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Rates of elementary processes in the chain reaction between hydrogen and oxygen

I. Reactions of oxygen atoms

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The rates of reaction of 3P oxygen atoms with hydroxyl and hydrogen have been measured in a flow system at pressures around 2 mmHg.

The former reaction,



occurred in the products of the rapid reaction between H and NO_2 , and was followed by measurements of atomic oxygen concentrations. k_{-4} was found to be $5 \pm 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 265 and 293 °K. This result, when combined with data on the reverse reaction at elevated temperatures, gives a value of k_{-4} which is virtually independent of temperature and equal to about 1/20 of the bimolecular collision frequency.

The reaction



was studied in the absence of molecular oxygen and found to have a rate constant of $6 \times 10^{-13} T^{\frac{1}{2}} \exp(-8900/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the range 409 to 733 °K. This is in good agreement with values obtained at higher temperatures. The rate constant for $\text{O} + \text{D}_2$ was significantly less than that for $\text{O} + \text{H}_2$ at temperatures between 491 and 671 °K.

INTRODUCTION

Few reliable data regarding the kinetics of individual steps in the chain reaction between hydrogen and oxygen are available, and in this series of papers values for the rate constants of some of these reactions are reported. Initiation reactions will not be considered, since the mode of initiation is still uncertain in the unsensitized hydrogen + oxygen reaction. The primary concern of these papers is with the simple, unsensitized reaction and emphasis is placed on the well-established propagation and branching steps



Reaction (2) can either participate as part of the propagation chain or alternatively as a termination step by means of wall deactivation of HO_2 radicals. This paper reports kinetic measurements on reactions (3) and (-4) , while a second paper (Clyne & Thrush 1963) discusses the kinetics of formation and removal of HO_2 and the role of surface deactivation of HO_2 in the hydrogen + oxygen reaction.

In view of the large number of reported determinations of the rate constants k_1 to k_4 and their reverse processes, it is desirable to consider critically the nature

of the methods used for these determinations and their limitations. The methods fall into three principal groups, (i) measurements of explosion limits and reaction rates for mixtures of $\text{H}_2 + \text{O}_2$ and $\text{CO} + \text{O}_2$ with added hydrogen in closed systems (Baldwin 1956; Karmilova, Nalbandyan & Semenov 1958; Azatyan, Voevodskii & Nalbandyan 1961); (ii) sampling of flames, especially at low temperatures (Fenimore & Jones 1959, 1961); and (iii) rate measurements in flow systems at low pressures, with the use of electric discharges to generate atomic species (Harteck & Kopsch 1931; Kaufman 1961; Clyne & Thrush 1961*a*). The first technique has been used mainly in studies of explosion limits, where the rates of chain branching and terminating reactions are equal. The temperature range of such measurements is naturally limited but the rate constants obtained are usually self-consistent and are generally in fair agreement with those obtained by other methods. For example, data on the second explosion limit in the $\text{H}_2 + \text{O}_2$ system yield the ratio k_2/k_4 , while first explosion limit data give ratios of k_4 to the rate constant of H atom removal at the vessel wall. Making an assumption about the latter, Nalbandyan & Voevodskii (1948) derive $k_4 = 4.3 \times 10^{-12} T^{\frac{1}{2}} \exp(-18000/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, as compared to Schott & Kinsey's (1958) value of $2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1650°K, obtained by measurements of the rise of OH radical concentrations in shock-heated hydrogen + oxygen mixtures. Determinations of individual rate constants are thus very useful in deriving the value of other velocity constants from explosion limit data, since assumptions about unknown rates of atomic combination processes are then unnecessary for the interpretation of the ignition-limit data. In their flame studies Fenimore & Jones (1959, 1961) have measured several of the rate constants k_1 to k_4 using sampling techniques, while much information is now becoming available from discharge-flow experiments at temperatures near 300°K. When the $\text{H} + \text{O}_2$ and $\text{O} + \text{H}_2$ systems are studied by this method, reactions (1) to (4) and their reverse processes can proceed at comparable rates leading to complex reaction schemes. For this reason, little weight can be given to early work based exclusively on product analyses, such as the determination of the activation energy of reaction (3) by Harteck & Kopsch (1931).

In view of the complexities mentioned above, it is clearly important to follow the concentrations of the labile species throughout the reaction, and also to establish the overall stoichiometry of the reaction. The concentrations of H and O atoms in the reacting gases can be determined by measurement of the intensities of the chemiluminescent HNO and NO_2 (air afterglow) emissions, respectively, as described later. In studies complementary to ours, Del Greco & Kaufman (1962) have used electronic absorption spectroscopy to follow the concentrations of hydroxyl radicals in flow systems.

EXPERIMENTAL

Ground-state atoms were generated by dissociation of purified molecular gases in an electrodeless electric discharge at 18 Mc/s. From the discharge tube, partially dissociated gas entered a 25 mm diameter Pyrex flow tube along the length of which were inlets for the admission of reactant gases at 25 cm intervals. Under steady-state flow conditions, the time t for a total flow of gas ΣF to travel a distance x along the

tube is given by $t = xAp/RT\Sigma F$, where p is the total gas pressure and A is the cross-section area of the tube. Low concentrations of atoms were used so that temperature rises due to chemical reaction were less than 10°C , and radial concentration gradients in the 25 mm tube were calculated to be negligible. The influence of back diffusion of active species upon the measured rate constants was also small and the appropriate corrections of 2 to 8 % of the observed rate constants were made for this effect. The axial pressure gradient was measured as less than 5 % of total pressure for the whole length of the flow tube, and corrections were made to the observed rates of atom removal.

Rates of reaction of atoms were measured by determining the atom concentrations remaining in the gas stream at the fixed observation point (10 cm downstream from the last inlet jet) when the same reactant partial pressures were added at the various inlets, each corresponding to a different reaction time. From such data a plot of the reduction in atomic concentration against reaction time t can be made. It can be seen that this atomic decay is to be attributed exclusively to the reaction (11) of atoms A with reactant molecules R , since the atom concentration at the fixed observation point is constant in the absence of added reactant. The following analysis is used. We suppose that three concurrent reactions remove atoms,



The rate of reaction of atoms is of the form

$$-d[A]/dt = 2k_9[A]^2[M] + [A](k_{10} + k_{11}[R]).$$

On integration we obtain

$$\ln\left(\frac{[A]}{[A]_0}\right) - \ln\left(\frac{2k_9[A][M] + k_{10} + k_{11}[R]}{2k_9[A]_0[M] + k_{10} + k_{11}[R]}\right) = (k_{10} + k_{11}[R])t.$$

where $[A] = [A_0]$ when $t = 0$. The total flow time to the observation point is $(t_1 + t_2)$, and reactant can be added at time $t = t_1$ when the atom concentration is $[A]_1$. Let the atom concentration at the observation point be $[A]_2$ when no reactant R is added, and $[A]_3$ when R is added at $t = t_1$. It can be shown that

$$\ln\left(\frac{[A]_1}{[A]_0}\right) - \ln\left(\frac{2k_9[M][A]_1 + k_{10}}{2k_9[M][A]_0 + k_{10}}\right) = -k_{10}t_1,$$

$$\ln\left(\frac{[A]_2}{[A]_0}\right) - \ln\left(\frac{2k_9[M][A]_2 + k_{10}}{2k_9[M][A]_0 + k_{10}}\right) = -k_{10}(t_1 + t_2),$$

$$\ln\left(\frac{[A]_3}{[A]_1}\right) - \ln\left(\frac{2k_9[M][A]_3 + k_{10} + k_{11}[R]}{2k_9[M][A]_1 + k_{10} + k_{11}[R]}\right) = -(k_{10} + k_{11}[R])t_2,$$

and therefore

$$\ln\left(\frac{[A]_3}{[A]_2}\right) - \ln\left(\frac{2k_9[M][A]_3 + k_{10} + k_{11}[R]}{2k_9[M][A]_1 + k_{10} + k_{11}[R]}\right) \times \left(\frac{2k_9[M][A]_1 + k_{10}}{2k_9[M][A]_2 + k_{10}}\right) = -k_{11}[R]t_2.$$

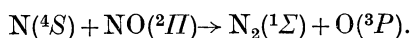
Provided that $k_{10} + k_{11}[R] \gg 2k_9[A][M]$ and $k_{10} \gg k_9[M]([A]_1 - [A]_2)$, this equation reduces to the simple form

$$\ln([A]_3/[A]_2) = -k_{11}[R]t_2.$$

The condition for reaction (9) to be much slower than reaction (10) or (11) was easily fulfilled by working with low concentrations of atoms. The method is very useful for the determination of the rates of third-order combination reactions, such as the $\text{H} + \text{NO} + M$ reaction (Clyne & Thrush 1961*b*, 1962) and the $\text{H} + \text{O}_2 + M$ system described here, since the measurements give the required third-order rate constants without involving large corrections for concomitant atomic recombination processes. It should be noted that the addition of small quantities of NO for photometric studies merely increases k_{10} slightly and emphasizes rather than impairs the accuracy of this kinetic method.

Measurements of the reactant flow rates F were made with calibrated capillary flowmeters; the corresponding partial pressures p_i of the reactants were then given by $p_i = Fp/\Sigma F$. Details of the flow tube and furnace were as previously described.

Oxygen, nitrogen and hydrogen atoms ($\frac{1}{4}$ to 1 %) in the presence of their parent molecular gases were generated by a discharge in the pure O_2 , N_2 and H_2 . Atomic species with argon or helium as carrier were produced by discharges in mixtures of the pure molecular gases (1 %) with dry inert gas (99 %). The products of such discharges contained about 1 % each of atomic and molecular species. Oxygen atoms in a nitrogen carrier were also generated by addition of the stoichiometric quantity of nitric oxide to a stream of partially dissociated nitrogen from the discharge



Considerations of spin correlation in this very rapid reaction indicate that only ground-state oxygen 3P atoms are produced. Oxygen atoms obtained from the $\text{N} + \text{NO}$ reaction exhibited indistinguishable chemical properties from those produced by discharges in oxygen. Other evidence for the lack of significant concentrations of excited atoms in the products of discharges in N_2 , O_2 and H_2 includes the work of Tanaka, Jursa & Le Blanc (1957) on nitrogen atoms and the absence of atomic emission from the products of hydrogen discharges. Recent work (Foner & Hudson 1962) shows that while significant concentrations of excited atoms are present less than 1 msec from the discharge, these do not persist.

Pressures of atomic hydrogen and oxygen in the system were determined photometrically or by NO_2 titration. In the first method, small amounts of nitric oxide were added to the gas stream just before the observation point, an E.M.I. type 9558 photomultiplier cell equipped with infra-red (Wratten 88 A) and green (Wratten 61) transmission filters. The intensity I_a of the green-grey air afterglow produced is given by $I_a = I_{0a}[\text{O}][\text{NO}]$ (Kaufman 1958) and the intensity of the infra-red HNO emission spectrum by $I_b = I_{0b}[\text{H}][\text{NO}]$ (Clyne & Thrush 1961*b*, 1962). $I_a/[\text{NO}]$ and $I_b/[\text{NO}]$ were then proportional to $[\text{O}]$ and to $[\text{H}]$, respectively. The constants of proportionality I_0 were determined by simultaneous measurement of $I[\text{NO}]$ and atom concentration. $[\text{O}]$ was determined by NO_2 titration (Kaufman 1958), and $[\text{H}]$ with the use of the isothermal wire calorimeter (Clyne & Thrush 1961*b*).

These calibrations allowed the rapid computation of $[O]$ and $[H]$ from measurements of $I_a/[NO]$ and $I_b/[NO]$ in mixed $O + H$ systems. In such systems the photo-current observed with the 61 filter is directly proportional to I_a , since the HNO emission spectrum has no detectable intensity at energies greater than 6000 \AA . However, the air afterglow spectrum has an appreciable intensity in the near infra-red in the region of transmission of the 88 Å filter. A small correction for this effect was made by use of the experimentally determined relation.

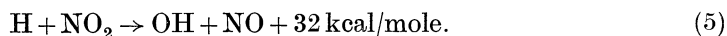
$$I_b = I_{88\text{Å}} - 0.032I_{61}.$$

For $[H]/[O] = 100$ this correction was 15 % of $I_{88\text{Å}}$, so that $[H]$ in the presence of $[O]$ could be measured accurately only when the concentration of the latter species was small, as in the products of reaction of H with NO_2 and with O_2 .

RESULTS

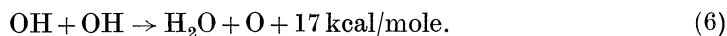
Reaction of O (3P) with OH (2II)

Ground-state hydroxyl radicals were generated by addition of nitrogen dioxide to a stream of hydrogen atoms in an argon carrier



The rate constant of reaction (5) is near the bimolecular collision frequency and it has an activation energy near zero (Ashmore & Tyler 1962; Rosser & Wise 1961).

Hydroxyl radicals undergo a fairly rapid bimolecular reaction (6) (Del Greco & Kaufman 1962; Clyne 1962), thus generating the oxygen atoms which are observed:



Under conditions where the concentration of H_2 in the flow system is negligible, as in the $Ar + H$ mixtures used here, reaction of OH with H_2 can be neglected as a rate-determining step for hydroxyl removal, and it will be shown that measurements of the rates of decay of oxygen atom concentrations in the $O + OH$ system lead to a value for the rate constant k_{-4} .

The variation of $[H]$ and $[O]$ in the $H + NO_2 + Ar$ reaction products was studied as a function of reaction time t , of total pressure and of concentration of added nitrogen dioxide, $[NO_2]_0$. Since nitric oxide is a stoichiometric product of the $H + NO_2$ reaction (Clyne & Thrush 1961*a*), the values of $I_a/I_{0a}[NO_2]_0$ and $I_b/I_{0b}[NO_2]_0$ measured in the reaction products are equal to $[O]$ and $[H]$ respectively. Further, the initial concentration of hydroxyl $[OH]_0$ produced in reaction (5) is equal to $[NO_2]_0$. When $5 \times 10^{-3} \text{ mmHg}$ of NO_2 was added to $1 \times 10^{-2} \text{ mmHg}$ of hydrogen atoms, measurements of I_a showed that 10^{-5} to 10^{-6} mmHg of atomic oxygen was present in the reaction products. Figure 1 shows that for a constant reaction time of 0.03 s, $[H]$ was a linear function of the concentration of added NO_2 , while $[O]$ was practically independent of $[OH]_0$ over a wide range. The rate of decay of $[O]$ was measured at a total pressure of 1.1 mmHg, under which conditions there was found to be no detectable removal of atomic hydrogen from the system. The rate of removal of

oxygen atoms was proportional to $[O]^2$ and was independent of the concentration of atomic hydrogen present,

$$-d[O]/dt = k'[O]^2.$$

Figure 2 shows a typical oxygen atom decay plot. No significant dependence of k' upon total pressure was observed in the range 1.09 to 2.23 mmHg, nor was there any difference between values of k' determined at 293 and 265 °K. The value of k' was much larger than the reported constant for the reaction $O + O + M \rightarrow O_2 + M$ (Morgan, Elias & Schiff 1960).

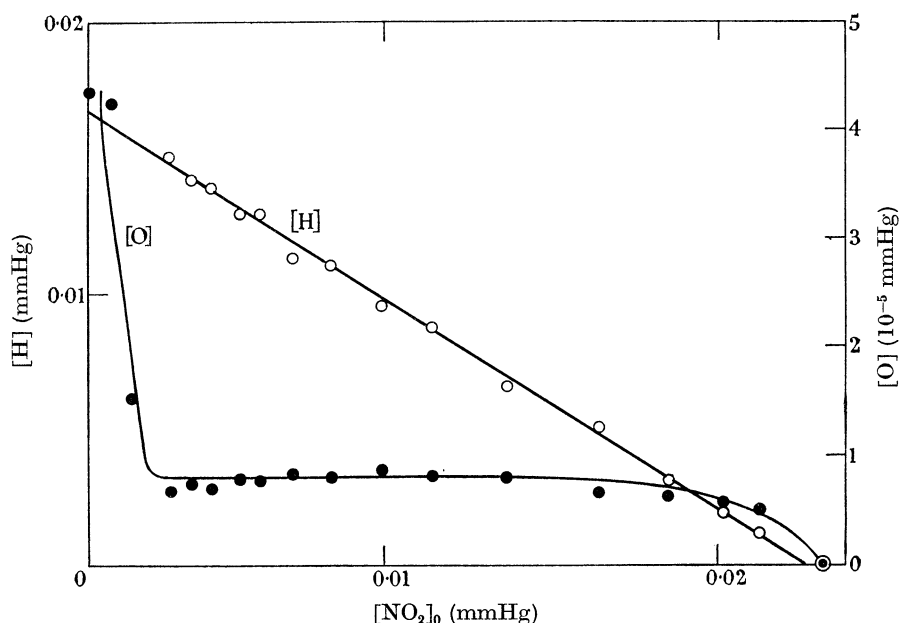
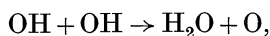


FIGURE 1. The variation of atom concentrations in the reaction between atomic hydrogen and nitrogen dioxide at 293 °K for a constant reaction time of 0.03 s. Total pressure, 1.09 mmHg.

It has been previously established (Clyne & Thrush 1961*a*; Del Greco & Kaufman 1962) that the oxygen atoms observed in the $H + NO_2$ reaction products are produced by reaction (6),



but it is necessary to consider carefully the possible reactions which may remove oxygen atoms, since the very small concentrations observed clearly indicate that most of the O atoms are rapidly removed from the reaction system. Third-order atomic combination processes involving oxygen atoms cannot contribute appreciably to O atom decay under our conditions, and atomic oxygen can thus be removed by means of either reaction (–4) or (7),



Reaction (−4) is a very rapid process with a rate constant around $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 293 °K while k_7 is known to be about $10^{-11.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Kistiakowsky & Kydd 1957; Ford & Endow 1957) under these conditions. However, nitrogen dioxide is removed in the $\text{H} + \text{NO}_2$ reaction by the extremely rapid reaction (5) in competition with reaction (7), and reaction (7) will therefore become rate determining for O atom removal only when $[\text{H}]$ is very small, as shown by the tailing of the oxygen atom concentration plot near the point of critical atom removal in figure 1. It follows that under conditions where hydrogen atoms are

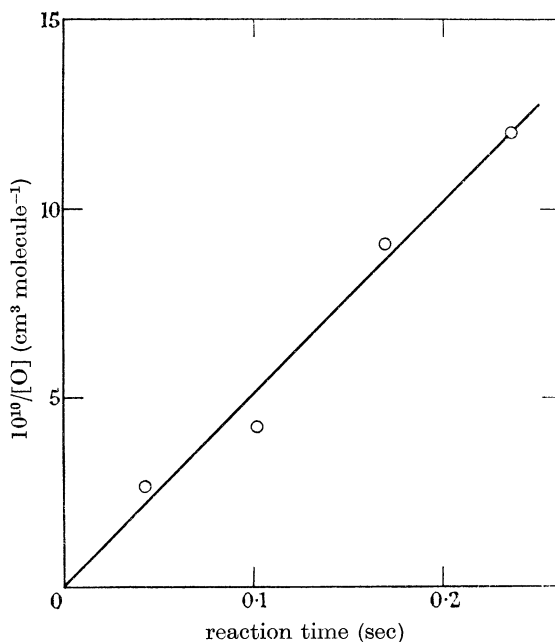


FIGURE 2. Second-order decay plot for oxygen atoms in their reaction with hydroxyl at 293 °K and a total pressure of 1.1 mmHg, using argon carrier gas.

present in excess, reaction (−4) is dominant for oxygen atom removal. Reactions (6) and (−4) thus determine oxygen atom production and removal and OH removal, and assuming steady-state concentrations of oxygen atoms,

$$\frac{1}{[\text{OH}]} = \frac{1}{[\text{OH}]_0} + 3k_6 t$$

and

$$k_{-4}[\text{O}] = k_6[\text{OH}],$$

hence

$$[\text{O}] = \frac{k_6}{k_{-4}(1/[\text{OH}]_0 + 3k_6 t)}.$$

k_6 is known to be $2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 °K (Del Greco & Kaufman 1962); it follows that for a typical reaction time of 0.05 s and a value for $[\text{OH}]_0$ of 10^{-2} mmHg , $1/[\text{OH}]_0$ is very much less than $3k_6 t$, and therefore

$$[\text{O}] = \frac{1}{3k_{-4}t},$$

or

$$-d[\text{O}]/dt = 3k_{-4}[\text{O}]^2.$$

The correction to the observed value of $-d[O]/dt$ to allow for the rate of reaction $O + NO + M \rightarrow NO_2 + M$ was about 5 % of the total rate. This reaction scheme is in agreement with the observed second-order removal of $[O]$ and with the lack of dependence of $d[O]/dt$ upon $[H]$, $[OH]_0$ and total pressure. The sharp drop in oxygen atom concentration at the left-hand side of figure 1 is due to the presence in the discharge products of a higher concentration of oxygen atoms than that given by the steady state established by reactions (6) and (-4) . Values of k_{-4} determined from the data were $5 \pm 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 293 and 265 °K.

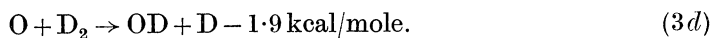
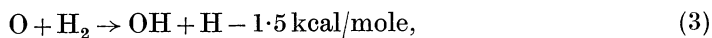
The validity of the assumption of a steady-state concentration of atomic oxygen in this system can be tested in the following manner. For a steady-state assumption to be a good approximation, the difference between the rates of formation and removal of oxygen atoms ($k_2[OH]^2 - k_{-4}[O][OH]$) must be much smaller than either of the individual terms $k_2[OH]^2$ and $k_{-4}[O][OH]$. The difference between these terms is the observed *net* rate of removal of atomic oxygen, $k'[O]^2$, which was typically $6 \times 10^{11} \text{ molecule cm}^{-3} \text{ s}^{-1}$; while the value of $k_2[OH]^2$ calculated from Del Greco & Kaufman's (1962) data under similar conditions was about $6 \times 10^{13} \text{ molecule cm}^{-3} \text{ s}^{-1}$. It follows that a steady-state concentration of oxygen atoms is rapidly established in our system.

Titration of atomic hydrogen with NO₂

The linear variation in figure 1 of $[H]$ with the concentration of added NO_2 , $[NO_2]_0$, shows that reaction of H with NO_2 is rapid and stoichiometric. Thus by observation of the critical NO_2 concentration $[NO_2]_{00}$ for extinction of the HNO emission, the stoichiometry point of the reaction is obtained. When the point of critical H atom removal is measured 15 cm downstream from the point of addition of NO_2 in our flow system, reaction (6) (followed by reaction (-4)) will have proceeded virtually to completion (Del Greco & Kaufman 1962). Each NO_2 molecule added removes one H atom with the formation of one OH radical. This OH radical then regenerates $\frac{1}{3}H$ in the reaction time which elapses between addition of NO_2 and the gas passing the observation point. It follows that the stoichiometry point observed under these conditions is such that $[H]_0 = \frac{2}{3}[NO_2]_{00}$ where $[H]_0$ is the initial concentration of atomic hydrogen. This relationship can be tested by independent measurement of $[H]_0$ with the use of the isothermal wire calorimeter (Clyne & Thrush 1961*b*). Considering the errors known to be associated with the wire calorimeter, the uncorrected experimental value for $[H]_0/[NO_2]_{00}$ of 0.53 is in good agreement with the predicted value of 0.67. Titration of atomic hydrogen with NO_2 to the critical extinction of the HNO emission or air afterglow spectrum can therefore be used for the measurement of atomic hydrogen concentrations. Unfortunately, the method cannot be used at elevated temperatures if H_2 is present, but at 300 °K the rate of reaction (1) is slow enough for its effect on the stoichiometry to be neglected if $[H]/[H_2]$ is greater than $\frac{1}{4}$ (Del Greco & Kaufman 1962; Clyne & Thrush 1961*a*). The titration method is therefore limited to room temperature systems where molecular hydrogen is not the carrier gas.

Reaction of O(³P) with H₂ and with D₂

Measurements of the rates of decay of atomic oxygen in the presence of molecular hydrogen and deuterium give the necessary information for the calculation of the rate constants k_3 and k_{3d} ,



Hydrogen atoms are a product of reaction (3), and when molecular oxygen is the carrier gas for the atomic species, HO₂ is formed in the three-body process (2). Reaction of atomic oxygen with these HO₂ radicals must be considered to contribute

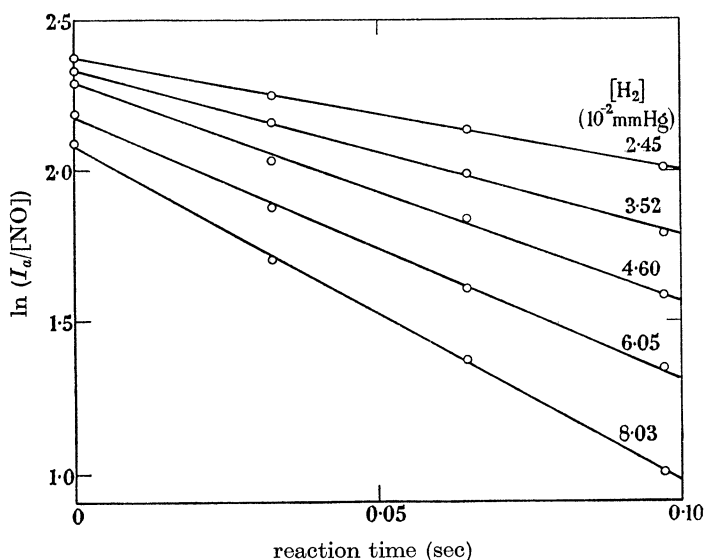


FIGURE 3. The O + H₂ reaction. Variation of atomic oxygen concentration with reaction time for various concentrations of molecular hydrogen at 441 °K. Reagent pressures: O, 0.0033 mmHg; H₂, 0.025 to 0.080 mmHg; N₂, 2.15 mmHg.

to oxygen atom removal in the O + H₂ system. It follows that a simple kinetic scheme in this system obtains only when the carrier gas is inert. For this reason ground state oxygen atoms for use in the kinetic study of the O + H₂ reaction were generated by addition of the stoichiometric quantity of nitric oxide to a stream of partially dissociated nitrogen, as described on page 547. Small amounts of nitric oxide were added to the reaction products. The photocurrent of a 1 P 28 phototube fitted with a Wratten 61 filter (which absorbs red light) was measured at a fixed point in the flow system. Under these conditions the contribution to the total photocurrent by the HNO emission was negligible, and I_a was equated to the total photocurrent. $I_a/[NO]$ is proportional to [O]. Excess hydrogen or deuterium ($[\text{H}_2] \gg 5[\text{O}]$) was added to the flow system upstream from the photo tube.

It was found that for both H₂ and D₂, plots of $\ln [\text{O}]$ against reaction time t were linear with slopes proportional to $[\text{H}_2]$. Typical data are shown in figure 3 and in

table 1. Table 2 shows that $(1/[H_2]) d \ln [O]/dt$ was independent of total pressure between 1.71 and 2.77 mmHg. The absence of any significant dependence upon total pressure is not unexpected, since the only third-order reaction which could be important is spin forbidden:

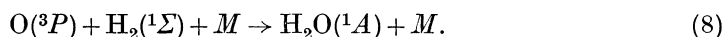


TABLE 1. THE VARIATION OF $d/dt \ln (I_a/[NO])$ WITH $[H_2]$ AT 554 °K
AND 2.18 MMHG TOTAL PRESSURE

$[H_2]$ (molecules cm^{-3})	$\frac{d}{dt} \ln \left(\frac{I_a}{[NO]} \right)$ (s^{-1})	$\frac{1}{[H_2]} \frac{d}{dt} \ln \left(\frac{I_a}{[NO]} \right)$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
4.17×10^{14}	3.84	9.19×10^{-15}
6.03	5.63	9.33
7.91	7.38	9.31
9.78	9.38	9.59
13.70	11.36	8.27

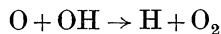
TABLE 2. THE VARIATION OF $1/[H_2] (d/dt) \ln (I_a/[NO])$ WITH TOTAL
PRESSURE AT 623 °K

total pressure (mmHg)	$\frac{1}{[H_2]} \frac{d}{dt} \ln \left(\frac{I_a}{[NO]} \right)$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
1.71	2.08×10^{-14}
2.11	1.99×10^{-14}
2.77	2.02×10^{-14}

The kinetic data can be represented by the equation

$$-d[O]/dt = k'''[O][H_2]$$

for both isotopic species of hydrogen. The equilibrium constant of reaction (3) is around unity, but since the final concentration ratio $[H]/[H_2]$ was typically 0.1–0.2, and OH is rapidly removed from the system, the reverse reaction (–3) can be neglected in comparison to reaction (3) as a rate-determining step. The relative magnitudes of k_1 , k_{-4} and k_6 (Del Greco & Kaufman 1962, this work) show that reaction (–4),



is predominant for OH removal. k_{-4} is much greater than k''' in these circumstances and hence

$$-d[O]/dt = 2k_3[O][H_2].$$

The analysis predicts that for every oxygen atom removed, one hydrogen atom is formed. If secondary reaction (1) rather than (–4) were predominant for hydroxyl removal, two H would be produced for every O reacted. The stoichiometry of the overall reaction was therefore tested in the following manner. The pressure in the flow tube was adjusted so that addition of a 20-fold excess of H_2 to O atoms in a nitrogen carrier resulted in at least 98 % removal of atomic oxygen at the downstream photomultiplier. A small amount of NO was added to the reaction system.

The infra-red photocurrent I_b due to $\text{H} + \text{NO}$ was measured under these conditions. The air afterglow intensity I_a was then determined at the same point when the hydrogen flow was added *downstream* from the photomultiplier tube. In this way the ratio of $[\text{O}]$ consumed to $[\text{H}]$ formed was determined as 1.0 ± 0.1 at 660°K . This experiment confirms that the slow primary step (3) is followed by the rapid reaction (–4). Values of k_3 were thus determined for H_2 in the range 409 to 733°K as shown in table 3. By substitution of deuterium for hydrogen as reactant, with unaltered flow conditions, the ratio k_3/k_{3d} was determined at four temperatures from 491 to 671°K . The values are also shown in table 3. Figure 5 is a plot of $(\log_{10} k_3 - \frac{1}{2} \log_{10} T)$ against $1/T$; the data can be represented by the expression

$$k_3 = 6 \times 10^{-13} T^3 \exp(-8900 \pm 700/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

or by

$$k_3 = 2 \times 10^{-11} \exp(-9400 \pm 700/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

No significant variation of k_3/k_{3d} with temperature is apparent from the data.

TABLE 3

(a) *Variation of k_3 with temperature*

$T (^\circ\text{K})$	$k_3 (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
733	$3.6 \pm 0.3 \times 10^{-14}$
623	$1.0 \pm 0.1 \times 10^{-14}$
554	$4.3 \pm 0.4 \times 10^{-15}$
494	$1.5 \pm 0.2 \times 10^{-15}$
441	$5.3 \pm 0.6 \times 10^{-16}$
409	$2.5 \pm 0.4 \times 10^{-16}$

(b) *Variation of k_3/k_{3d} with temperature*

$T (^\circ\text{K})$	k_3/k_{3d}
671	1.2 ± 0.2
648	1.1 ± 0.2
522	1.6 ± 0.2
491	1.7 ± 0.2

DISCUSSION

 $\text{O} + \text{OH}$

The value of k_{-4} reported here is about twice that obtained by Del Greco & Kaufman (1962), who also used the $\text{H} + \text{NO}_2$ reaction for the generation of hydroxyl radicals. They introduced atomic oxygen from a separate discharge system to the products of the $\text{H} + \text{NO}_2$ reaction, with simultaneous measurements of the consequent acceleration in the rate of OH removal. The satisfactory agreement between Del Greco & Kaufman's and our values of k_{-4} confirm the correctness of the postulated mechanism for the production and removal of O and OH in the $\text{H} + \text{NO}_2$ system.

Comparison of our value of k_{-4} at room temperatures may be made with values indirectly obtained at temperatures above 700°K . These high temperature values

of k_{-4} can be deduced by combining values for the rate constant of the reverse reaction k_4 with the equilibrium constant k_4/k_{-4} . The main uncertainty in the calculation of k_4/k_{-4} lies in the value for the dissociation energy of the hydroxyl radical used to determine the heat of reaction. Possible errors due to this cause will be reduced if calculations are performed at the higher temperatures to find k_{-4} from k_4 rather than using the low-temperature value of k_{-4} to calculate k_4 . Values so obtained are plotted in figure 4 which also show our data. The high-temperature

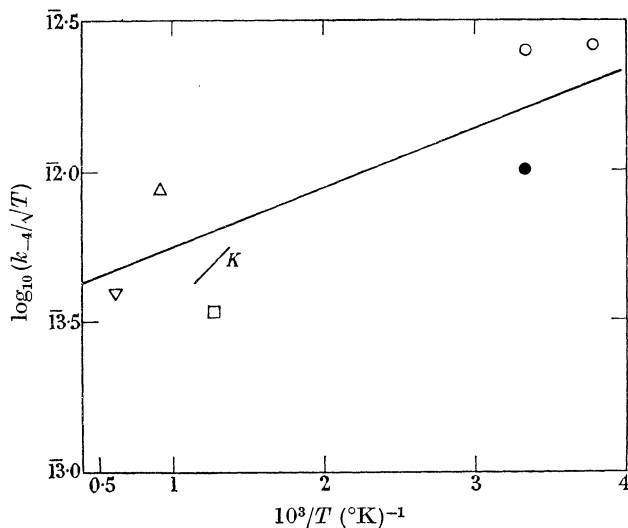


FIGURE 4. The variation of $\log_{10}(k_{-4}/\sqrt{T})$ with $1/T$ from 250 to 2000 °K. k_{-4} is expressed in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Direct determinations of k_{-4} : O, this work; ●, Del Greco & Kaufman (1962). Indirect determinations of k_{-4} (from measurements of k_4 and use of *JANAF* values of $\Delta H_f^\circ(\text{OH})$): Δ, Fenimore & Jones (1959); ▽, Schott & Kinsey (1958); □, Baldwin (1956); K, Karmilova *et al.* (1958).

data are from Schott & Kinsey's (1958) work on shock-heated hydrogen + oxygen mixtures at 1650 °K, sampling of hydrogen + nitrous oxide flames burning at 1100 °K (Fenimore & Jones 1959), and from explosion limit data on the hydrogen + oxygen reaction at 793 °K (Baldwin 1956) and from 733 to 893 °K (Karmilova *et al.* 1958). $\Delta H_f^\circ(\text{OH})$ at 298 °K is 9.3 kcal/mole (Barrow 1956; *JANAF tables* 1960), and using the tabulated values of $\Delta H_f^\circ(\text{OH})$ at temperatures in the range 250 to 1800 °K (*JANAF tables* 1960), these data lead to values of k_{-4} between $10^{-10.5}$ and $10^{-11.0} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at the elevated temperatures of the various systems used. On a collisional basis or for a linear transition state k_{-4} would be expected to be proportional to $T^{0.5}$ ($T^{1.0}$ for a bent transition state) and figure 4 therefore shows a plot of $\log_{10} k_{-4} - \frac{1}{2} \log_{10} T$ against $1/T$. It is evident from this plot that when values of k_{-4} at elevated temperatures are calculated using $\Delta H_f^\circ(\text{OH}) = 9.3 \text{ kcal/mole}$ at 298 °K, $k_{-4} T^{-\frac{1}{2}}$ shows a small negative temperature coefficient. Since it is unlikely that reaction (-4) has a negative activation energy, this observation suggests that $\Delta H_f^\circ(\text{OH})$ may be slightly smaller than the value quoted.

Our data support a value of $\Delta H_f^\circ(\text{OH}) = 10.2 \pm 0.5 \text{ kcal/mole}$ at 298 °K. This corresponds to zero activation energy for the $\text{O} + \text{OH}$ reaction, and a significantly

higher value of this quantity would imply a pre-exponential factor greater than the collision number for the $\text{H} + \text{O}_2$ reaction. The main uncertainty in $\Delta H_f^0(\text{OH})$ is in the dissociation energy of the OH radical and the data presented here suggest a value of about 1 kcal/mole lower than 101.5 ± 0.5 kcal/mole given by Barrow (1956).



The activation energy found for reaction (3) is appreciably higher than the value of 6 ± 1 kcal/mole reported by Harteck & Kopsch (1931) who measured the temperature coefficient of water formation in the reaction of hydrogen with the products of a discharge through oxygen. It is doubtful whether the method of these authors provides an accurate measure of the activation energy of reaction (3). Water is formed mainly in the secondary reaction (1),

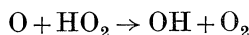
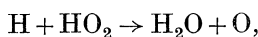


which competes with $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \quad (-4)$

for OH removal, so that the amount of water formed does not provide an unequivocal measure of the extent of reaction (3). In a system where hydrogen atoms are formed in the presence of a large excess of molecular oxygen, the reaction



followed by reactions of the type



must also be considered, since we show in part II that water is a product of the reaction between hydrogen atoms and molecular oxygen. Reaction (2) would be more rapid at low than at room temperatures and could occur to a considerable extent in the cold trap used to condense the products. For these reasons it is doubtful whether the earlier work leads to a reliable value of E_3 . It is also evident that measurements of the rate of oxygen atom removal in the $\text{O} + \text{H}_2$ system lead simply to a determination of k_3 only when O_2 is substantially absent from the system, as in our experiments.

More recently the rate constant of reaction (3) has been determined by three different methods in combustion processes. From a study of the effect of small additions of hydrogen on the first explosion limit of mixtures of oxygen with carbon monoxide between 846 and 930 °K, Azatyan *et al.* (1961) obtained

$$k_3 = 1.1 \times 10^{-10} \exp(-11700 \pm 700)/RT \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

Fenimore & Jones (1961) report rate constants of 4.2×10^{-13} and $5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction (3) at temperatures of 1660 ° and 1815 °K in low-pressure flames. The third determination is that of the chain propagation step in the hydrogen + oxygen system, for which Baldwin (1956) gives a rate constant of $3.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reactions concerned in this system are (3) followed by (1). From recent data on reaction (1) (Kaufman & Del Greco 1962) it is clear that (3) is the rate-determining step and Baldwin's value refers to k_3 .

Figure 5 is an Arrhenius plot of these and our data, and it can be seen that the best straight line through our points represents a satisfactory compromise between the various sets of high-temperature data. The agreement between these data is considered satisfactory in view of the difficulty of determining individual rate constants in complex combustion reactions, and the small ranges of $1/T$ which can be used in such work.

It is interesting to compare our rate constant of $10^{-10.5} \exp(-9400 \pm 700/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the $\text{O} + \text{H}_2$ reaction with the value of $10^{-10.9} \exp(-5500/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained by Ashmore & Chanmugam (1953) for the closely related

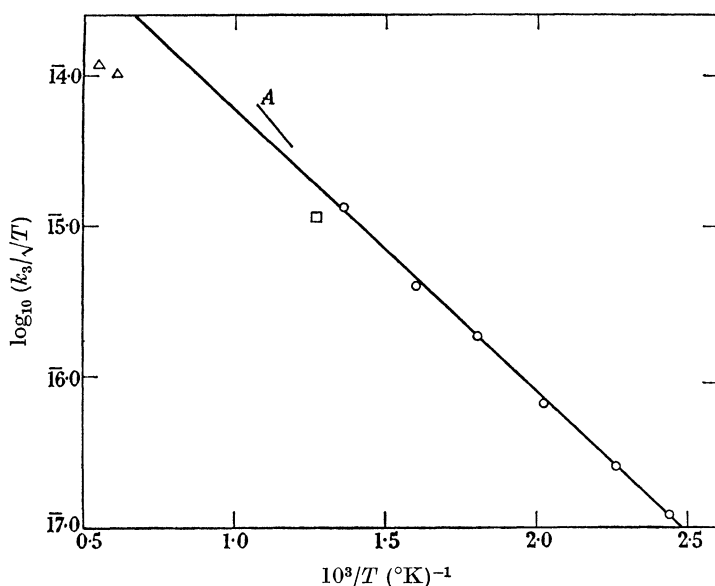


FIGURE 5. The variation of $\log_{10}(k_3/\sqrt{T})$ with $1/T$. k_3 is expressed in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. \circ , This work; \square , Baldwin (1956); Δ , Fenimore & Jones (1961); A, Azatyan *et al.* (1961).

reaction $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} - 1.1 \text{ kcal}$. Using the ratio of the rate constants for isotopic hydrogen species obtained by a competitive method (Bigeleisen, Klein, Weston & Wolfsberg 1959), it has been possible to estimate the vibration frequencies of the transition state in this reaction, and to show that the observed rate constant is in good agreement with the value predicted by the transition state theory. For the $\text{O} + \text{H}_2$ reaction, this theory gives a calculated pre-exponential factor of $10^{-10.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, neglecting vibrational contributions and assuming a linear transition state with $\text{O}-\text{H}$ and $\text{H}-\text{H}$ distances of 1.1 and 0.9 Å, respectively.

Substitution of deuterium for hydrogen in our experiments is not as accurate as the competitive method for the determination of the ratio of the rate constants of the $\text{O} + \text{H}_2(k_3)$ and $\text{O} + \text{D}_2(k_{3d})$ reactions. The values obtained for this ratio were between 1.1 and 1.7 (see table 3) and no significant temperature variation could be detected. Since the mean ratio of the rate constants observed is close to the value of 1.34 for the ratios of the pre-exponential factors predicted both on a collisional

basis and theoretically by Bigeleisen *et al.* (1959), it is concluded that the activation energies of the $O + D_2$ and $O + H_2$ reactions are very close to each other as is predicted by the calculations of Wheeler, Topley & Eyring (1936). Data for the $Cl + H_2$ and $Cl + HD$ reactions yield a calculated activation energy for the $Cl + D_2$ reaction which is 1.2 kcal/mole greater than for the $Cl + H_2$ reaction (Bigeleisen *et al.* 1959).

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REFERENCES

- Ashmore, P. G. & Chanmugam, J. 1953 *Trans. Faraday Soc.* **49**, 254.
 Ashmore, P. G. & Tyler, B. J. 1962 *Trans. Faraday Soc.* **58**, 1108.
 Azatyan, V. V., Voevodskii, V. V. & Nalbandyan, A. B. 1961 *Kinetika i Kataliz*, **2**, 340.
 Baldwin, R. R. 1956 *Trans. Faraday Soc.* **52**, 1344.
 Barrow, R. F. 1956 *Ark. Fys.* **11**, 281.
 Bigeleisen, J., Klein, F. S., Weston, R. E. & Wolfsberg, M. 1959 *J. Chem. Phys.* **30**, 1340.
 Clyne, M. A. A. 1962 *9th Symp. on Combustion*. New York: Academic Press.
 Clyne, M. A. A. & Thrush, B. A. 1961*a* *Trans. Faraday Soc.* **57**, 2176.
 Clyne, M. A. A. & Thrush, B. A. 1961*b* *Trans. Faraday Soc.* **57**, 1305.
 Clyne, M. A. A. & Thrush, B. A. 1962 *Disc. Faraday Soc.* **33**, 139.
 Clyne, M. A. A. & Thrush, B. A. 1963 *Proc. Roy. Soc. A*, **275**, 559 (part II).
 Del Greco, F. P. & Kaufman, F. 1962 *Disc. Faraday Soc.* **33**, 128.
 Fenimore, C. P. & Jones, G. W. 1959 *J. Phys. Chem.* **63**, 1154.
 Fenimore, C. P. & Jones, G. W. 1961 *J. Phys. Chem.* **65**, 993.
 Foner, S. N. & Hudson, R. L. 1962 *J. Chem. Phys.* **37**, 1662.
 Ford, H. W. & Endow, N. 1957 *J. Chem. Phys.* **27**, 1156.
 Harteck, P. & Kopsch, U. 1931 *Z. Phys. Chem. B*, **12**, 327.
JANAF thermochemical tables 1960 Dow Chemical Company, Midland, Michigan.
 Karmilova, R. V., Nalbandyan, A. B. & Semenov, N. N. 1958 *Zh. Fiz. Khim.* **32**, 1193.
 Kaufman, F. 1958 *Proc. Roy. Soc. A*, **247**, 123.
 Kaufman, F. 1961 *Progress in reaction kinetics*, vol. 1 (Ed. G. Porter). London: Pergamon Press.
 Kistiakowsky, G. B. & Kydd, P. H. 1957 *J. Amer. Chem. Soc.* **79**, 4825.
 Morgan, J. E., Elias, L. & Schiff, H. I. 1960 *J. Chem. Phys.* **33**, 930.
 Nalbandyan, A. B. & Voevodskii, V. V. 1948 *Mechanism of hydrogen combustion*. Moscow.
 Tanaka, Y., Jursa, A. & Le Blanc, F. 1957 *The Threshold of Space* (Ed. Zelikoff, M.), p. 89.
 Rosser, W. A. & Wise, H. 1961 *J. Phys. Chem.* **65**, 532.
 Schott, G. L. & Kinsey, J. L. 1958 *J. Chem. Phys.* **29**, 1177.
 Wheeler, A., Topley, B. & Eyring, H. 1936 *J. Chem. Phys.* **4**, 178.