^{-1}$. [b] From slopes in Fig. 2, hr.$^{-1}$. [c] From intercepts in Fig. 2, mole l.$^{-1}$hr.$^{-1}$. [d] Mole$^{-0.5}$ l.$^{0.5}$, k_i taken as 0.60 hr.$^{-1}$. [e] Bromobenzene diluent. [f] 100°. [g] Benzoyl peroxide.

When the rate of decomposition of AIBN was measured in oxidizing ethylbenzene at 80° several of the complications present in the oxidation of cumene were removed. Since the oxidation was considerably slower, smaller amounts of hydroperoxide were formed and autocatalysis was no longer troublesome. Moreover, the hydrocarbon concentration was more nearly constant than in the cumene oxidations. However, a correction was necessary that could be ignored in the oxidation of cumene. The amount of nitrogen evolved by the decomposition of the azo compound was not insignificant when compared to the amount of oxygen absorbed in the oxidation of ethylbenzene and the observed decrease in gas volume had to be corrected.

In Fig. 2 a plot of the log of the rate as a function of time is shown for the AIBN-catalyzed oxidation of ethylbenzene where a linear relationship was followed up to 90% catalyst decomposition. The value of k_i calculated from the slope of this line is 0.63 hr.$^{-1}$.

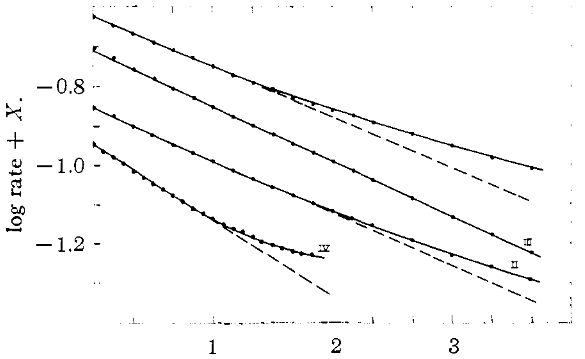

Fig. 2.—Log of the rate (mole l.$^{-1}$ hr.$^{-1}$) as a function of time for the catalyzed oxidation of cumene and ethylbenzene: I, 6.8 *M* cumene, 80°, $[\text{AIBN}]_0 = 0.0094$ *M*, $X = 0$; II, 3.7 *M* cumene, 80°, $[\text{AIBN}]_0 = 0.0047$ *M*, $X = 0.2$; III, 7.7 *M* ethylbenzene, 80°, $[\text{AIBN}]_0 = 0.0094$ *M*, $X = 0.6$; IV, 6.6 *M* cumene, 100°, $[\text{BP}]_0 = 0.01025$ *M*, $X = -0.3$.

Toluene was oxidized slowly at 80° in the presence of AIBN and its rate curve is open to considerable doubt since a correction amounting to about 30% had to be applied to the change in gas volume because of the nitrogen evolved in the decomposition of AIBN. The best straight line drawn through a plot of the log of the rate as a function of time gave a rather high value for k_i, 0.72 hr.$^{-1}$.

The conclusion that the presence of oxygen does not influence the rate of decomposition of AIBN is in agreement with the results of Hammond and Boozer which demonstrate that the rate of production of radicals from AIBN in chlorobenzene solution in the presence of oxygen is equivalent to the maximum rate of production of free radicals from AIBN in deoxygenated chlorobenzene solutions containing iodine.[3,6] It was demonstrated that iodine does not affect the rate of decomposition of AIBN, but from the results cited it cannot be stated definitely that oxygen does not affect the rate of decomposition of AIBN and that the fraction of AIBN molecules that produce free radicals upon decomposition is the same in the presence of either oxygen or iodine. However, the present results demonstrate that this is the case and that the rate of decomposition of AIBN is the same in the presence of either oxygen or iodine.

Decomposition of Benzoyl Peroxide.—The decomposition of benzoyl peroxide (BP) in cumene at 100° was also investigated. Here an appreciable effect of oxygen on the rate of decomposition was expected since BP is known to undergo an induced decomposition reaction

$$\text{R}\cdot + (\text{R'CO}_2)_2 \longrightarrow \text{R'CO}_2\text{R} + \text{R'CO}_2\cdot$$

Oxygen has been observed to retard the decomposition of BP in acetic anhydride solution[7] and the possibility that oxygen can completely eliminate induced decompositions (by converting alkyl to peroxy radicals) has been considered.[8]

A plot of the log of the rate of oxidation as a

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[5] F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

[6] C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3233 (1955).

[7] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

[8] J. L. Bolland, *Trans. Faraday Soc.*, **44**, 669 (1948).

function of time for the BP-catalyzed oxidation of cumene at 100° gave a linear relationship (Fig. 2) over somewhat more than the first half-life of the catalyst. Autocatalysis then became evident. The rate constant for the decomposition of BP calculated from the slope of this line is 0.90 hr.$^{-1}$. This value of the decomposition rate constant is considerably below the value of 1.35 hr.$^{-1}$ calculated from the data of Barnett and Vaughan for the decomposition of BP in cumene at 100° in the absence of oxygen.[9]

A comparison of the decomposition rate constants of BP, as calculated from the data of other workers, suggests that oxygen may indeed completely eliminate the induced decomposition reaction. Nozaki and Bartlett attempted to separate the unimolecular decomposition of BP from the induced decomposition by a kinetic method.[7] Their results indicate that the unimolecular reaction occurs at the same rate in many aromatic solvents. A decomposition rate constant for BP at 100° in the absence of induced decomposition of 1.53 hr.$^{-1}$ is suggested. Hammond has eliminated the induced decomposition of BP by the use of iodine as a radical trap.[10] The rate constant observed in benzene solution at 79° was 0.093 hr.$^{-1}$, which when corrected to 100° (E_{act} taken as 33.3 kcal. mole^{-1}) gives a decomposition rate constant of 1.39 hr.$^{-1}$. Data on the rate of decomposition of BP in dioxane solution containing 3,4-dichlorostyrene as a radical trap indicate a decomposition rate constant of 1.49 hr.$^{-1}$ at 100°.[11]

TABLE II

SUMMARY OF DECOMPOSITION RATE CONSTANTS FOR BENZOYL PEROXIDE

Solvent	Temp., °C.	Radical trap	k, hr.$^{-1}$	E_{act}, kcal. mole^{-1}	Calcd. k at 100°, hr.$^{-1}$	Ref.
Cumene	90	.....	0.429	31	1.35	9
Cumene	100	Oxygen	.90	..	0.90	This work
Benzene	79.8	.....	.118	33.3	1.53	7
Benzene	79	Iodine	.093	33.3	1.39	10
Dioxane	80	3,4-Dichlorostyrene	.151	31	1.49	11

It is not understood why the "true" unimolecular decomposition rate constant observed in cumene solution at 100° is considerably below the rate constants calculated for dioxane or benzene solutions. Errors in the energies of activation employed may be involved or there may be a solvent effect on the rate of the dissociation. The latter seems likely since even the over-all rate of decomposition of BP in cumene at 100° is below the rates calculated for the dissociation step in benzene or dioxane solutions at this temperature.

Initiation Efficiencies.—Some interesting calculations of relative initiation efficiencies can be made from the data of Table I in conjunction with the data of Melville and Richards on the oxidation of cumene.[12] As mentioned previously, the intercepts (A) of the straight lines of Fig. 2 are functions of several rate constants and the efficiency of initiation. If the value of $k_3k_6^{-0.5}$ is known the efficiency of initiation can be calculated from A, or if the value of $k_3k_6^{-0.5}$ is unknown, relative initiation efficiencies may be obtained.

In this manner it is calculated that AIBN is 1.5 times as efficient as α,α'-azocyanocyclohexane[12] in initiating oxidation chains in cumene at 80°. Moreover, the data indicate that at 100° BP is only 0.32 as efficient as α,α'-azocyanocyclohexane in initiating oxidation chains. In the oxidation of olefins not containing an aromatic nucleus BP is usually found to be more efficient than azo compounds as an oxidation initiator.[13] The low efficiency calculated for BP in initiating the oxidation of cumene may be connected with the fact that a substantial decomposition product of BP in cumene arises from substitution in the aromatic ring[14] and this process may not lead to the initiation of an oxidation chain.

In Table I values for $k_3(e/k_6)^{0.5}$ are listed for cumene, ethylbenzene and toluene. These values are in agreement with the relative oxidation rates obtained by other methods,[4] and probably involve differences not only in k_3 but also in k_6 and e.

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(9) B. Barnett and W. E. Vaughan *J. Phys. Colloid Chem.*, **51**, 942 (1947).

(10) G. S. Hammond, THIS JOURNAL, **72**, 3737 (1950).

(11) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

(12) H. W. Melville and S. Richards, *J. Chem. Soc.*, 944 (1954).

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

(14) C. S. Rondestvedt, Jr., and H. S. Blauchard, THIS JOURNAL, **77**, 1769 (1955).