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Studies of the reactions of hydroxyl radicals. I

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This paper describes how the homogeneous decomposition of hydrogen peroxide vapour has been successfully used as a source of hydroxyl radicals in a kinetic study of the relative rates of reaction of hydroxyl radicals with methane, carbon monoxide, formaldehyde and hydrogen peroxide. It has been found that the method is of general applicability provided subsequent reactions of radicals formed can be controlled.

With hydroxyl radicals so produced from the decomposition of hydrogen peroxide, surprisingly consistent values were obtained for the relative rates of reaction of methane and carbon monoxide with hydroxyl radicals. Thus, within an accuracy of 10 %, the ratios of rate constants for reaction of hydroxyl radicals with methane and carbon monoxide were found to be 3.6 at 650 °C, 2.1 at 525 °C and 0.85 at 400 °C. The rates of reaction of hydroxyl radicals with formaldehyde and hydrogen peroxide were less accurately determined because of expected additional reactions. Within an accuracy of about 50 % it was estimated that hydroxyl radicals reacted ten times as fast with hydrogen peroxide as with carbon monoxide at 525 °C. At the same temperature hydroxyl radicals reacted 33 ± 6 times as fast with formaldehyde as with methane.

Data were obtainable at temperatures as low as 400 °C even though heterogeneous decomposition of hydrogen peroxide was relatively more important at these temperatures. This was because heterogeneous decomposition of hydrogen peroxide did not cause oxidation of the other gases which were also present. A preliminary account (Hoare 1962) of this work has previously been published.

INTRODUCTION

The thermal decomposition of hydrogen peroxide vapour has been shown by Hoare, Protheroe & Walsh (1958, 1959) and Forst (1958) to occur by a second-order mechanism with an activation energy of 48 ± 4 kcal/mole. The decomposition occurs by a non-chain process and it was thought likely to be a useful source of hydroxyl radicals. Experiments were therefore devised to determine the relative rates of reaction of hydroxyl radicals so produced, with various additives.

EXPERIMENTAL

Helium, used as a carrier gas, was saturated by passing it over Becco 98 % hydrogen peroxide contained in two saturators. Analysis showed that saturation was achieved even at the fastest flow rates by having the first saturator at 5 °C above the second saturator. The saturation vapour pressures so calculated were in agreement with the data published by the manufacturers and Maass & Hiebert (1924). The rates of flow of helium and the reactant gases injected into it were recorded by Manostat flowmeters and were easily kept constant or adjusted by Edwards needle valves. A pre-heater ensured that at the fastest flow rates used the gases attained the temperature of the reaction vessel within a quarter of its length and were within 4 degC at its mouth. A more efficient preheater would have caused too much heterogeneous decomposition of hydrogen peroxide. The reaction vessel was of silica 20 cm long and 3.9 cm internal diameter. It had a volume of 241 ml. Heterogeneous

decomposition was minimized in the pre-heater and reaction vessel by coating with boric acid. The traps, designed by Volman (1946), were efficient in condensing at least 99 % of the hydrogen peroxide and formaldehyde issuing from the reaction vessel. Hydrogen peroxide was titrated with 0.02M potassium permanganate in very dilute acid solution (which did not rapidly oxidize formaldehyde). Formaldehyde was estimated by oxidation with 0.05M iodine in alkaline solution, unreacted iodine being released by acidification and titrated with sodium thiosulphate. The presence of any unreacted hydrogen peroxide did not appreciably affect the accuracy of the estimation of formaldehyde, but in acid solution, merely produced the calculated equivalent amount of iodine.

Samples of the gases (before and after reaction) were taken in calibrated sample tubes varying between 2 and 20 ml. in volume. They were analysed by gas chromatography at room temperature, a molecular sieve being used to separate methane, carbon monoxide and oxygen and silica gel to separate carbon dioxide and ethane. Paired thermistors were able to detect as little as 0.001 mmHg pressure of these gases in one atmosphere of helium carrier gas.

The gases, used from cylinders without further purification, were of research grade. The methane was 99.5 % pure and contained 0.003–0.043 % oxygen, 0.012–0.060 % ethane, 0.020–0.090 % carbon dioxide and 0.36–0.44 % nitrogen. The carbon monoxide was 99 % pure and contained 0.18 % oxygen, 0.75 % nitrogen and 0.085 % carbon dioxide. The oxygen and helium contained no impurities that were important in the present study.

Under nearly all conditions the mass balance obtained for the products indicated that no important product except water had been omitted in the analysis.

RESULTS

The first experiments were carried out at 525 °C. At this temperature the rate constants for homogeneous decomposition of hydrogen peroxide were in good agreement with those obtained by Hoare *et al.* (1959). It was found that the decomposition of hydrogen peroxide was at least 75 % homogeneous but that no matter how much methane was added some oxygen was formed by heterogeneous reaction (mostly in the preheater). The chief reaction product when methane was added, was ethane with some formaldehyde and carbon monoxide but no carbon dioxide. With the possible exception of formaldehyde, no change was observable in the products as the rate of flow was varied from 6.5 to 46 ml./s although a little hydrogen peroxide remained undecomposed at the fastest flow rate.

When carbon monoxide was added to this reaction system carbon dioxide was formed and the relative quantities of ethane and carbon dioxide produced depended upon the relative quantities of methane and carbon monoxide added to the helium gas stream (table 1). Clearly methane and carbon monoxide were reacting in competition for hydroxyl radicals, giving methyl radicals and carbon dioxide respectively as products.

These experiments were repeated at 600 and 650 °C. There was still no effect of flow rate upon the products (table 1, expts. 192 and 194) but the increased temperature favoured the production of ethane instead of carbon dioxide. In order to study

this system further, experiments were performed at 400 and 450 °C. At these temperatures the decomposition of hydrogen peroxide was predominantly heterogeneous, (with an apparent activation energy of 10 kcal/mole). As might be expected, the heterogeneous decomposition of hydrogen peroxide did not cause oxidation of methane or carbon monoxide. Thus the oxidation of methane proceeded to an

TABLE 1. EFFECT OF ADDING METHANE AND CARBON MONOXIDE TO DECOMPOSING HYDROGEN PEROXIDE

Pressures (mmHg) at 25 °C and flow rate (ml./s) at 1 atm total pressure at 25 °C.

expt. no.	CH ₄	CO	O ₂	C ₂ H ₆	CH ₂ O	CO ₂	flow rate	A	k ₁ /k ₂
525 °C									
159	20.5	2.70	(0.185)	0.27	0.110	0.048	19	1.8	2.1
158	21.2	8.3	0.30	0.23	0.120	0.120	19	1.9	2.1
160	19.2	30.8	0.170	0.24	0.096	0.46	19	2.0	2.2
161	5.2	34.3	0.160	0.098	0.063	0.80	19	2.1	2.1
170	21.6	0.190	0.145	0.27	0.120	0	19	—	—
91	22.6	0.075	0.36	0.22	0.067	0	19	—	—
89	21.7	0.088	0.32	0.190	0.160	0	46	—	—
600 °C									
236	20.7	8.4	0.26	0.34	0.067	0.108	19	2.8	3.0
237	5.8	9.0	0.25	0.185	0.035	0.24	19	2.6	2.8
238	5.3	25.8	0.24	0.145	0.019	0.555	19	2.7	2.7
650 °C									
184	19.5	8.25	0.32	0.35	0.033	0.088	19	3.5	3.8
185	20.2	3.00	0.29	0.39	0.037	0.037	19	3.3	3.6
186	5.15	9.75	0.33	0.177	0.015	0.22	19	3.2	3.5
187	5.15	28.9	0.30	0.170	—	0.525	19	3.6	3.6
192	21.2	0.072	0.30	0.395	0.038	0	19	—	—
194	17.8	0.063	0.11	0.40	0.034	0	46	—	—
400 °C									
232	100	12.2	0.22	0.015	0.220	0.035	3.5	0.87	0.87
233	90	37.4	0.47	0.010	0.190	0.105	3.5	0.83	0.83
217	100	0	(1.10)	0.019	0.130	0	3.5	—	—
450 °C									
252	48.5	21.7	0.51	0.064	0.130	0.107	6.5	1.08	1.25
253	50.0	6.3	0.46	0.072	0.130	0.031	6.5	1.11	1.28

extent compatible with extrapolation of the results at higher temperatures (where hydrogen peroxide decomposed with an activation energy of 48 kcal/mole). Longer contact times were needed in order to obtain sufficient decomposition of hydrogen peroxide and, because of the lower concentrations of methyl radicals produced, the reaction of methyl radicals with oxygen to give formaldehyde was more important than their combination to give ethane. However, the trend noted at higher temperatures was continued, i.e. lowering the temperature favoured the production of carbon dioxide instead of methyl radicals.

If, at 525 °C, carbon monoxide alone were added to the helium carrier gas stream then carbon dioxide was the main product (table 2). At 650 °C more carbon dioxide

TABLE 2. THE EFFECT OF ADDING CARBON MONOXIDE TO DECOMPOSING HYDROGEN PEROXIDE VAPOUR

Pressures (mmHg) at 25 °C and flow rate (ml/s) at 1 atm total pressure at 25 °C.

expt. no.	CO	O ₂	CO ₂	flow rate	H ₂ O ₂ decomposed	H ₂ calculated
400 °C						
164	25.6	0.53	0.113	6.5	0.96	0.11
229	4.3	0.46	0.060	3.5	0.93	0.02
228	15.9	0.51	0.140	3.5	1.08	0.04
230	44	0.48	0.36	3.5	1.10	0.11
525 °C						
173	0.95	0.56	0.08	46	1.25	0
174	3.12	0.45	0.32	46	1.28	0
175	8.70	0.29	0.79	19	1.36	0
176	21.5	0.27	0.98	6.5	1.36	0.08
177	67	0.145	1.34	6.5	1.36	0.13
650 °C						
188	0.74	0.26	0.66	46	1.36	0
189	3.00	0.023	1.10	46	1.36	0

TABLE 3. THE EFFECT OF ADDING METHANE AND OXYGEN TO DECOMPOSING HYDROGEN PEROXIDE VAPOUR

Pressures (mmHg) at 25 °C and flow rate (ml/s) at 1 atm total pressure at 25 °C.

expt. no.	CH ₄	O ₂	C ₂ H ₆	CH ₂ O	CO	CO ₂	flow rate	$\frac{\text{CH}_4}{\text{CH}_2\text{O}}$
450 °C								
263	6.2	0.76	0.026	0.125	0.051	0	3.5	49
225	6.6	6.6	0.005	0.165	0.085	0	6.5	40
223	6.1	14.6	0.007	0.170	0.175	0	3.5	36
222	12.5	12.6	0.015	0.28	0.244	0.011	3.5	45
525 °C								
88	39	0.61	0.23	0.22	0.060	0	46	180
85	8.8	0.26	0.130	0.185	0.140	0	46	47
86	5.3	0.32	0.080	0.115	0.180	0	46	46
87	2.3	0.33	0.032	0.087	0.190	0	46	27
154	8.0	1.40	0.115	0.180	0.200	0.010	46	44
155	5.1	1.11	0.073	0.136	0.230	0.010	46	38
156	1.88	1.30	0.045	0.066	0.170	0.014	46	29
168	7.6	12.1	0.044	0.23	0.63	0.011	46	33
169	2.1	13.9	0.007	0.063	0.36	0.015	46	33
650 °C								
190	1.88	0.22	0.098	0.010	0.225	0.008	46	188
209	1.82	1.00	0.093	0.019	0.28	0.025	46	96
206	1.49	10.6	0.048	0.043	0.67	0.050	46	35
250	1.14	24.0	0.025	0.051	0.86	0.011	46	22
249	1.14	21.5	0.023	0.051	0.82	0.013	19	22
256	4.3	21	0.090	0.100	2.40	0.214	3.5	43
257	4.3	20	0.100	0.115	1.16	0.067	6.5	37
260	4.0	27	0.094	0.128	1.13	0.089	19	31
259	4.3	20.5	0.105	—	0.91	0.051	46	—

was produced under similar conditions while less was produced at 400 °C. Examination of the yields of carbon dioxide and oxygen and of the material balance indicates that at 400 and 525 °C with the higher pressures of added carbon monoxide (expts. 164, 228, 230, 176 and 177) some hydrogen may have been formed. Further experiments confirmed that hydrogen was indeed formed, though in quantities difficult to estimate accurately (e.g. 0.2 mmHg).

TABLE 4. THE EFFECT OF VARYING THE OXYGEN AND HYDROGEN PEROXIDE PRESSURES IN A STUDY OF THE INDUCED OXIDATION OF METHANE

Pressures (mmHg) at 25 °C with a flow rate of 19 ml./s at 25 °C. Nitrogen was used instead of helium as a carrier gas in expts. nos. 131 and 153; no carbon dioxide was produced.

expt. no.	CH ₄	O ₂	C ₂ H ₆	CH ₂ O	CO	H ₂ O ₂ added
525 °C						
170	21.6	0.145	0.27	0.12	0.19	1.36
151	21.0	2.6	0.23	0.22	0.35	1.36
152	19.8	8.4	0.176	0.26	0.50	1.36
153	18.3	8.0	0.138	0.32	0.53	1.36
157	19.8	29	0.102	0.37	0.78	1.36
118	21.0	0.08	0.122	0.034	0.004	0.29
131	22.0	0.08	0.112	0.085	0	0.29
117	20.9	1.90	0.116	0.043	0.009	0.29
116	22.1	2.7	0.107	0.068	0.010	0.29
115	19.0	8.8	0.080	0.083	0.073	0.29
114	20.7	35	0.050	0.142	0.18	0.29
650 °C						
192	21.2	0.36	0.395	0.038	0.072	1.36
196	20.5	2.5	0.34	0.067	0.21	1.36
197	19.6	9.8	0.305	0.130	0.22	1.36
200	20.5	30	0.18	0.157	0.178	1.36
205	19.3	8.8	0.165	0.045	0.010	0.29

Comparison of tables 1 and 2 shows that addition of methane (e.g. expts. 158 and 175) reduced the yield of carbon dioxide whereas addition of carbon monoxide (e.g. expts. 160 and 170) had little effect upon the yield of ethane. This suggests that the hydroxyl radicals consumed by carbon monoxide are usually replaced by other reactive entities but, in the absence of added oxygen, the hydroxyl radicals consumed by reaction with methane are not usually replaced. In expt. 189 the low amounts of oxygen produced when carbon monoxide alone was added indicate that a chain oxidation of carbon monoxide may have occurred.

When methane alone was added to the helium gas stream it was found that at high methane pressures the main carbon-containing products were ethane and formaldehyde but that as the pressure of methane was reduced, less ethane but more carbon monoxide was produced (table 3, expts. 85 to 88). Addition of small quantities of oxygen did not greatly affect the amounts of carbon monoxide and formaldehyde produced but larger additions resulted in increased yields of carbon monoxide (table 3) presumably due to a chain oxidation of formaldehyde.

It was found that even at 650 °C the products were not greatly affected by flow rates (table 3, expts. 256 to 259) when these rates were greater than 6.5 ml./s. However, at 650 °C the formaldehyde equilibrium pressure was very dependent upon the oxygen pressure. At 600 °C the dependence on oxygen pressure was less marked, while at 450 °C it was quite small.

Addition of oxygen reduced the amount of ethane produced and increased the amounts of formaldehyde and carbon monoxide (table 4). Reduction in the pressure of hydrogen peroxide reduced the yield of methyl radicals (as calculated from the yields of ethane and formaldehyde) by a factor roughly proportional to the square root of the hydrogen peroxide pressure. The yield of carbon monoxide, a secondary product, was naturally affected to a greater degree.

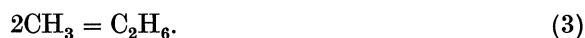
DISCUSSION

(a) *Reaction of hydroxyl radicals with methane and carbon monoxide*

The results shown in table 1 indicate clearly that a competition occurred between methane and carbon monoxide for the hydroxyl radicals produced the decomposition of hydrogen peroxide



Reaction (1) produced methyl radicals which, at the higher temperatures and in the presence of very little oxygen, yielded ethane:



When small amounts of oxygen were added to the system, formaldehyde was the chief oxidation product presumably formed by the reaction



Reaction (4) has for long been postulated as the chief mode of oxidation of methyl radicals at temperatures of 500 °C. It would lead to straight chain oxidation of methane because of the regeneration of hydroxyl radicals. Hoey & Kutschke (1955), Sleppy & Calvert (1959) and Hoare & Wellington (1960) have shown that at temperatures up to 200 °C the oxidation of methyl radicals yields equimolar quantities of methanol and formaldehyde; Shahnin & Kutschke (1961) have shown that some methyl hydroperoxide is also formed. However, at temperatures approaching 500 °C little methanol is normally found (Jost 1946) and methyl hydroperoxide was shown by Egerton, Minkoff & Salooja (1956) to be a minor by-product. This is in accord with the small amounts of methanol and alkyl hydroperoxide which were detected in the present work.

If the great majority of methane and carbon monoxide molecules reacted *only* according to reactions (1) and (2) respectively, then the ratio

$$\frac{2(\text{C}_2\text{H}_6) + (\text{CH}_2\text{O})}{\text{CO}_2} \times \frac{\text{CO}}{\text{CH}_4} \quad (A)$$

should represent the ratio of the rate constants of reactions (1) and (2) no matter how the concentrations of radicals varied along the length of the reaction vessel. The ratio A is found to be remarkably constant, at each temperature used, over a large range of CH_4/CO ratios (table 1). It seems therefore that reactions (1) and (2) do indeed predominate.

In order to obtain more correct values of k_1/k_2 it was desirable to have as little oxidation of methyl radicals as possible. Nevertheless, some oxygen was always produced by the heterogeneous decomposition of hydrogen peroxide and a correction of the ratio A has therefore been made in table 1 to allow for the carbon monoxide normally produced from formaldehyde in the absence of added carbon monoxide. The values for k_1/k_2 so obtained can be used to evaluate $E_1 - E_2$. The value of 7.0 ± 1.5 kcal/mole derived for $E_1 - E_2$ makes this work consistent with that of Westenberg & Fristrom (1961) who obtained a value of 15 for k_1/k_2 at about 1800 °K.

Later work with flames by Fristrom (1963) and Fenimore & Jones (1963*a*) yielded similar values for k_1/k_2 to those obtained by Westenberg & Fristrom, but their values for $E_1 - E_2$ (3.5 and 0 kcal/mole, respectively) are completely in disagreement with the present work. Unless the temperature range is large, estimates of k_1/k_2 are probably more accurate than estimates of $E_1 - E_2$. Baldwin, Jackson, Walker & Webster (1964) overcame this difficulty by combining the results of Fenimore & Jones (1963*a, b*) at 1275 °K with their own at 500 °C. For the reaction



they found $k_{1a}/k_2 = 95 \exp(-5160/RT)$ which compares with $160 \exp(-7000/RT)$ for k_1/k_2 as derived above. Since reactions (1) and (1*a*) may be expected to occur at similar rates, this agreement is satisfactory. The rather large value for the ratio of steric factors P_1/P_2 can most simply be explained by considering that there are great steric restrictions on the approach of a hydroxyl radical towards a carbon monoxide molecule to give a linear carbon dioxide molecule.

Separate values for k_1 and k_2 have been derived by Avramenko & Lorentso (1949) and Avramenko & Kolesnikova (1950). This work is open to severe criticism (Steacie 1954) but it does yield values of k_1/k_2 which are surprisingly close to those given in table 1. However, the Russian work yields a value for $E_1 - E_2$ of 1.5 kcal/mole which is in complete disagreement with the present work.

(b) Reaction of hydrogen atoms

Hydrogen atoms are produced by reaction (2). If these hydrogen atoms reacted to any great extent with methane, e.g.



they would have caused the ratio A (table 1) to be considerably greater in experiments where much carbon dioxide was produced (expts. 160 and 161) than in experiments where little was produced (expt. 159). The experiments referred to show this not to occur. In addition, considerable quantities of hydrogen would have been formed contrary to the balance of products obtained.

Hydrogen atoms are not likely to combine with each other by a third order reaction, because the reaction



is more likely even when the pressure of oxygen is only 0.1 mmHg. However, it is also possible for hydrogen atoms to react with undecomposed hydrogen peroxide by the reactions



and



These reactions have been studied by Baldwin *et al.* (1964) who have found k_7/k_{7a} to be approximately 6 at 440 °C and k_6/k_{7a} to be 2.9×10^{-3} (mmHg of hydrogen) $^{-1}$. In the present experiments, helium (third body coefficient in reaction (6) = 0.36) at 1 atm pressure was used, so that the value of the relative rate constants $k_6 M/k_7$ would be 0.14 at 440 °C and less at higher temperatures.

The rate constants given by Baldwin & Walsh (1954) and Steacie (1954) show that at 525 °C reaction (6) is likely to occur about 100 times faster than reaction (5) at equal methane and oxygen pressures. It can be concluded that k_7/k_5 is of the order of 700. This calculation supports the experimental finding that reaction (5) does not take place to any great extent under present conditions.

Reaction (7) results in the regeneration of a hydroxyl radical and this explains the chain character of the processes occurring in some of the experiments recorded in table 2. It is clear that addition of methane, by yielding methyl radicals which in turn yield ethane, causes chain ending but addition of carbon monoxide, as reported earlier, merely propagates the chains (expts. 160 and 170). In some experiments (e.g. expt. 177) considerable amounts of carbon dioxide were produced so that an appreciable number of the hydrogen atoms produced by reaction (2) would react by the less frequent reaction (7a) to give hydrogen molecules. (k_7/k_{7a} , which is equal to 6 at 440 °C, will not change greatly with temperature.) This accounts for the hydrogen produced in these experiments.

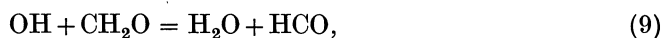
At 650 °C oxygen was consumed (expt. 189), and little hydrogen produced, in a chain reaction the mechanism of which is not clear. The reaction



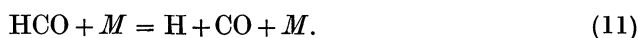
and reaction (6) do not seem likely to have caused much consumption of oxygen while hydrogen peroxide remained. Thus Baldwin *et al.* (1964) find $(k_7 + k_{7a})/k_8$ to be 336 at 500 °C and the ratio will not be much less than 100 at 650 °C.

(c) Reactions of formaldehyde

Tables 3 and 4 show that carbon monoxide was produced from formaldehyde as the pressure of oxygen was increased. Addition of oxygen also increased the rate of reaction of methyl radicals with oxygen so that more formaldehyde and less ethane were produced. If formaldehyde in turn reacted with hydroxyl radicals, then carbon monoxide could be formed by the following sequence of reactions:



or

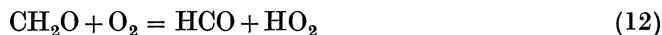


If reaction (9) were as exclusively responsible for the oxidation of formaldehyde as reaction (1) is for methane, then an equilibrium concentration of formaldehyde would be set up in due course so that the rate of oxidation of methane to formaldehyde was equal to the rate of oxidation of formaldehyde, i.e.

$$k_1(\text{CH}_4)(\text{OH}) = k_9(\text{OH})(\text{CH}_2\text{O}) \quad (\text{neglecting ethane production}).$$

Under such conditions $k_9/k_1 = \text{CH}_4/\text{CH}_2\text{O}$ and so the theory can be tested by testing the constancy of $\text{CH}_4/\text{CH}_2\text{O}$.

It is also possible that oxidation of formaldehyde occurred by the reaction



in spite of the high activation energy (*ca.* 35 kcal/mole) expected for such a reaction.

The reaction



is slightly exothermic and must also be considered. However, the results shown in table 3 indicate that the $\text{CH}_4/\text{CH}_2\text{O}$ was constant and did not increase as the oxygen pressure was increased as it would have done if reaction (12) were important. In fact, oxidation would have depended considerably on the contact time, because reaction (12) would have continued even after all the hydrogen peroxide had been decomposed.

At 450 and 525 °C, under conditions such that an equilibrium concentration of formaldehyde had probably been reached, the ratio $\text{CH}_4/\text{CH}_2\text{O}$ was almost independent of the oxygen pressure. At 650 °C, presumably because of the intrusion of new reactions of formaldehyde, the $\text{CH}_4/\text{CH}_2\text{O}$ ratio was very variable and tended to be larger than that which might be predicted from the values obtained at 450 and 525 °C. Increase in the pressure of oxygen favoured a chain reaction which, by increasing the equilibrium concentration of formaldehyde, reduced the $\text{CH}_4/\text{CH}_2\text{O}$ ratio to a value compatible with those found at 450 and 525 °C. This suggests that the chain oxidation of formaldehyde at 650 °C as well as the normal oxidation at 450 and 525 °C proceeds by reaction (9) rather than by (13).

We can therefore find k_9/k_1 by assuming that in the present experiments hydroxyl radicals alone react with both methane and formaldehyde so that formaldehyde will attain an equilibrium value. The best values of k_9/k_1 have been chosen (from table 3) as 40, 33, and 22 at 450, 525 and 650 °C, respectively, from the data for $\text{CH}_4/\text{CH}_2\text{O}$ when the oxygen pressure was high, the ethane yield low and $d\text{CH}_2\text{O}/dt = 0$. These values are in fairly good agreement with the values derived by Blundell, Cook, Hoare & Milne (1964) from experiments on the oxidation of methane but would not lead to an activation energy difference $E_1 - E_9$ as large as the value of 8.5 kcal/mole which can be derived for the corresponding reactions of methyl radicals with formaldehyde and methane (as given by Toby & Kutschke, 1959 and Dainton, Ivin & Wilkinson, 1959).

(d) Reactions of hydroperoxy radicals

Hydroperoxy radicals may be produced (as shown above) by reactions (10) and (6) when oxygen is added to the system and they are also formed by the reaction



if the quantities of added methane or carbon monoxide are small. It is difficult to estimate the relative rates of reactions (2) and (14) or (1) and (14) because of the variable degree of heterogeneous reaction of hydrogen peroxide and of hydroperoxy radicals. Baldwin *et al.* (1964) give a value of k_{14}/k_2 of 16 at 500 °C which is a little greater than an approximate value of 10 which can be derived from the results given in table 2 for reactions at 525 °C.

Hydroperoxy radicals may react either with formaldehyde by reaction (13) or with carbon monoxide by the reaction



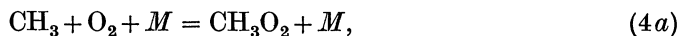
Blundell *et al.* (1964) have obtained a value of 320 for k_{13}/k_{15} at 525 °C so that reaction (15) like reaction (13) will not normally be expected to be important under the conditions used in this work. This is substantiated by the constancy of the values of k_1/k_2 obtained in table 1 and the fact that no carbon dioxide is formed except where reaction (2) is of importance. HO_2 radicals probably react together to give hydrogen peroxide or, on the surface, to give water.

(e) *Reactions of methyl radicals*

The results were not conclusive as to the order of the reaction of methyl radicals with oxygen (which is determined in part II). The predominance of formaldehyde rather than methanol as a product suggested, however, that the second-order reaction



was more important than the reaction



which was reported to predominate at temperatures up to 200 °C (Hoare & Walsh 1957).

(f) *Chain ending*

The power of the method used to determine relative rate constants lies in the fact that a complete mechanism is not needed and minor reactions do not do more than slightly alter the accuracy with which ratios of velocity constants may be obtained. Thus a chain ending reaction has not been specified and subsequent studies (part II, following) have led to similar values of k_1/k_2 at reduced total pressure even after allowing for ethylene which was not estimated in the present work because of the small quantities produced.

As shown in table 4, the extent of reaction is proportional to the square root of the initiation reaction, suggesting that a chain reaction which is terminated by a reaction between radicals may be taking place. The chain length is very small and is least at low oxygen pressures. The reaction



is clearly one chain ending reaction, but there is likely to be another and this could be



(g) Conclusion

The use of hydrogen peroxide to find relative rate constants for reactions of hydroxyl radicals has been shown to give particularly accurate results in some cases. The power of the method is enhanced because complete mechanisms need not be specified. The rate constant ratios derived from this work are shown in table 5. In general, rate constant ratios are needed more than absolute rates in the interpretation of kinetic data and simplification of expressions derived by steady state treatments. However, the use of one absolute rate constant, e.g. the value of $k_2 = 1.2 \times 10^8 \text{ l. mole}^{-1} \text{ s}^{-1}$ at 525°C (Fenimore & Jones 1963*b*) enables other rate constants to be calculated from table 5 with an accuracy almost equal to that of the assumed absolute rate constant.

TABLE 5. RELATIVE RATES OF REACTION OF HYDROXYL RADICALS

reactants compared	650 °C	600 °C	525 °C	450 °C	400 °C
$\text{CH}_4:\text{CO}$	3.6	2.8	2.1	1.25	0.85
$^*\text{H}_2:\text{CO}$	5.8	4.9	3.7	2.6	2.0
$\text{CH}_2\text{O}:\text{CH}_4$	22	—	33	40	—
$\text{H}_2\text{O}_2:\text{CO}$	—	—	10	—	—

* Calculated from the results of Baldwin *et al.* (1964).

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