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Mass Spectrometric Investigation of the Hydrogen-Oxygen and Methyl-Oxygen Reactions*

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The reactions of hydrogen and of methyl radicals with oxygen have been studied by means of a mass spectrometer designed to detect free radicals. The reactants were present at low pressures in a stream of helium. Radicals detected were OH and HO2 in the hydrogen-oxygen reaction, and CH3O, CH3O2, OH, HO2, CH_2 , and probably CHO in the methyl-oxygen reaction. A rough value of 10^{-3} to 10^{-4} was obtained for the collision efficiency of the oxygen+methyl radical reaction.

INTRODUCTION

IN recent years the mass spectrometer has been used for the detection and identification of stable intermediates and free radicals produced in a number of organic reactions. In particular it has been used to study the low pressure oxidation of hydrogen and the lower hydrocarbons.1-3

In the low pressure hydrogen-oxygen flame, H atoms, O atoms, and OH radicals have been detected.² The HO2 radical has been formed by adding hydrogen atoms to a stream of oxygen.^{2,3}

Although the methane-oxygen reaction has been examined in some detail with a mass spectrometer,^{1,2} the reaction of methyl radicals with oxygen has been studied only briefly by this means.¹ There has, however, been some work on the latter reaction in photochemical systems.4-9

The present work includes a brief re-examination of the H_2-O_2 reaction and, to help elucidate various combustion processes, a study of the $CH_3 - O_2$ reaction.

EXPERIMENTAL

The reactor and associated pumping system were similar to those described by Ingold and Lossing.¹⁰ In the majority of experiments it was found to be desirable to add oxygen to the second reactant below the heated zone. For this purpose a movable furnace was wound around a quartz tube 3 mm in diameter through which the oxygen entered. (See Fig. 1.) The furnace element was 0.028-in. chromel-A wire. The furnace and tube could be moved simultaneously from a position just above the leak into the mass spectrometer to a position 6 cm back from the leak. The quartz tube ended in a fine nozzle about 5 mm below the furnace. Oxygen entering the tube at about 10-cm pressure passed into the reacting mixture at a pressure of a few microns. This system prevented fluctuations of the oxygen pressure in the reactor. Moreover, the oxygen was always added in the same position relative to the second reactant regardless of the position of the furnace in the reactor. Helium at 1-cm pressure passing down the main reactor tube at about 5000 cm/sec was the carrier for the second reactant.

The mass spectrometer itself was similar to the one used by Lossing and Tickner,11 but with slit sizes chosen to give a mass resolution of 1 in 200.

MATERIALS

The oxygen, hydrogen, and helium were the standard compressed gases used without further purification. The mercury dimethyl was obtained from Delta Chemicals Ltd., New York.

THE HYDROGEN-OXYGEN REACTION

Results

Hydrogen at about 100 microns pressure was added to the helium gas stream. Oxygen issued from the quartz tube at 10 microns. With the furnace at 1000°C and 1.5 cm above the leak about 3% of the oxygen was consumed. This was estimated by measuring the change in the mass 32 peak when the hydrogen stream was shut off. However, even this low extent of reaction was sufficient for a number of products to be identified. Table I gives some typical values obtained for the peak heights of masses 32, 33, and 34 in the presence and absence of hydrogen, using an electron accelerating potential of 50 volts.

When H_2O_2 was added to the mass spectrometer to obtain its mass spectrum, it underwent a slow catalyzed decomposition. Therefore, although the 33/34 ratio for

^{*} This work was done under Defence Research Board Grant 5001-10 Project No. D44-50-01-10. ¹ G. C. Eltenton, J. Chem. Phys. 15, 455 (1947). ² S. N. Foner and R. L. Hudson, J. Chem. Phys. 21, 1374, 1608

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G. Hoey and K. O. Kutschke, private communication.

¹⁰ K. U. Ingold and F. P. Lossing, J. Chem. Phys. 21, 1135 (1953).

¹¹ F. P. Lossing and A. W. Tickner, J. Chem. Phys. 20, 907 (1952).

 H_2O_2 could be determined accurately, the 32/34 ratio could not be obtained since part of the 32 peak was due to oxygen gas and part to O_2^+ from H_2O_2 . This means that the change in the oxygen concentration will be larger than is shown in Table I by an amount given by the 32/34 ratio for H₂O₂. However, this ratio is unlikely to be greater than unity, and is probably of the order of the 33/34 ratio. For this reason the extent of the $H_2 - O_2$ reaction can only be given approximately.

It should be noted that although water is the end product of reaction under normal conditions, not much more than half the oxygen consumed is converted to water under the present conditions. The increase in the water peak cannot therefore be used to measure the degree of reaction.

In Table I any uncertainties in the measurement of oxygen isotope ratios and residuals are cancelled out by taking differences. With 50-volt ionizing electrons the 33/34 ratio for H_2O_2 was found to be 0.096, so the contribution of H_2O_2 to mass 33 is 0.06, leading 0.32 which must be due to the HO₂ radical. The presence of H_2O_2 and HO_2 was confirmed with 20-volt ionizing electrons.[†] At this electron energy the 33/34 ratio for H_2O_2 is only 0.033. A typical spectrum is shown in

TABLE I. Products of $H_2 - O_2$ reaction (50-volt electrons) peak heights in arbitrary units.

Mass No.	H ₂ present	H2 absent	Difference
32	71.1	74.3	3.2
33	0.98	0.60	0.38
34	1.55	0.93	0.62

Fig. 2. In arbitrary units the peak heights are 32, 16.0; 33, 0.50; and 34, 1.49. These figures demonstrate conclusively the presence of H_2O_2 and the HO_2 radical.

By the use of low electron energies OH radicals were also shown to be abundant. No hydrogen or oxygen atoms could be detected, nor was any H_2O_4 found.

Discussion

One of the principal reasons for studying the $H_2 - O_2$ reaction was to compare the present method, in which the reactants were present in very low concentration in a large excess of inert carrier gas, with the low pressure flame technique used by Eltenton¹ and by Foner and Hudson.² The success in detecting HO₂, and the relatively large amount formed compared with the extent of reaction shows that the present method can be very useful in detecting radicals.

Hydrogen atoms have been detected in a similar reaction system in some thermal decomposition reactions.12 The failure to detect them in this work means that their concentration must have been exceedingly

[†] Actual electron energies are lower than indicated voltages by about 1 volt because of contact potentials, space charge, etc. ¹² F. P. Lossing, unpublished results.



low, which would account for the small amount of reaction.

The HO₂ radical has been postulated as an intermediate in the H_2-O_2 reaction.¹³ The present results, in agreement with those of earlier workers,^{2,3} establish that both HO_2 and OH are formed in this reaction. H_2O and H_2O_2 were the only stable products.

THE METHYL-OXYGEN REACTION

Results

The decomposition of mercury dimethyl under conditions similar to those employed in this investigation gave only ethane, methane, and methyl radicals.¹¹ Because of the simplicity of the products and the high



¹³ C. N. Hinshelwood, Proc. Roy. Soc. (London) A188, 1 (1946).



yield of methyl,¹⁰ $Hg(CH_3)_2$ was used as the source of methyl for studying the CH_3-O_2 reaction.

Preliminary experiments were done with a premixed stream of oxygen and mercury dimethyl each at about 10 microns pressure. With the furnace at 640°C, where, in the absence of oxygen, almost no $Hg(CH_3)_2$ was decomposed, the mass 31 peak decreased when the oxygen was shut off. This indicated that CH₃OH or the radical CH₃O was formed by the direct oxidation of $Hg(CH_3)_2$. Under the same conditions no change was detected in the 47 peak (CH₃O₂), but the 33 peak decreased, this decrease being greater than could be accounted for by the contribution of O¹⁶O¹⁷ from the oxygen. The presence of the HO₂ radical was confirmed by cutting off the $Hg(CH_3)_2$ from the premixed stream. Although the oxygen isotope contribution to 33 remained constant, the peak dropped, its decrease being greater than could be accounted for by the 31/33 ratio for CH₃OH, assuming that all of the 31 peak came from CH₃OH. The H₂O₂ contribution to 33 was negligible, and HO₂ must therefore have been present.

With the oxygen and $Hg(CH_3)_2$ entering the reactor separately, the optimum position of the furnace for radical detection was between 1 and 2 cm from the leak. Unless otherwise stated the furnace was at 1000°C and the $Hg(CH_3)_2$ and oxygen were at about 10 and 20 microns pressure, respectively, in 1 cm of helium. Under these conditions the following radicals were detected:

 CH_3 —Large amounts of methyl were present, as is to be expected since the amount of oxidation was small.

 CH_2 —With 12.5 volt ionizing electrons the remaining 14 peak (about 5 mm) disappeared when the oxygen was cut off. It also disappeared as the temperature was lowered, and reappeared as the temperature was raised. At this low electron energy the 14 peak was probably due to methylene radicals. Although ethylene was detected it does not necessarily confirm the presence of CH_2 , as there is some doubt about the efficiency of recombination of methylene.¹⁴ However, the identification of ketene in the products was considered to be strong evidence for the existence of methylene.¹⁴

 CH_3O_2 —With 50-volt electrons, the 47 peak decreased from 5 mm to zero as the temperature was lowered. Since no $CH_3O_2CH_3$, $C_2H_5O_2$, or CH_3O_2H were detected, and since the 46 peak was much too small for there to be any interfering isotopic contribution, the presence of the CH_3O_2 radical was indicated. Its concentration was, however, too low for detection at low electron energies.

CH₃O—With CH₃OCH₃ in the reactor the electron energy was set at a value below the appearance potential of the CH₃O⁺ ion from CH₃OCH₃ and CH₃OH (*ca* 11.5 volts). After removing the ether, the flow system was reactivated and the temperature of the furnace was raised. The 31 peak increased from zero to a maximum value of about 3 mm at 900°C, and as the temperature was further raised to 1000°C the peak dropped to about 2 mm, indicating that this radical is unstable at these high temperatures. At this electron energy the CH₃O⁺ ion could not arise from any stable product and, moreover, it is unlikely that this amount (3 mm at 11.5 volts) could arise from the CH₃O₂ radical (which was only 5 mm at 50 volts). The CH₃O radical was, therefore, probably present.

OH—The hydroxyl radical was detected at low electron energies (ca 15.5 volts) by changing the furnace temperature and by cutting off the oxygen.

 HO_2 —Table II gives the peak heights at masses 32, 33, and 34 at 50 volts, in the presence and absence of $Hg(CH_3)_2$. The change in 32 gives only a rough measure of the degree of reaction as CH_3OH (mass 32) was a very probable reaction product. The increase in the oxygen contribution to 32 when the $Hg(CH_3)_2$ was cut off would be offset therefore by the disappearance of the CH_3OH contribution.

It might be argued that the change in the peak height at mass 33 was due to the isotope contribution of CH₃OH. However, this is unlikely, since the 32 peak height was only about 70.0, of which most must be due to oxygen. Experiments at low electron energies showed that HO₂ was present. Figure 3 shows a typical spectrum obtained with 20-volt electrons. The relative peak heights are 32, 112; 33, 3.9; 34, 4.5. Even with the most adverse assumption that all the 32 is due to CH₃OH, the 33 peak cannot be accounted for completely. Since it is very unlikely that at this electron energy more than a small fraction of the 32 is due to CH₃OH, an appreciable concentration of HO₂ radicals was present. The above results also show the presence of H₂O₂.

CHO—The evidence for this radical was inconclusive. At low electron energies (*ca* 13 volts) the 29 peak disappeared when the $Hg(CH_3)_2$ was cut off, but changing the oxygen pressure caused only a slight alteration in

¹⁴ E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954), second edition, pp. 375, 523.

peak height. At this electron energy the 29 peak could not be entirely due to the $C_2H_5^+$ ion from ethane, but in view of the essentially negative results with oxygen the small intensity difference cannot be ascribed to the CHO radical with certainty. Some confirmation was provided by the identification of acetaldehyde in the products, but it is possible that this was formed by the oxidation of ethane.

No $C_2H_5O_2$ or C_2H_5O radicals, and no hydrogen atoms were detected. The major stable products were H₂O, CO, and CO2 and, of course, methane and ethane as unreacted products of the Hg(CH₃)₂ decomposition. Less important stable products were H_2O_2 (shown to be present at 50 volts and 20 volts), hydrogen (in very small amounts) and acetylene (shown to be present at an electron energy of 12 volts). At 13.5 volts the only appreciable peaks in the 35-50 mass range were at masses 42 and 44; they were probably due to ketene and acetaldehyde, respectively. Using 50-volt electrons both these compounds were shown to be present. At 13 volts the only appreciable peak in the mass range 50-100 was at mass 56. When the $Hg(CH_3)_2$ or oxygen were cut off this peak disappeared; it was most probably methyl ketene or perhaps acrolein. The detection of CH₃OH was made difficult by the identity of its mass with that of oxygen, and the fact that oxygen was present in large excess. However, some slight evidence for its presence was obtained at electron energies below the ionization potential of oxygen. The detection of C_2H_4 was also difficult because of the low appearance potential of the $C_2H_4^+$ ion from C_2H_6 . However, the appearance potential of the $C_2H_3^+$ ion from C_2H_4 is about 0.6 volts lower than its appearance potential from C_2H_6 . At low electron energies the mass 27 peak increased slightly when oxygen was added; this increase was attributed to ethylene formation.

No $CH_3O_2CH_3$, CH_3O_2H , CH_3OCH_3 , or H_2CO_2 were detected. Because of the interference from other products at parent mass numbers it was not possible to check for O atoms or CH_2O .

It was difficult to estimate the degree of reaction, but it appeared to be small. It was not possible to use the change in mass 15 at low electron energies as the oxygen pressure was altered, since methyl is known to be a product in the CH_4-O_2 reaction.^{1,2} Assuming that the amount of CH_3OH produced was small the change in the mass 32 peak when the $Hg(CH_3)_2$ pressure was altered indicated that about 3% of the oxygen was consumed.

Discussion

Eltenton¹ found that methyl could be readily detected in the decomposition of lead tetramethyl when oxygen was used as the carrier gas, and he therefore concluded that methyl was rather stable to oxygen—a conclusion which was supported by his measurements of methyl in CH_4-O_2 flames. However, he did attribute

TABLE II. Products of CH_3-O_2 reaction (50-volt electrons) peak heights in arbitrary units.

Mass No.	Hg(CH ₃) ₂ present	Hg(CH ₃) ₂ absent	Difference
32	69.8	72.0	2.2
33	0.63	0.31	0.32
34	0.98	0.59	0.39

his mass 30 peak to formaldehyde rather than to ethane, which was probably correct since he was using a very large excess of oxygen. On the other hand, a number of workers have studied the influence of oxygen on photochemically produced methyl.⁴⁻⁹ The general conclusion is that quite small partial pressures of oxygen will completely inhibit ethane formation, indicating that the removal by oxygen

$$CH_3 + O_2 \rightarrow ?$$
 (1)

must be fast, since the competing reaction

$$CH_3 + CH_3 \rightarrow C_2H_6$$
 (2)

has a collision efficiency of unity.[‡]

Marcotte and Noyes⁴ have estimated the steric factor for the reaction

$$CH_3+O_2 \rightarrow CHO+H_2O$$

to be 2×10^{-4} , with zero activation energy. Van Tiggelen has suggested an activation energy of 1.5 kcal for this reaction,⁷ and zero for the reaction⁸

$$CH_3+O_2\rightarrow H_2CO+OH.$$

For the reaction

 $CH_3 + O_2 \rightarrow CH_3O_2$,

Blaedel *et al.*⁶ have estimated an activation energy of 3 kcal, and Hoey and Kutschke⁹ have calculated an activation energy of 0.4 kcal and a steric factor of 7×10^{-3} .

In a system involving two competing reactions of very different rates it is usually difficult to measure the steric factor and activation energy of the slow reaction. This was particularly true in the present work, since large oxygen pressures shortened the life of the mass spectrometer filament. Moreover, the amount of reaction (1) could only be estimated roughly. Any calculation of the collision efficiency of this reaction must therefore be very approximate. However, by comparing the present results with those of Ingold and Lossing¹⁰ for reaction (2) under similar conditions, the collision efficiency of reaction (1) is found to be of the order of 10^{-3} to 10^{-4} .

In view of the large number of reactions which might possibly give the detected products,¹⁴ the following are

[‡] See reference 14, p. 538.

only tentatively suggested.

 $CH_3 + O_2 \rightarrow CH_3O_2$ $CH_3 + O_2 \rightarrow H_2CO + OH$ $CH_3 + O_2 \rightarrow CH_2 + HO_2$ $CH_{3}O_{2}+CH_{3}\rightarrow CH_{3}O_{2}CH_{3}$ $CH_{3}O_{2}+RH \rightarrow CH_{3}O_{2}H+R$ $CH_{3}O_{2}CH_{3} \rightarrow 2CH_{3}O$ $CH_{3}O_{2}H$ \rightarrow CH₃O+OH CH₃O \rightarrow H₂CO+H $CH_{3}O + RH \rightarrow CH_{3}OH + R$ $+O_2 \rightarrow HO_2$ Η

The CHO radical, if present, might be formed by either

$$H_2CO+O_2 \rightarrow HO_2+CHO$$

or perhaps

 $CH_3 + O_2 \rightarrow CHO + H_2O.$

It would be removed by two fast reactions:

$$CHO+O_2 \rightarrow HO_2+CO,$$

$$CH_3+CHO \rightarrow CH_3CHO.$$

CO, CO_2 , and H_2O were naturally to be expected as products. H₂O₂ could be formed from HO₂ and a H atom or by the combination of two OH radicals. Ketene could come from the reaction¹⁴

$$CH_2+CO\rightarrow CH_2CO.$$

Acetylene and methyl ketene or acrolein (mass 56) cannot be accounted for as easily and were probably secondary products produced after several reaction steps. CH₃O₂CH₃ and CH₃O₂H are very unstable with respect to O-O bond scission even at room temperatures. At 1000°C their lifetime will be less than 10⁻⁶ sec. With a flow rate of only 5000 cm/sec in the reactor, their absence from the products was not surprising. Their decomposition would account for the CH₃O and OH radicals.

Although most of the radicals reported here were detected by Eltenton¹ in the $CH_4 - O_2$ flame, the present method has the advantage that, because of the low concentration of reactants, the concentration of intermediates relative to final products is much higher than in low-pressure flames. For this reason their detection is easier and the whole mass spectrum is less complicated.

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Spectroscopic Properties of Organic Photoconductors. I. Absorption Spectra of Cationic Dye Films

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The absorption spectra of solid films of six photoconductive dyes are reported. The transitions in the solid state correspond to those of the "isolated" cations in solution. However, the longest-wavelength singlet-singlet absorption band is split into components separated by 1000 cm^{-1} or more. Other bands are unaffected, except for a general decrease of oscillator strength. The results are interpreted in terms of light absorption by a single molecule, followed by exciton motion in the lowest excited state.

HE electronic energy levels of organic crystals generally are nearly identical with those of the individual molecules, and the molecules act in various ways as though they were isolated. In a number of highly conjugated solids, however, there is sufficient interaction among neighbors to permit excited electrons to migrate through a "conduction band"-a communal energy level extending through large regions of the lattice. These are the organic semi- and photoconductors. The best known of these are, at present, the photoconductive films of cationic dyes, which have recently been investigated in detail by

* This work was supported by the Charles F. Kettering Foundation.

Vartanian¹ and Nelson.² These systems are of special interest because their solid-state behavior is largely determined by well-known properties of their isolated components.

The present series of papers on the absorption, reflection, and action spectra³ of certain of these photoconductive dye films (referred to, below, as I,

³ An excitation, or action spectrum of photoconduction is the relationship between the wavelength of incident light and the photocurrent produced.

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