

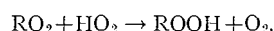
MERCURY-PHOTOSENSITIZED OXIDATIONS OF HYDROCARBONS

PART II. THE MERCURY-PHOTOSENSITIZED OXIDATION OF ISOBUTANE¹

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ABSTRACT

The mercury-photosensitized oxidation of isobutane has been studied over a wide range of pressures of the hydrocarbon and oxygen, in a conventional static photochemical apparatus at the temperatures of 30° C and 100° C. The main products of the reaction are tertiary butyl hydroperoxide, together with tertiary butyl alcohol, acetone, and corresponding small quantities of formaldehyde and methyl alcohol. Isobutyraldehyde was also detected; ditertiary butyl peroxide being notably absent. Peroxide yields suggest that a reaction between an excited isobutane molecule and oxygen is important in the initiation processes and that peroxide is formed in the reaction



INTRODUCTION

The mercury-photosensitized oxidations of methane, ethane, and propane have previously been studied in flow systems (1, 2, 3). The original classical concept of the peroxide chain reaction



occurring at 25° C was modified in the most recently published work of this type by Watson and Darwent (4), who explained the low yields of peroxide obtained in the ethane oxidation by suggesting the following reaction



as the source of hydroperoxide rather than reaction [19]. These workers found that the yields of peroxide decreased on raising the reaction temperature or on lowering the flow rate. They attributed these effects to thermal and photochemical decomposition of the peroxide. The hydroperoxide was characterized as ethyl hydroperoxide by Gray (1), and so this work provides no evidence on the nature of the mutual interaction of HO₂ radicals.

In an effort to elucidate further the nature of certain aspects of hydrocarbon oxidation mechanisms we have studied the mercury-photosensitized oxidation of isobutane in a static photochemical apparatus employing low light intensities.

EXPERIMENTAL

The apparatus and photochemical techniques employed were the same as those described in Part I (K. M. Bell and C. A. McDowell. *Can. J. Chem.* This issue). Using a modification of the ferrous thiocyanate method of Young, Voigt, and Nieuland (5), 5×10^{-9} mole of peroxides could be determined. The method is non-stoichiometric, and a calibration curve was prepared using purified solutions of tertiary butyl hydroperoxide. The hydroperoxide was also determined gas chromatographically, dinonyl phthalate on chromosorb being used as the column material. The other products were determined and identified by their characteristic elution times on different columns. Formaldehyde

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was estimated by the method of Bricker and Johnson (6). In all cases the final yield of product was limited by the slow removal of the mercury vapor (see Part I). The rate of removal was greater at 30° C than 100° C. For a mixture of 50 mm Hg of isobutane and 100 mm Hg of oxygen, Φ (the quantum yield of removal of excited 6^3P_1 Hg atoms) was 6×10^{-4} at 30° C and 2×10^{-4} at 100° C.

RESULTS

The main product of the oxidation was tertiary butyl hydroperoxide, together with smaller yields of tertiary butyl alcohol, acetone, methyl alcohol, formaldehyde, and isobutyraldehyde. Evidence was also obtained for a trace of isobutyl alcohol. Tests were specifically made for ditertiary butyl peroxide but none could be detected under conditions where the lower limit of detection corresponded to a quantum yield of 0.02. It is also to be noted that we were unable to detect isobutylene oxide despite several attempts using our gas chromatographic apparatus. Close agreement was obtained between the total peroxide determined colorimetrically, and tertiary butyl hydroperoxide determined gas chromatographically.

The yield of peroxide was directly proportional to the integrated absorbed light intensity (Fig. 1) for constant incident intensity, and also to the average absorbed

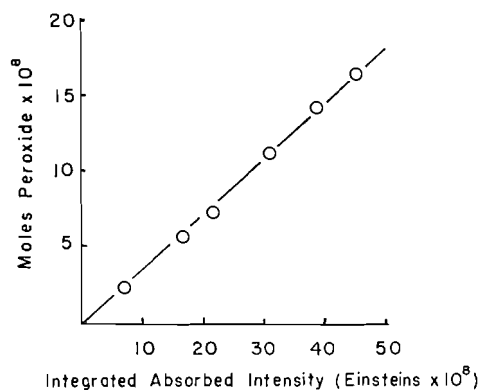


FIG. 1. Yield of peroxide as a function of the integrated absorbed intensity, for constant incident intensity, in the mercury-photosensitized oxidation of isobutane at 30° C, $p_{O_2} = p_{C_4H_{10}} = 100$ mm Hg.

intensity when a given isobutane-oxygen mixture was illuminated for a given time (500 seconds) at varying light intensities (Fig. 2). The integrated absorbed light intensity was obtained from the sum of the average numbers of quanta absorbed between determined short time intervals during the course of the reaction (see Part I). The time of illumination (500 seconds) for the intensity variation was the minimum required to obtain an accurately determinable quantity of peroxide at the lowest intensity, so minimizing the change in absorbed intensity, which in no case was greater than 15% of the total.

The quantum yield of peroxide was constant for a given isobutane-oxygen ratio for oxygen pressures in excess of 30 mm Hg, but increased as the fraction of isobutane in the mixture increased (Fig. 3). The yield of tertiary butyl alcohol underwent the same variation with varying light intensity as the peroxide (Fig. 4), and was constant in the region of constant peroxide (Fig. 5). The total yield of (tertiary butyl alcohol + acetone) was approximately proportional to the corresponding yield of peroxide (Fig. 6).

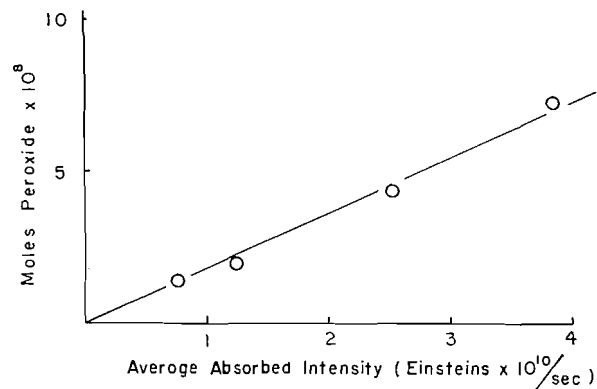


FIG. 2. Yield of peroxide as a function of the average absorbed intensity, varying the incident intensity and illuminating for constant time (500 seconds), in the mercury-photosensitized oxidation of isobutane at 30° C, $p_{O_2} = p_{C_4H_{10}} = 100$ mm Hg.

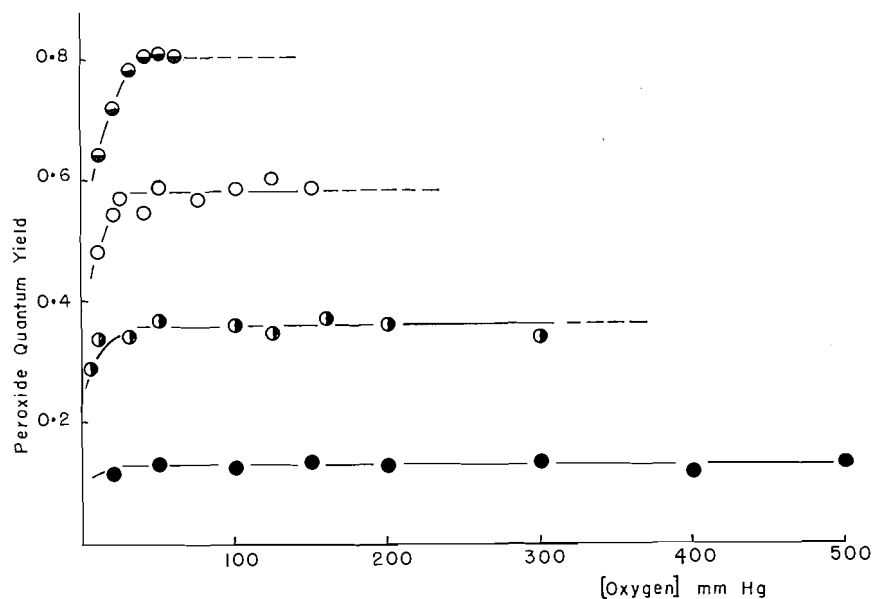


FIG. 3. Peroxide quantum yield as a function of the concentration of reactants at fixed hydrocarbon-oxygen ratios, in the mercury photosensitized oxidation of isobutane at 30° C. \bullet $p_{C_4H_{10}}:p_{O_2} = 10:1$; \circ $p_{C_4H_{10}}:p_{O_2} = 3:1$; \ominus $p_{C_4H_{10}}:p_{O_2} = 1:1$; \bullet $p_{C_4H_{10}}:p_{O_2} = 1:10$.

At 100° C an almost identical set of results was obtained (Tables I and II), modified

TABLE I
Quantum yields of products in the isobutane mercury-photosensitized oxidation at 30° C

$p_{C_4H_{10}}/p_{O_2}$ (ratio)	(mm Hg)	% Hg(6^3P_1) quenched by C_4H_{10}	Total peroxide	t -BuOOH	t -BuOH	Acetone	Isobutyraldehyde
1/10	40/400	3	0.13	N.D.	0.065	N.D.	0.08
1/1	220/220	24	0.36	0.33	0.12	0.02	0.12
3/1	330/110	48	0.58	0.55	0.23	0.03	0.09
10/1	400/40	76	0.80	0.76	0.36	0.06	0.05

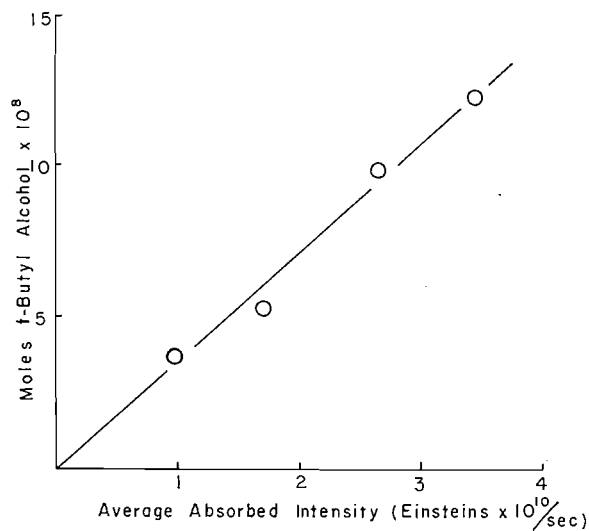


FIG. 4. Tertiary butyl alcohol as a function of the average absorbed intensity, varying the incident intensity and illuminating for constant time (1000 seconds), in the mercury-photosensitized oxidation of isobutane at 30° C, $p_{C_4H_{10}} = 400$ mm Hg; $p_{O_2} = 40$ mm Hg.

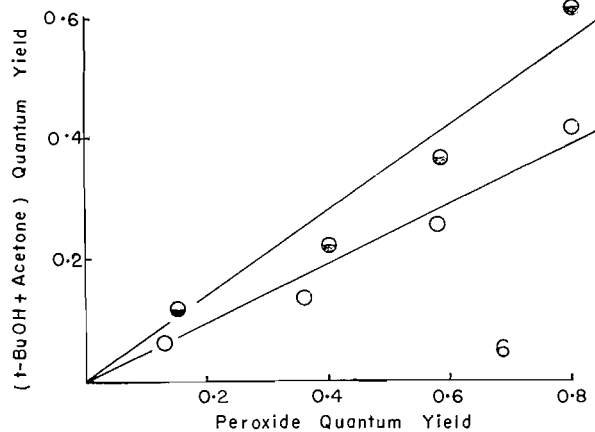
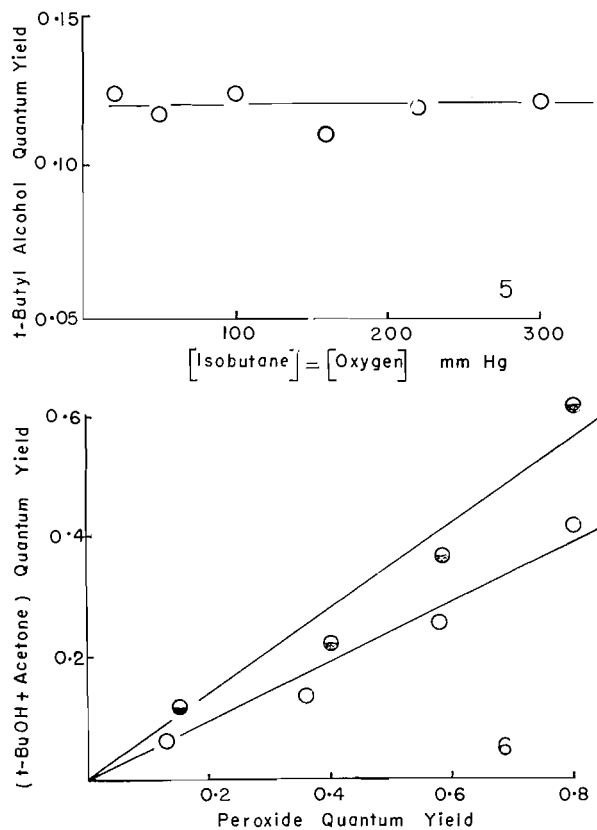


FIG. 5. Tertiary butyl alcohol quantum yield as a function of the concentration of reactants at fixed hydrocarbon-oxygen ratio = 1:1 in the mercury-photosensitized oxidation of isobutane at 30° C.

FIG. 6. Quantum yields of (t-butyl alcohol + acetone) as a function of tertiary butyl hydroperoxide quantum yield in the mercury-photosensitized oxidation of isobutane. \circ 30° C; \bullet 100° C.

TABLE II
Quantum yields of products in the isobutane mercury-photosensitized oxidation at 100° C

$p_{C_4H_{10}}/p_{O_2}$		% Hg(6^3P_1) quenched by C_4H_{10}	Total peroxide	<i>t</i> -BuOOH	<i>t</i> -BuOH	Acetone	CH ₃ OH	CH ₂ O	Isobutyraldehyde
(ratio)	(mm Hg)								
1/10	40/400	3	0.15	0.12	0.04	0.08	N.D.	0.07	0.06
1/1	220/220	24	0.40	0.38	0.08	0.14	N.D.	0.12	0.09
3/1	330/110	48	0.58	0.55	0.13	0.24	N.D.	0.16	0.07
10/1	400/40	76	0.80	0.75	0.20	0.42	0.17	0.23	0.035

only by an increased yield of acetone relative to tertiary butyl alcohol, and an increased total yield of (tertiary butyl alcohol + acetone). With the increase in acetone, methanol and formaldehyde were detected. The variation with conditions for all products was the same at 100° C as at 30° C. Small quantum yields of isobutyl alcohol verging on the lower limit of detection ($\phi \approx 0.02$ – 0.03) were observed at the higher isobutane–oxygen ratios.

Results showing the thermal stability of the peroxide to both homogeneous and heterogeneous decomposition during the course of an experiment, are given in Table III, the

TABLE III
Thermal stability of peroxide at 30° C and 100° C
($p_{O_2} = p_{C_4H_{10}} = 100$ mm Hg)

Period of illumination (seconds)	Period of shielding (seconds)	Peroxide	Temp. (°C)
500	—	0.36	30
500	1000	0.35	30
500	—	0.40	100
500	1000	0.39	100

products being left in the reaction cell for 1000 seconds, with the lamp shielded, after a 500-second period of illumination. The hydrocarbon conversion was never greater than 1%, and in the case of the colorimetric peroxide determination often less than 0.1%, thus minimizing photochemical decomposition with subsequent reaction of intermediate and final products.

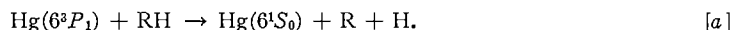
DISCUSSION

Variation of the concentrations of the reactants in a mercury-photosensitized oxidation will possibly have an effect on the initiation reactions. The rate of initiation will depend upon the relative quenching cross sections of the two gases and also upon the numbers of radicals produced as a result of each quenching process. Values of the quenching cross section of oxygen have been variously reported in the literature lying in the range 13.2–19.9 Å² (7, 8). Burgess and Robb in a recent paper (9) adopted a value for $\sigma_{O_2, Hg(6^3P_1)}$ of 17.2 Å² and for $\sigma_{C_4H_{10}, Hg(6^3P_1)}$ of 6.9 Å², both determined in the same way. Using these values the number of excited mercury atoms quenched by each gas is given by

$$\frac{Z_{O_2, Hg(6^3P_1)}}{Z_{C_4H_{10}, Hg(6^3P_1)}} = 3.2 \frac{n}{(1-n)}$$

where n is the mole fraction of oxygen in the mixture (see Table I).

Radicals are produced from the hydrocarbon quenching reaction [a],



Radical yields in mercury-photosensitized decompositions are usually below unity. For isobutane a yield of 0.2 radicals has been determined by Darwent and Winkler (10), indicating that reaction [b] must occur.

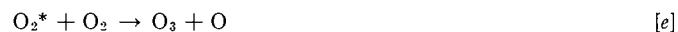
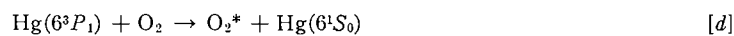


In this equation RH^* represents an excited RH molecule.

In the presence of oxygen it is possible that reaction [c] will occur.



Burgess and Robb (9) postulated that each O_2 -Hg quenching collision led to three radicals in the sequence of reaction [d] to [i] since reaction [e] was stated to have an efficiency close to unity.



In a subsequent paper Callear, Patrick, and Robb (11) while studying the O_2 -Hg(6^3P_1) reaction found the net efficiency of process [e] including reaction [j]



to be 0.14, due to deactivation of the active species in reaction [k]



This seems to contradict the value adopted in their earlier paper. In hydrocarbon-oxygen mixtures the reactions [l] and [m]



and

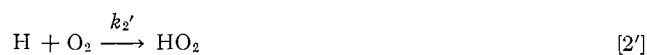


are also possibilities.

The situation is obviously complex since efficiencies cannot be accurately assigned to all the above reactions. One simplification which can be made is to operate at a constant ratio of hydrocarbon to oxygen. Under these conditions the rate of initiation should not vary, provided the over-all gas pressures are adequate to provide complete quenching of all the excited mercury atoms. Using different ratios it is possible to assign efficiencies to some of the above reactions.

The fact that the quantum yields of peroxide were below unity and independent of

the hydrocarbon-concentration variation in a mixture containing a fixed hydrocarbon-oxygen ratio (Fig. 3) indicates the absence of a peroxide chain reaction at the temperatures studied. The operation of the simple mechanism below:



leads, on applying the stationary state hypothesis, to the kinetic equation

$$d[\text{ROOH}]/dt = R_1 = \phi I_a$$

where ϕ is the effective primary radical yield in all initiation processes.

For a given hydrocarbon-oxygen ratio the total yield of peroxide should be proportional to the absorbed light intensity as observed (Fig. 2). Yields of tertiary butyl alcohol vary in a manner parallel to those of the hydroperoxide (Figs. 4 and 5) suggesting that the tertiary butoxy radical, which must be the immediate precursor of the alcohol, in the absence of ditertiary butyl peroxide, originates in reaction [4]



with subsequent hydrogen abstraction from the parent hydrocarbon as follows,

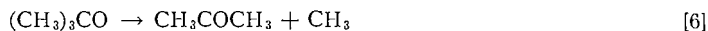


Reaction [4] is not a terminating step and, therefore, does not affect the rate equation for peroxide production. In addition to reaction [5] a similar type of process, namely [3'], merits some consideration.



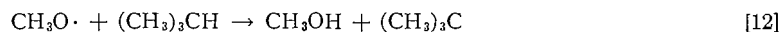
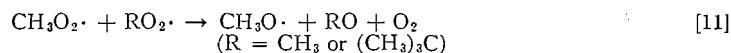
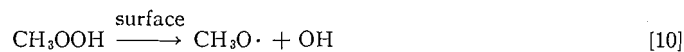
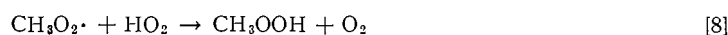
It is difficult to decide definitively between the two reactions [3'] and [5]. If [3'] is assumed to be the process leading to the production of tertiary butyl alcohol this would imply a primary radical yield of greater than unity for those mixtures with an isobutane-oxygen ratio of 10:1, since [3'] is a terminating reaction. The value of 0.8 found for the quantum yield of tertiary butyl hydroperoxide suggests that [3] alone is the main terminating reaction. For these reasons, reaction [5] would seem to be a better suggestion for the production of tertiary butyl alcohol. Figure 5, however, shows that the quantum yield of tertiary butyl alcohol is constant and independent of pressure for a fixed ratio of isobutane-oxygen and this is predicted by equation [3']. The inclusion of equation [5] and omission of [3'] would lead to a decrease in alcohol and an increase in acetone production for lower values of isobutane in the fixed isobutane-oxygen ratio. Either equation [5] or [3'] leads to the same expected change in the rate of formation of alcohol and acetone with variation in light intensity. The kinetic data we have obtained is in favor of reaction [3'] as being the process responsible for the formation of the tertiary butyl alcohol. It would, however, also be reasonable to include reaction [5] on the basis of the values and trends observed for the quantum yields of tertiary butyl alcohol. It must, however, be pointed out that the constant value found for the ratio tertiary butyl alcohol - acetone for varying values of the ratio [isobutane]-[oxygen] (see Table II) is predicted

by neither [3'] nor [5] if either is in competition with equation [6], which is obviously the source of the acetone found.



However, the process represented by equation [6] may not necessarily be so simple as there indicated. Should equation [6] be more complex than indicated it is possible that the inclusion of equation [5] may give the correct form of the variation of the quantum yields of tertiary butyl alcohol with hydrocarbon concentration.

The decomposition of the tertiary butoxy radical indicated in equation [6] is almost complete at temperatures about 190° C, even in the presence of an excess of a hydrocarbon containing a weak R—H bond (13, 14, 15, 16). At room temperature, it appears that the abstraction predominates because it requires a much lower activation than the decomposition. At 100° C the increasing yields of acetone are a measure of increasing extent to which the decomposition reaction [6] occurs. There is much uncertainty regarding the reaction of the resulting methyl radicals with oxygen to form methyl alcohol and formaldehyde (1, 16, 17, 18, 19, 20, 21). Below are listed some of the reactions considered possible at 100° C in the absence of significant yields of methyl hydroperoxide.



It is not, of course, possible to assign individual efficiencies to reactions [7]–[13] given above. Tables I and II show that the peroxide yields and the variations of these with the composition of the reactants are about the same at 30° and 100°. Similar reactions as indicated in [7]–[13] must have about the same efficiencies at both these temperatures.

Close agreement between the total peroxide and tertiary butyl hydroperoxide indicates that neither the mutual interaction of hydroperoxy radicals nor abstraction from the parent hydrocarbon to form hydrogen peroxide occurs to any appreciable extent. The exothermicity for abstraction by the tertiary butyl peroxy radical from the isobutane molecule, equation [5']



is about 1.5 kcal mole⁻¹, and the activation energy has been determined by Burgess and Robb (9) to be 16 kcal mole⁻¹, thus accounting for the radical–radical reaction at 30° C. Abstraction from the isobutane molecule by the tertiary butoxy radical, equation [5], is exothermic by about 16 kcal mole⁻¹, and the activation energy is presumably less than for the peroxy abstraction, equation [5'], being sufficiently low to exclude the occurrence of the radical–radical reaction at 30° C.

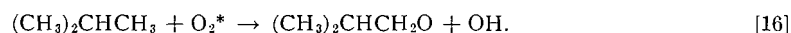
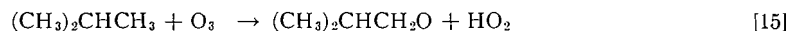
The above isobutane–oxygen reaction scheme predicts that, providing [HO₂] = [RO₂], the quantum yield of peroxide should be proportional to the sum of the reactions involving the RO· radical, i.e. tertiary butyl alcohol + acetone. Figure 6 shows that this is what our experimental results indicate.

The yields of peroxide which are formed in the main terminating reaction [3] increase with the increasing role of hydrocarbon in the excited mercury quenching processes (Tables I and II) and suggest that reaction [c] in the initiation processes has an efficiency close to unity. Low peroxide yields ($\phi < 0.15$) for the oxygen-isobutane = 10:1 mixtures are attributed to a low efficiency of reaction [e]. The value for ϕ in this case is close to that determined by Callear, Patrick, and Robb (11) for the oxygen-mercury reaction.

The detection of small yields of isobutyraldehyde was surprising. This is regarded as being formed from the isobutoxy radical according to equation [14]



In the absence of significant quantities of the corresponding hydroperoxide the isobutoxy radicals will probably be formed as primary products without going through the isobutyl peroxy stage, where the opportunity for formation of the hydroperoxide exists. The data in Table II show that the ratio isobutyraldehyde-tertiary butyl peroxide increases with the increase in the percentage of the excited mercury atoms quenched by molecular oxygen. This suggests that the reactions [15] and [16] may be of some importance:



Both of these are very exothermic.

The occurrence of [14] and [15] maintains the balance of hydroperoxy radicals at high oxygen-hydrocarbon ratios where each effective oxygen quenching process has the potentiality of producing three $\text{RO}_2\cdot$ radicals and only one HO_2 radical (reactions [c] to [i]).

Hydrogen abstraction by oxygen from the isobutoxy radical must have a lower activation energy than abstraction by the isobutoxy radical from the parent hydrocarbon, in view of the low yields of isobutyl alcohol found. Hydrogen abstraction from the tertiary butoxy radical by oxygen does not occur to any extent because the product of this reaction, namely isobutylene oxide, was not detected. A small fraction of the formaldehyde yields is attributable to decomposition of the isobutoxy radical occurring at 100° C where the quantum yields of the aldehyde are lower. The over-all increase in the yield of (acetone + *t*-butyl alcohol) at 100° C suggests reaction [4] may have a small activation energy. The slight increase in peroxide at 100° C for oxygen-rich mixtures is explained if the efficiency of [e] increases with increasing temperature.

A pressure of ~ 3 mm Hg of oxygen will give complete quenching in a system containing mercury vapor at its room temperature equilibrium vapor pressure. The tail-off in peroxide yield at oxygen pressures below 30 mm Hg may be attributable to a competition between deactivation processes and reaction with oxygen for removal of active isobutane molecules as portrayed by equations [17] and [18]



The slow, absolute rate of reaction of mercury with the isobutane oxidation system will not be significant in reducing the rate of production of radicals in the initiation processes (see Part I).

ACKNOWLEDGMENTS

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