pendence suggest that the charge of the product ion of equation 4 is more negative than -1. Since TaX_6^- is stable over a considerably larger HF concentration range than NbX_6^- and since the high reactivity of the latter ion was attributed to one oxide ion in the complex,[2] it appears that TaX_6^- is not oxygenated. Thus in reaction (4) probably only chloride ions could be liberated. The HCl dependence of K_{12} is remarkably small and the sum of chloride and oxonium ions liberated is therefore probably not larger than one. Hence, since $n = 2$, the most probable formula of the product tantalum complex becomes $HTaX_5F_3^{-2}$ and equation (4) reduces to

$$TaX_5F^- + 2HF + H_2O \rightleftarrows HTaX_5F_3^{-2} + H_3O^+ \qquad (7)$$

The corresponding molarity constants K^*_{12} become 2.5 and 0.53 for 9 *M* HCl and 3 *M* HCl, respectively.

Summary

1. The anion exchange behavior of tantalum was studied for a number of HCl–HF mixtures. It was found to adsorb very strongly under most conditions, even in 9 *M* HCl.

2. The species TaX_5F^- and $HTaX_5F_3^{-2}$ have been tentatively identified and the molarity constants for the probable reaction

$$TaX_5F^- + 2HF + H_2O \rightleftarrows HTaX_5F_3^{-2} + H_3O^+$$

were estimated to be 2.5 and 0.53 for 9 *M* HCl and 3 *M* HCl solutions, respectively.

OAK RIDGE, TENNESSEE RECEIVED MAY 19, 1950

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

The Oxidation of Free Methyl Radicals

BY J. H. RALEY, L. M. PORTER, F. F. RUST AND W. E. VAUGHAN

Introduction

The development of the free radical theory of hydrocarbon oxidation by molecular oxygen has resulted in general acceptance of the reaction

$$R + O_2 \longrightarrow ROO \qquad (1)$$

(where R is a free radical derived from the hydrocarbon RH) as representative of the initial union of oxygen and a carbon atom in the original molecule. It is also recognized that, in many instances, the peroxy radical is converted to a hydroperoxide, ROOH, by interaction with RH or some other material serving as a hydrogen atom donor, and that subsequent processes are dependent on the behavior of this hydroperoxide. However, in the absence of an efficient hydrogen atom donor or in the presence of a sufficiently high free radical concentration, processes other than hydroperoxide formation must predominate. It was toward the elucidation of these steps that the present investigation was directed. Methyl was selected for study since it is the simplest alkyl radical and is conveniently obtained in high concentrations by the vapor phase decomposition of di-*t*-butyl peroxide.[1,2] In addition, the decomposition of methyl *t*-butyl peroxide was utilized as a source of certain free radicals believed to be intermediates in the methyl radical oxidation.

Experimental

Materials.—The preparation and purification of di-*t*-butyl peroxide and methyl *t*-butyl peroxide have been described previously.[3] Commercial oxygen and helium were used without further purification.

Method.—The apparatus was similar to that employed in kinetic studies of the vapor phase decomposition of di-*t*-alkyl peroxides.[1] Liquid di-*t*-butyl peroxide was forced into the 1-l. spherical reaction vessel by a small pressure of helium, and the decomposition of the vapor was followed for a short time. Oxygen was then admitted and its partial pressure estimated by interpolation of total pressure measurements before and after its introduction. Methyl *t*-butyl peroxide was admitted as a vapor by expansion from a 5-l. storage bulb since injection of the liquid resulted in instantaneous, complete decomposition.

The reaction was halted by opening the vessel to a trap held in a block of mercury and cooled by liquid nitrogen. The residual gas was then slowly pumped through a Dry Ice-cooled scrubbing trap to a calibrated reservoir, and duplicate samples were taken for mass spectrometric analysis. The temperature of the mercury block was then raised to $-120°$ and a second portion of gas measured and sampled. At $-120°$ ethane is readily separated from formaldehyde and other less volatile products. In most instances the condensate in the traps was dissolved in pyridine and aliquots taken for analysis.

Analysis.—**Methanol** was determined by a procedure similar to that of Elving and Warshowsky.[4] It was identified in the condensed product by conversion to the 3,5-dinitrobenzoate (m. p. 107–107.5°, lit. for CH_3OH 107.0°, mixed m. p. 107–107.3°).

***t*-Butyl alcohol** was taken as the difference between the methanol and total alcohol contents, the latter being determined by a modified procedure based on that described by Skrabal[5] and Fischer and Schmidt.[6]

Formaldehyde was estimated colorimetrically with chromotropic acid.[7,8]

Acetone was taken as the difference between the formaldehyde and total carbonyl contents, the latter being determined by the procedure of Mitchell, *et al.*[9]

Water was determined with the Karl Fischer reagent according to the procedure of Bryant, *et al.*[10] Because of the large number of components in the reaction product, the analysis for water was carried out preferably on the condensate from a duplicate run. The product was condensed directly into the reagent solution held in a collection trap at liquid nitrogen temperature, and a second portion of the reagent, handled in a similar manner except for exposure to reaction product, was used as a blank.

Free acid was titrated directly and assumed to be formic.

Di-*t*-butyl Peroxide and Oxygen.—The reaction of oxygen and free methyl radicals, the latter

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[1] Raley, Rust and Vaughan, THIS JOURNAL, **70**, 88 (1948).

[2] Rust, Seubold and Vaughan, *ibid.*, **70**, 95 (1948).

[3] Rust, Seubold and Vaughan, *ibid.*, **72**, 338 (1950).

[4] Elving and Warshowsky, *Ind. Eng. Chem., Anal. Ed.*, **19**, 1006 (1947).

[5] Skrabal, *Z. Anal. Chem.*, **119**, 222 (1940).

[6] Fischer and Schmidt, *Ber.*, **59**, 679 (1926).

[7] MacFadyen, *J. Biol. Chem.*, **158**, 107 (1945).

[8] Bricker and Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945).

[9] Mitchell, Smith and Bryant, THIS JOURNAL, **63**, 573 (1941).

[10] Bryant, Mitchell and Smith, *ibid.*, **62**, 3504 (1940).

supplied by decomposing di-*t*-butyl peroxide, has been examined at 120–160° (Table I). The decomposition of the peroxide to methyl radicals, *viz.*

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO \qquad (2a)$$
$$(CH_3)_3CO \longrightarrow CH_3 + (CH_3)_2CO \qquad (2b)$$

is not influenced detectably by the presence of oxygen, since the amounts of free methyl released, as calculated from the "normal" decomposition rate constant or from the acetone found, agree within the experimental error.[11] In addition, only traces of *t*-butyl alcohol have been noted in the product. Therefore, reactions of the intermediate *t*-butoxy radical other than decomposition are neglected.

TABLE I

DI-*t*-BUTYL PEROXIDE AND OXYGEN, *P* IN MM.

Temp., °C. →	120.1	147.2		159.8
Di-*t*-butyl peroxide	157.8	170.5	175.4	173.3
Oxygen	167.9	202.1	203.7	194.8
Peroxide decomposed^a	125.5	154.8	154.6	170.1
Oxygen consumed	168	185	181	161
CH_3 released, calcd. from k^a	251	309.6	309.2	340.2
Calcd. from acetone formed	258	307	. . .	329
CH_3 accounted for (based on C)	228	303	. . .	336
O_2 accounted for	119	172	. . .	140
CH_3 oxidized^b	206	279	. . .	253
Product	Moles/100 moles CH_3 oxidized			
CH_3OH	56.7	61.6		61.3
CO	27.3	23.0	Product	23.8
HCO_2H	11.4	9.3	analyzed	7.5
H_2CO	0.6	3.6	for H_2O	4.5
CO_2	4.0	2.5	only	2.9
	100.0	100.0		100.0
H_2O	. . .	11.1^c	^{c}	. . .
H_2	2.2	0.6		0.3

[a] Calculated from the rate constant, $k = 3.2 \times 10^{16} \cdot e^{-39,100/RT}$ (sec.$^{-1}$).[1] Each peroxide molecule was assumed to give two methyl radicals. [b] Calculated from: CH_3 oxidized = (CH_3 accounted for) − ($CH_4 + 2C_2H_6$). [c] The mm. of products volatile at −195° from the duplicate runs were: CO (64.2, 64.4), H_2 (1.8, 1.8) and CH_4 (0.8, 0.8). Therefore, the amounts of water formed were assumed to be identical.

It is particularly noteworthy that in all experiments where the available oxygen was not exhausted, ethane and methane formation after the oxygen had been admitted was vanishingly small (Table II).

TABLE II

EFFECT OF OXYGEN ON C_2H_6 AND CH_4 FORMATION, *P* IN MM.

Temp., °C. →	159.8	147.2		122.1	120.1
Oxygen remaining	34	17	12	10	<0.2
Total CH_3 released^a	340	310	238	284	251
CH_3 released before O_2 added^a	81	28	19	1	1
Total CH_3 found as CH_4 + C_2H_6	84	24	19	2	22

[a] Calculated from decomposition rate constant.

In view of this suppression of the normal reactions of free methyl, it is reasonable to conclude that the only significant reaction of this radical is a combination with oxygen.[12] Therefore the step

$$CH_3OO + CH_3 \longrightarrow CH_3OH + H_2CO \qquad (3)$$

proposed by Blaedel, Ogg and Leighton[13] for the photoöxidation of methyl iodide at 0° is not considered to be important in the present system.[14] In addition, the reaction suggested by Bates and Spence, also for the methyl iodide photoöxidation

$$CH_3 + O_2 \longrightarrow H_2CO + OH \qquad (4)$$

is not believed to play a significant role since it leads to no plausible mode of methanol formation.[15] Furthermore, it implies a low stability of the peroxy radical which is not in harmony with the known action of oxygen as an inhibitor of various chain reactions.

The most likely fate of the methylperoxy radical is a transformation to the methoxy (CH_3O) radical, since, as will be shown in a following section, the latter readily gives rise to methanol, formaldehyde and carbon monoxide as final products. The presently suggested path for this transformation at high peroxy radical concentrations is

$$CH_3O_2 + CH_3O_2 \longrightarrow 2CH_3O + O_2 \qquad (5)$$

Disproportionation of the methoxy radicals

$$CH_3O + CH_3O \longrightarrow CH_3OH + H_2CO \qquad (6)$$

could then follow to produce methanol and formaldehyde.

This mechanism could account for the nearly equimolar production of the alcohol and aldehyde and the virtual absence of carbon monoxide observed at 0° by Bates and Spence. However, since in our experiments the methanol yield exceeds 50%, it is clear that an additional methanol producing reaction is required. Abstraction of a hydrogen atom from the di-*t*-butyl peroxide by the methoxy radical is not probable since such attack would be reflected in an accelerated rate of peroxide decomposition. Similarly, reaction with acetone would probably be followed by oxidative degradation of the ketone and this is not observed. However, reactions which could account for the high methanol yield as well as the conversion of formaldehyde to carbon monoxide without the formation of equivalent quantities of water and/or hydrogen are

$$CH_3O + H_2CO \longrightarrow CH_3OH + HCO \qquad (7a)$$
$$CH_3O + HCO \longrightarrow CH_3OH + CO \qquad (7b)$$

The formation of methyl hydroperoxide as an intermediate by a reaction between the methylperoxy radical and a hydrogen atom donor cannot be ruled out. However, since this peroxide is reported to produce high yields of water by thermal decomposition,[16] reaction (5) is thought to represent the predominant fate of CH_3O_2.

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[11] *Cf.* also ref. 1.

[12] From measurements on the acetone photosensitized oxidation of methane, van Tiggelen (*Ann. Mines Belg.*, **43**, 117–144 (1941)) concludes that the reaction of methyl radicals and oxygen has an activation energy of only 1.5 kcal.

[13] Blaedel, Ogg and Leighton, THIS JOURNAL, **64**, 2500 (1942).

[14] Evidence for the elimination of a process analogous to (3), namely, the reaction between *t*-butylperoxy and ethyl free radicals, by the introduction of molecular oxygen is reported by Seubold, Rust and Vaughan *ibid.*, **73**, 18 (1951).

[15] Bates and Spence, *ibid.*, **59**, 1689 (1931), suggested: $OH + CH_3I \longrightarrow CH_3OH + I$ for methanol production in their system.

[16] Medvedev and Podyapolskaya, *Acta Physiochim. U. R. S. S.*, **2**, 487 (1935).

Formic acid, carbon dioxide, water, and perhaps a portion of the carbon monoxide probably arise from oxidation of the formyl radical but the mechanisms of these reactions cannot be specified on the basis of these experiments.

Decomposition of Methyl *t*-Butyl Peroxide.—The thermal decomposition of methyl *t*-butyl peroxide was used to produce free methoxy radicals; that this reaction furnishes these fragments has already been established by the data for the pyrolysis in the presence of cyclohexene.[3] The decomposition products in the absence of any additive are listed in Table III. The formation of ketone, methane and ethane is consistent only with the intermediate existence of *t*-butoxy and methyl radicals. Chain decomposition involving attack on the peroxide by these species or by methoxy radicals is presumably minor since the structurally similar methyl *t*-butyl ether does not show a high reactivity toward *t*-butoxy and methyl radicals.[17] The principal mode of decomposition, therefore, is believed to be

$$CH_3OOC(CH_3)_3 \longrightarrow CH_3O + (CH_3)_3CO \quad (8)$$

TABLE III

DECOMPOSITION PRODUCTS OF METHYL *t*-BUTYL PEROXIDE; TEMPERATURE 140.0°; PEROXIDE, 90 MM.; TIME, 23.3 HR.

Product[a]	Moles/100 moles peroxide dec.	CH_3O	Equivalent $(CH_3)_2CO$	CH_3
Ketone[b]	85		85	
CH_3OH	53	53		
CH_4	44			44
CO	33	33		
t-C_4H_9OH	12		12	12
C_2H_6	11			22
H_2	2			
H_2CO	1	1		
		87	97	78

[a] Gaseous products determined in a duplicate run. [b] Assumed to be only acetone.

The data show that the released methoxy radicals produce methanol and formaldehyde and that the latter is subsequently converted to carbon monoxide with the liberation of very little molecular hydrogen.[18] In addition, it may be noted that the methanol yield far exceeds the sum of the formaldehyde and carbon monoxide yields. These results, therefore, are in accord with expectations based on the reactions of methoxy radicals and formaldehyde suggested in the previous section.

Acknowledgment.—We are indebted to Mr. Edward D. Peters and Dr. Frederick T. Weiss of the Analytical Department of this Company for developing suitable procedures for the semimicro analysis of the various reaction products.

Summary

The oxidation of free methyl radicals at 120–160° produces methanol, carbon monoxide, formic acid, formaldehyde, carbon dioxide, water and traces of hydrogen. Since no methane or ethane is formed, it is concluded that the only significant reaction of free methyl is a combination with oxygen to form the methylperoxy (CH_3OO) free radical. Transformation of the methylperoxy radical to the methoxy radical is also proposed and ultimate formation of methanol, formaldehyde and carbon monoxide attributed to reactions of the latter radical. These reactions are also observed with methoxy radicals obtained by the pyrolysis of methyl *t*-butyl peroxide. The major reactions of the formyl radical probably involve hydrogen atom donation to other free radicals and oxidation.

EMERYVILLE 8, CALIFORNIA RECEIVED MAY 9, 1950

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[17] The reactivity of methyl *t*-butyl ether may be estimated from the following data at 147.2°:

(*t*-BuO)$_2$ (mm.)	Additive (mm.)	time (min.)	Peroxide dec. (calcd.) (mm.)	Ketone (mm.)	CH_4 (mm.)	C_2H_6 (mm.)	CO (mm.)	H_2CO (mm.)	H_2 (mm.)
166	None	82	83	169	11.3	74.3	...	...	...
166	200 ether	82	83	165	31.3	48.3	6.0	1.4	0.2
172	226 acetone	53	..	...	CH_4/C_2H_6 = 0.27			...	...

From these data it may be calculated that a maximum of about 20% of the released radicals abstract a hydrogen atom from the ether. In the pyrolysis of methyl *t*-butyl peroxide such species as formaldehyde and the methoxy and formyl radicals should compete with the peroxide for reaction with free radicals.

[18] The failure to observe higher conversions of methoxy radicals to carbon monoxide in the pyrolysis of methyl nitrite (Steacie and Shaw, *Proc. Roy. Soc.* (*London*), **146**, 388 (1934)) is attributable to the rapidity of a reaction between alkoxy radicals and the parent molecule (Rice and Rodowskas, THIS JOURNAL, **57**, 350 (1935)).