will involve hydrogen ions. An analogous situation was encountered by King and Pandow[15] while studying the oxidation of bromide ion by cerium(IV). The following mechanism is postulated to explain the reduction of chromium(VI). It is based on the reactive species being $HCrO_4^-$ since it is the predominant species in these solutions. The steps are

$H^+ + HCrO_4^- = H_2CrO_4$ fast
$H_2CrO_4 + e^- = H_2CrO_4^-$ fast
$H^+ + H_2CrO_4^- = H_3CrO_4$ fast
$H_3CrO_4 + e^- = H_3CrO_4^-$ slow
Cr(IV) = Cr(III) fast

Acknowledgment.—The authors wish to thank E. I. du Pont de Nemours and Co., and the Wisconsin Alumni Research Foundation for financial assistance.

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[15] E. L. King and M. L. Pandow, THIS JOURNAL, **75**, 3063 (1953).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Oxidation of Lower Paraffin Hydrocarbons. II. Observations on the Role of Ozone in the Slow Combustion of Isobutane[1]

BY CLARENCE C. SCHUBERT, S.J., AND ROBERT N. PEASE

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The reaction of ozonized oxygen (*ca.* 3–6 mole % O_3) with isobutane in the temperature range 110 to 270° was compared with the slow uncatalyzed reaction with oxygen alone. The ratio of gram atoms of oxygen fixed in liquid product to moles of ozone added increased from 3.4 at 125° to 4.2 at 200° and 5.0 at 225°. The ozone-induced oxidation merges into the normal slow combustion reaction at *ca.* 265°. Approximately one third of the condensed products of the isobutane–ozone reaction at 150° was found to be *t*-butylhydroxymethyl peroxide. The same peroxide was indicated to be a product of the isobutane–oxygen reaction at 270° by a comparison of infrared spectra. It is proposed that ozone may be the active intermediate responsible for chain branching during the slow combustion of hydrocarbons in oxygen. Ozone might result from the reaction: $RO_2\cdot + O_2 \rightarrow O_3 + RO\cdot$ Ozone probably has the stability requirements to account for the cool flame reaction and negative temperature coefficient region observed in the combustion of hydrocarbons. Preliminary attempts to detect ozone during the normal slow reaction by observing the ultraviolet absorption in a 3-meter tube were unsuccessful due to general absorption in the 2500 Å. region.

The preceding paper in this series[2] described the reaction of ozonized oxygen with paraffins at low temperatures, *i.e.*, 25–50°. This study has been extended to include the temperature range 110–270°. At the higher temperatures employed the reaction with ozonized oxygen merges into the uncatalyzed slow combustion reaction. In this paper the oxidation of isobutane in the presence of ozone and in its absence are compared, with attention paid to the identification of peroxidic products.

Recently, Batten, *et al.*,[3] have investigated in a static system the slow oxidation of isobutane, and Neu[4] has reported on the oxidation of *n*-butane. Current theories relative to the slow combustion of hydrocarbons favor the postulation of peroxides or of aldehydes as the intermediates responsible for the termination of the initial induction period and for chain branching. These theories are reviewed by Batten, *et al.*[3] It is of interest that these authors conclude that peroxides in their normal state are not the substances responsible for the termination of the first induction period. This work may aid in deciding whether ozone is a likely candidate for the role of intermediate.

Three aspects of the slow oxidation reaction were considered: (1) the formation of liquid products from the reaction of ozonized oxygen with isobutane in the temperature range 110–270°; (2) the reaction without added ozone at *ca.* 270°; (3) the identification of the peroxidic material formed in the isobutane–ozone and the isobutane–oxygen reaction.

Experimental Method

Isobutane (C.P. grade from Matheson Co.) was mixed with varying amounts of ozonized oxygen, then passed through a heated glass reactor in a flow system. Condensible products were collected in a trap kept at 0° and weighed. The rate of production of this liquid condensate was taken as a rough measure of the extent of reaction. The reactor was a 5-cm. Pyrex cylinder of 640-ml. volume. Prior to initial use it was cleansed with hot concentrated nitric acid followed by rinses with distilled water and a final rinse with a saturated solution of boric acid. The reactor was mounted in a vertical position in a furnace; the reactant gases without preheating entered at the top and products emerged at the bottom where they were collected in a trap immersed in ice-water. Temperatures were measured by means of a thermometer placed in contact with the reaction vessel. Due to the exothermic nature of the reaction and the impossibility of preheating the ozone more rigid temperature control was precluded.

Commercial tank oxygen was ozonized by means of a Siemens type ozonizer constructed of Pyrex and provided with a grounded condenser jacket filled with circulating cooling water. Ozonized oxygen was mixed with isobutane in a 2 mm. capillary tube, then introduced directly into the reactor by a 5-cm. length of this same 2 mm. capillary. Ozone concentrations were measured by an infrared absorption method calibrated, in turn, by an absolute method similar to that described by Jahn[5] (decomposition at a heated platinum filament).

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[1] Taken from a thesis submitted by C. C. Schubert S.J. in partial fulfillment of the requirements for the Ph.D. degree. The work described in this paper was jointly supported by Contract NOrd-7920 with the U. S. Naval Bureau of Ordnance as coördinated by the Applied Physics Laboratory, The Johns Hopkins University; and by Contract N6-ori-105 with the Office of Naval Research as coördinated by Project Squid, Princeton University. Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

[2] C. C. Schubert S.J. and R. N. Pease, THIS JOURNAL, **78**, 2044 (1956).

[3] J. J. Batten, H. Gardner and M. Ridge, *J. Chem. Soc., London*, 3029 (1955); J. J. Batten and M. Ridge, *Australian J. Chem.*, **8**, 370 (1955).

[4] J. T. Neu, Abstracts 127th ACS Meeting, April 1955, paper No. 50, p. 16P. Also, *J. Phys. Chem.*, **60**, 320 (1956).

[5] S. Jahn, *Ber.*, **43**, 2319 (1910).

Results

The effect of the addition of varying amounts of ozone to isobutane–oxygen mixtures is made clear by a consideration of the data shown in Fig. 1. Curves A, B and C of Fig. 1 show the production of liquid condensate as a function of temperature for mixtures containing varying amounts of oxygen and ozone (see caption, Fig. 1). Curve D was obtained when no ozone was added to the introduced oxygen. No reaction is noticeable below 200° without ozone. Moreover, it was noted that the reaction with added ozone, which is already well advanced at 255°, would gradually cease entirely upon stopping the discharge in the ozonizer. With added ozone the production of liquid condensate gradually increases with rise in temperature until at 265–275° the reaction merges into the slow oxidation without ozone (see curve). Ozone consumption was virtually complete above 110° for the residence times employed, 3.5 to 7 minutes.

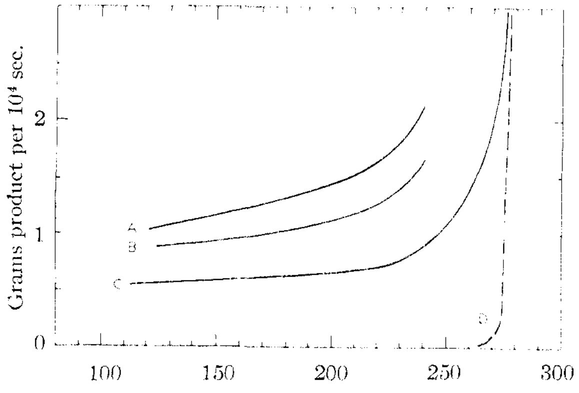

Fig. 1.—Production of liquid condensate from the reaction of ozonized oxygen with isobutane.

	H. C., ml./sec.	O_2, ml./sec.	Mole % O_3 in O_2
A	1	0.78	3.2
B	1	.4	4.9
C	1	.2	6.0
D	1	.78	0.0

A lower estimate (condensed liquid products only) of the efficiency of ozone in effecting oxidation was obtained from the data presented in Fig. 1, and combustion analyses of the liquid. The latter gave substantially constant composition of 10.2% H, 39.4% C and 50.4% O (by difference), with small variations depending on temperature and on make-up gas. The procedure was to compare gram-atoms of oxygen in the condensed liquid to gram-moles of ozone reacting.

The results indicate little variation with gas composition at any one temperature. As temperature was increased, the ratio rose slowly from 3.4 at 125° to 4.2 at 200°, and then more rapidly to about 5 at 225°.[6] Beyond this temperature the autocatalytic acceleration typical of the reaction without ozone set in (see Fig. 1). However, if the ozonizer were cut off, reaction dropped rapidly to negligible proportions until the temperature range 265–275° was reached. From this point onward the reaction went virtually to completion, with or without added ozone (see curve D, Fig. 1).

It should be emphasized that the above ratios are based only on liquid condensed at 0°. For this reason, analogous ratios obtained in the earlier work at 25–50° (ratios of 1.3–1.6) are not directly comparable. The latter, based on infrared spectroscopy, included carbon oxides but not water. Nevertheless it is clear that the ozone reaction triggers in a limited degree the normal oxidation chain at temperatures substantially below the normal range.

Experiments similar to those described above were performed with *n*-butane and propane. The reaction between ozonized oxygen and *n*-butane proceeds initially slower than in the case with isobutane, but the slow combustion reaction becomes self-sustaining at a lower temperature, 255°. Propane behaves in a comparable manner and becomes self-sustaining at 285°. A point worthy of emphasis is that which was noted also by Briner.[6] Ozone completely eliminates the first induction period.

Partial Analysis of Reaction Products. Identification of Peroxide.—It will be recalled that analysis by infrared spectrometry of the products of the room temperature reaction revealed the presence of *t*-butyl alcohol and acetone with lesser amounts of methanol, carbon dioxide, carbon monoxide and formic acid. The same is true of the reaction at 125° and above; but in addition we find in the liquid condensate substantial amounts of the addition product of *t*-butyl hydroperoxide and formaldehyde. This substance may have failed detection in the room temperature experiments because of its low volatility.

Isobutane at a flow rate of 1 ml./sec. and oxygen containing 3.26 mole % ozone at a flow rate of 0.8 ml./sec. were passed through the same Pyrex reactor previously described. Furnace temperature was maintained at 150°, residence time in the reactor was *ca.* 5 minutes. The gases emerging from the reactor were passed through a trap held at 0°. The liquid product which collected in the trap, when treated with an equal volume of saturated sodium chloride solution, formed two layers of which one was an oily substance comprising 70% by volume of the original material. The salting out procedure was repeated with another volume of saturated sodium chloride solution equal to the volume of the oil, whereupon another loss was entailed of approximately 5% of the remaining oil. Presumably most of this loss was that of water-soluble products, acetone, methanol, some *t*-butyl alcohol and, perhaps, minor amounts of hydrogen peroxide and water. The oily substance was dried with calcium sulfate (Drierite) for 16 hours. There followed a vacuum distillation, with the pot kept at 25°, which yielded 13 cuts. These cuts were then analyzed to give the results shown in Table I. In the determination of active oxygen the method of Liebhafsky and Sharkey,[7] which employs glacial acetic acid and hydrogen iodide, was used.

Examination of the infrared spectra of both vapor and liquid showed that fractions 1 to 8 contained principally *t*-butyl alcohol, acetone and methanol. Fractions 9–13 were of much lower vapor pressure, *ca.* 2 mm. at 25° and were, most probably, one and the same material, *t*-butyl hydroxymethyl peroxide. Chemical examination of the peroxidic material represented by fractions 9 to 13 showed that the peroxide split under the influence of solid potassium hydroxide to yield formaldehyde; when subjected to oxidation by warm dilute sulfuric acid and potassium dichromate, acetone was produced. Identification of the peroxidic material with *t*-butyl hydroxymethyl peroxide was established by the comparison of the infrared absorption spectrum of a pure synthetic sample of this peroxide, prepared essentially

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(6) Compare E. Briner and J. Carceller, *Helv. Chim. Acta*, **18**, 973 (1935).

(7) H. A. Liebhafsky and W. H. Sharkey, This Journal, **62**, 190 (1940). See also, C. N. Satterfield, R. Wilson and R. M. LeClair, *Anal. Chem.*, **26**, 1792 (1954).

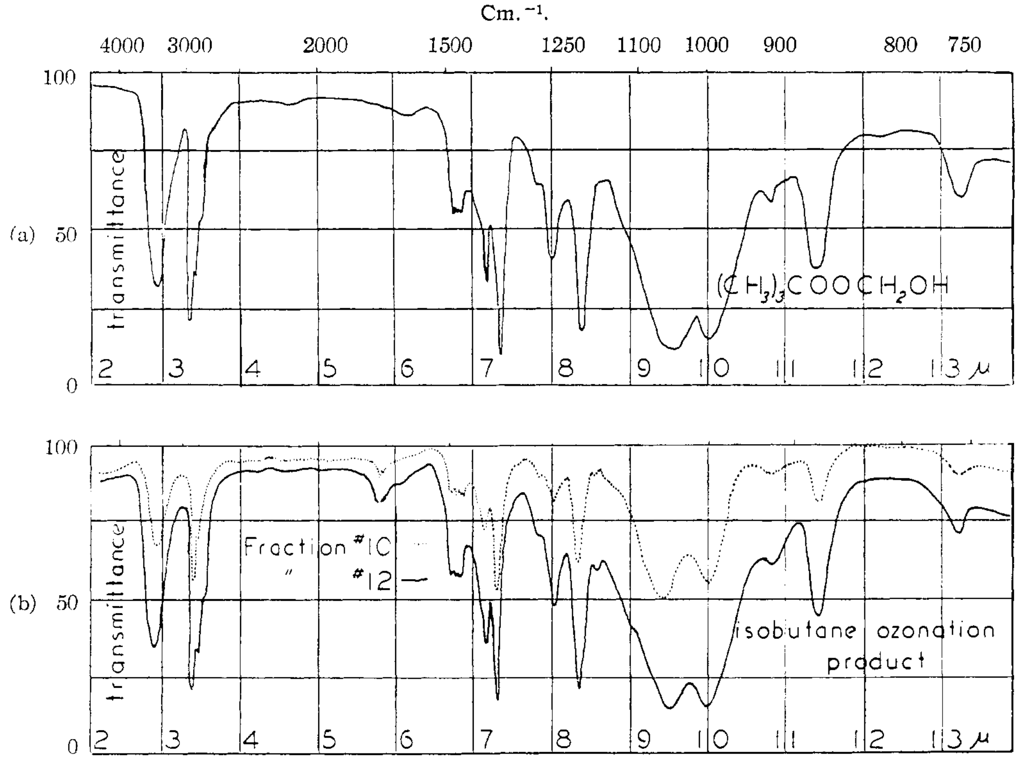

Fig. 2.—(a) Liquid *t*-butyl hydroxymethyl peroxide pressed between sodium chloride plates, no solvent; (b) fractions 10 and 12 from condensate of reaction of isobutane and ozonized oxygen at 150°.

according to the method of Dickey,[8] with the infrared spectrum of two of the fractions of the material obtained from the reaction between ozonized oxygen and isobutane. Figure 2a is the spectrum of the liquid synthetic *t*-butyl hydroxymethyl peroxide, Fig. 2b is a copy of the spectra of the fractions no. 10 and 12.

TABLE I

FRACTIONATION OF WATER-INSOLUBLE PORTION OF CONDENSATE FROM ISOBUTANE–OZONIZED OXYGEN REACTION AT 150°

Fraction	Wt., g.	$n^{25}D$	d^{25}_4	Active O, wt. %	C, %	H, %
1-8	6.1710	1.3675– 1.4002	. . .	2.0 to 10	. . .	. . .
9	1.0715	1.4068	0.990	12.1	. . .	. . .
10	1.3319	1.4092	.995	14.3	48.9	9.8
11	1.0764	1.4100	.994	13.3	. . .	. . .
12	0.6018	1.4115	.995	13.7	. . .	. . .
Residue	0.4767	1.4175	. . .	. .	. . .	. . .
Synthetic samples of *t*-butyl hydroxymethyl peroxide						
This work		1.4098	0.995	13.5	48.4	10.05
Dickey, *et al.*[8]		1.4128	.960	13.3	51.5	10.9
Theor. value for *t*-butyl hydroxymethyl peroxide				13.3	49.95	10.05

It is believed that the evidence obtained from these spectra and from the analytical data of Table I establishes the fact that *t*-butyl hydroxymethyl peroxide is produced in substantial amounts by the reaction between isobutane and ozonized oxygen.

Similar experiments without prior ozonization were less satisfactory owing to the autocatalytic nature of the process at the necessarily higher reaction temperatures (265–275°). Nevertheless, it was possible to draw some inferences from the analytical data. In particular the salting-out procedure mentioned above led to a residue whose infrared spectrum (Fig. 3a) bore some resemblance to that of *t*-butyl hydroxymethyl peroxide, with perhaps some admixture of the corresponding addition product with acetaldehyde (Fig. 3b). Infrared and ultraviolet spectra of the untreated gaseous products also indicated the presence of isobutene, formic acid, methanol, formaldehyde, acetone and carbon oxides.

Discussion

The tentative mechanism of the ozone reaction remains as before[2] except that now with evidence of

$$RH + O_3 \longrightarrow RO\cdot + HO_2\cdot \qquad (1)$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot \qquad (2)$$

$$RO\cdot \longrightarrow (CH_3)_2C{=}O + CH_3\cdot \qquad (3)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (4)$$

the presence of *t*-butyl hydroxymethyl peroxide it is presumed that the further reaction takes place

$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot \qquad (5)$$

with subsequent splitting of the peroxide

$$ROOH \longrightarrow RO\cdot + \cdot OH \qquad (6)$$

and the possibility of branching. However, since the reaction is strictly limited at 150–250° and substantial amounts of the peroxide are recovered as the hydroxymethyl addition product, it appears that 6 is not contributing largely.

As to the formation of *t*-butyl hydroxymethyl peroxide, it is tentatively assumed that the methyl radical formed in 3 reacts

$$CH_3\cdot + O_2 \longrightarrow CH_3O_2\cdot \qquad (7)$$

$$CH_3O_2\cdot \longrightarrow CH_2O + \cdot OH \qquad (8)$$

This is followed by

$$ROOH + CH_2O \longrightarrow ROOCH_2OH \qquad (9)$$

to yield *t*-butyl hydroxymethyl peroxide.

With respect to the normal autocatalytic oxidation at 275° and above, we are impressed by the

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[8] F. Dickey, F. Rust and W. Vaughan, THIS JOURNAL, **71**, 1432 (1949).

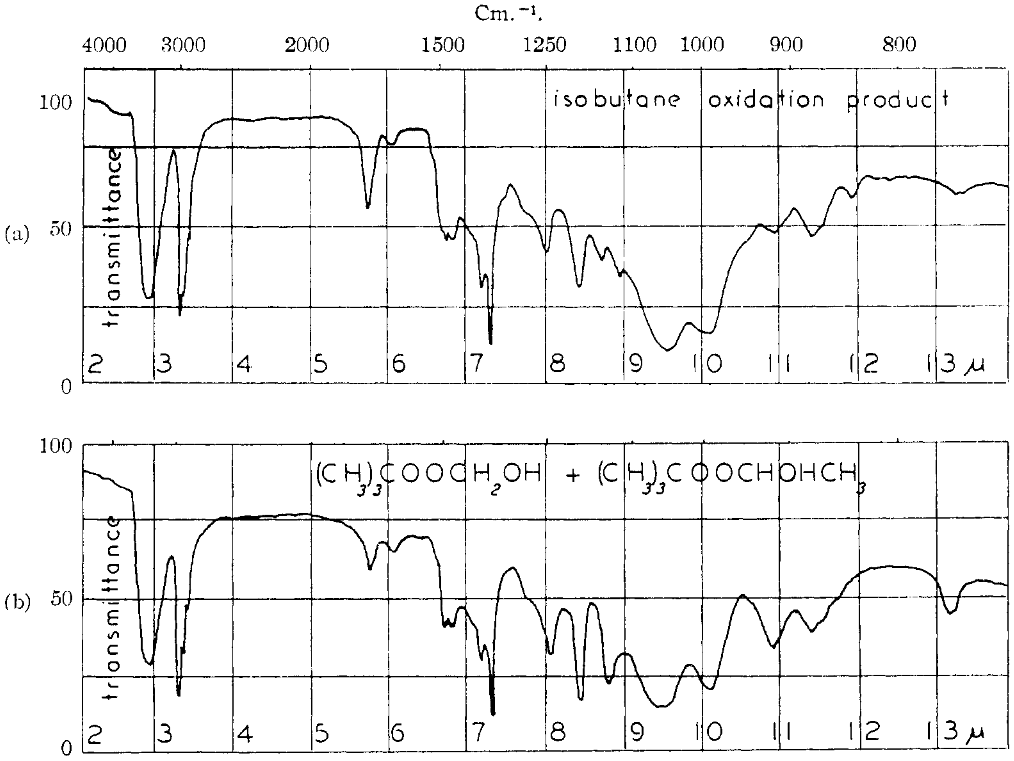

Fig. 3.—(a) Sample obtained from condensate of reaction between oxygen and isobutane at 270°; (b) synthetic mixture of approximately equal amounts of $(CH_3)_3COOCH_2OH$ and $(CH_3)_3COOCHOHCH_3$.

fact that added ozone will eliminate the induction period. Since ozone always seems to be present in air or oxygen in minimal amounts (formed presumably as a result of ionization by primary particles likewise present), there is the possibility that ozone is commonly the initiator of reaction. It may even be supposed that some regeneration of ozone occurs *via* reactions of the type[9]

$$RO_2\cdot + O_2 \longrightarrow RO\cdot + O_3 \qquad (10)$$

This would itself be a branching reaction to supplement 6.

With respect to the availability of ozone in the elimination of the normal low-temperature induction period in hydrocarbon oxidation, the review of rate data by Garvin[10] indicates that at 10^{-6} mole/liter the half-life at 300° is of the order of 100 sec. In going from 300 to 400° this is reduced to about 1 sec. In these terms, the negative temperature coefficient in this region might be explained. The new reaction at higher temperatures would then represent for the first time the direct attack of molecular oxygen on the hydrocarbon

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot \qquad (11)$$

However, it should be added that attempts to detect ozone in the normal oxidation *via* ultraviolet absorption *in situ* have so far been unsuccessful.

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(9) See comments by F. C. Dainton, *Trans. Faraday Soc.*, **42**, 225 (1946). Also, R. D. Cadle and H. S. Johnston, "Proceedings of the Second National Air Pollution Symposium," Sept. 1952, p. 32.

(10) D. Garvin, THIS JOURNAL, **76**, 1523 (1954).