

Atom—Molecule Kinetics at High Temperature Using ESR Detection. Technique and Results for O +H₂, O +CH₄, and O +C₂H₆

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could not be reached because of lower maximum chargeable plate potential. The lower observed quantum efficiency of the pinacyanole as compared with the rhodamine sensitization can be partly attributed to the lower collection efficiency. It is again postulated here that the sensitizations observed are chiefly electron-injection phenomena, analogous to electron-injecting dye sensitizations in Se.

The maximum quantum efficiency measured on the rhodamine B-sensitized S was of the order of 10^{-2} . This was approximately a factor of 10 lower than the reported maximum carrier-generation efficiency of the dye² at wavelengths between 5700 and 5900 Å. For the

² J. W. Weigl, J. Chem. Phys. **24**, 883 (1956).

particular sandwich structure used, the light absorption in the dye was largest in the region adjacent to the S-dye interface and the photoexcited-electron-generation efficiency of this region governed the over-all quantum efficiency. It is possible that the S overlay on rhodamine has enhanced the competitive energy dissipation processes at the expense of free-electron generation upon photoexcitation within the dye-surface layer.

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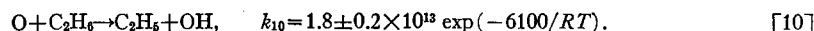
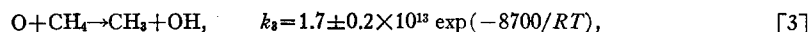
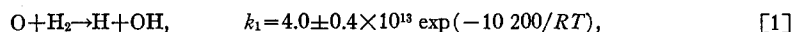
Atom-Molecule Kinetics at High Temperature Using ESR Detection. Technique and Results for $O + H_2$, $O + CH_4$, and $O + C_2H_6$

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A technique is described for the measurement of atom-molecule rate constants over the temperature range 300°–1000°K. It combines a heated fast-flow reactor with ESR atom detection, the ESR cavity being located at a fixed position outside the heated reactor. The system should be useful with a wide variety of reactions, and yields rate constants having $\pm 10\%$ precision independent of temperature. This is also the absolute accuracy when the reaction stoichiometry is known or can be determined by auxiliary mass-spectrometric analysis. Results on some O-atom reactions are (in cubic centimeters per mole-second units):



In the $O + CH_4$ case, the stoichiometry determined both in this work and by others indicates that the mechanism subsequent to the initial step may be



although [8] and [9] are not definitely established, and other mechanisms are discussed. Little can be said about the $O + C_2H_6$ mechanism at present. It is shown that the pre-exponential factors and activation energies for these three hydrogen abstraction reactions are in reasonable relation to each other.

INTRODUCTION

ALL of the chemical kinetic studies of elementary reactions using electron spin resonance (ESR) detection reported from this laboratory¹⁻⁴ have thus

far been confined to room temperature. With a few notable exceptions, the majority of absolute rate constant measurements in well-defined flow systems with any of the other means of atom or radical detection have also been carried out only at room temperature. Some of the important results which were accomplished over a significant temperature range include those of Clyne and Thrush⁵ on $O + H_2$ (409°–733°K), Elias and Schiff⁶ on $O + C_2H_4$ and $O + C_4H_{10}$ (223°–473°K),

¹ A. A. Westenberg and N. de Haas, J. Chem. Phys. **40**, 3087 (1964).

² A. A. Westenberg and N. de Haas, J. Chem. Phys. **43**, 1550 (1965).

³ G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, J. Chem. Phys. **44**, 2877 (1966).

⁴ A. A. Westenberg and W. E. Wilson, J. Chem. Phys. **45**, 338 (1966).

⁵ M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. (London) **A275**, 544 (1963).

⁶ L. Elias and H. I. Schiff, Can. J. Chem. **38**, 1657 (1960).

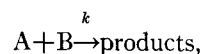
Kistiakowsky and Volpi⁷ on $\text{N} + \text{O}_2$ (400°–500°K), and Wong and Potter⁸ on $\text{O} + \text{H}_2$ and $\text{O} + \text{NH}_3$ (350°–600°K), besides the many shock-tube studies of dissociation-recombination kinetics over (sometimes) a range of several thousand degrees. Most of the data on the temperature dependence of rate constants have come from a variety of sources and techniques. In a few cases these diverse data may be correlated successfully, and a summary of these has been recently published.⁹ Nevertheless, it is clearly desirable to measure precisely the rate constants of elementary radical reactions over a wide temperature range with the same apparatus and in the same laboratory. In this paper we describe an adaptation of the ESR detection technique to a fast-flow system which has been successfully operated over the 300°–1000°K range and which is flexible enough for a wide variety of atom-molecule reactions. Results obtained with this system for the reaction of O atoms (³P) with H_2 , CH_4 , and C_2H_6 are reported. All bimolecular rate constants quoted in this paper are in cubic centimeters per mole·second.

EXPERIMENTAL METHOD

The obvious application of ESR detection in a fast-flow kinetic system^{3,4} in which the detectable atom or radical is measured at various positions downstream of a mixing point by moving the ESR cavity is not practical at high temperatures. We have been unable to think of any way of moving a cavity inside a furnace which does not have too many objectionable features, nor does the idea of using a series of fixed cavities seem attractive. Furthermore, signal intensities tend to decrease with increasing temperature, which is undesirable. Thus, the method we have adopted makes use of a *fixed* cavity located *outside* the heated section of flow tube and operated at room temperature. Since the cavity is fixed at one place on the flow tube, the spectrometer needs to be tuned only infrequently (usually once or twice a day) instead of after every movement of the cavity when that method is employed. This is a great simplification which facilitates the measurements considerably.

The feasibility of using a fixed detection cavity outside of the uniformly heated reaction section may be established by the following analysis. It appears that a similar method may have been used by Clyne and Thrush⁵ with their photomultiplier detector. However, we consider it important to set down the argument in some detail as it is not obvious at first sight and is crucial to the whole experiment. Consider a flow system which consists of a section with uniform cross section maintained at constant temperature T and velocity followed by a section having arbitrary geom-

etry and temperature-velocity distribution. The constant-temperature section is provided with a movable inlet through which a stable reactant B may be introduced. An atom or radical species A carried in an inert diluent gas flows past the inlet (where reaction starts) and is detected by the ESR cavity located at some point on the variable temperature section. Assume that A and B react in the gas phase according to



and that A may also be lost by another route (independent of B) which is first-order in A with rate constant k_w . Typically, the latter loss mechanism might be a wall reaction, although the only necessary condition is that it be first order. The rate equation for A is then

$$-d[\text{A}]/dt = k[\text{B}][\text{A}] + k_w[\text{A}]. \quad (1)$$

We now make the important stipulation that B is in large enough excess compared to A so that it is not appreciably consumed. Equation (1) may then be integrated over the constant temperature section to give

$$\ln[\text{A}]_0 - \ln[\text{A}]_t = k[\text{B}]t + k_w t, \quad (2)$$

where $[\text{A}]_0$ is the concentration at the movable inlet ($t=0$) and $[\text{A}]_t$ is the concentration at the end of the uniform region after time t . Since there could be an atom loss upstream of the inlet probe, $[\text{A}]_0$ could be a function of t , i.e., of the inlet position. Note that k and $[\text{B}]$ are the values pertaining to the constant temperature T .

In the variable-temperature region k , k_w , and $[\text{B}]$ are all functions of the time t' because they are temperature dependent. Integrating Eq. (1) over this region up to the ESR cavity position (denoted by the subscript c) gives

$$\ln[\text{A}]_t - \ln[\text{A}]_c = \int_t^t k[\text{B}]dt' + \int_t^t k_w dt' = K + K_w. \quad (3)$$

The key point in the analysis is now invoked, namely, that although the integrals K and K_w are functions of the unknown temperature-time history in the variable-temperature section, they are *independent* of the time t between the B inlet and the end of the constant-temperature section. Addition of Eqs. (2) and (3) yields

$$\ln[\text{A}]_0 - \ln[\text{A}]_c = k[\text{B}]t + k_w t + K + K_w. \quad (4)$$

For the condition $[\text{B}]=0$, this becomes

$$\ln[\text{A}]_0 - \ln[\text{A}]_{c, \text{B}=0} = k_w t + K_w \quad (5)$$

if we assume that even though $[\text{B}] \gg [\text{A}]$ everywhere, B is a small fraction of the total flow (or is replaced by an inert gas), so that t and t' are unaffected by making $[\text{B}]=0$. This is easily accomplished in practice.

⁷ G. B. Kistiakowsky and G. G. Volpi, J. Chem. Phys. **27**, 1141 (1957).

⁸ E. L. Wong and A. E. Potter, J. Chem. Phys. **43**, 3371 (1965).

⁹ R. M. Fristrom and A. A. Westenberg, *Flame Structure* (McGraw-Hill Book Co., New York, 1965), Chap. 14.

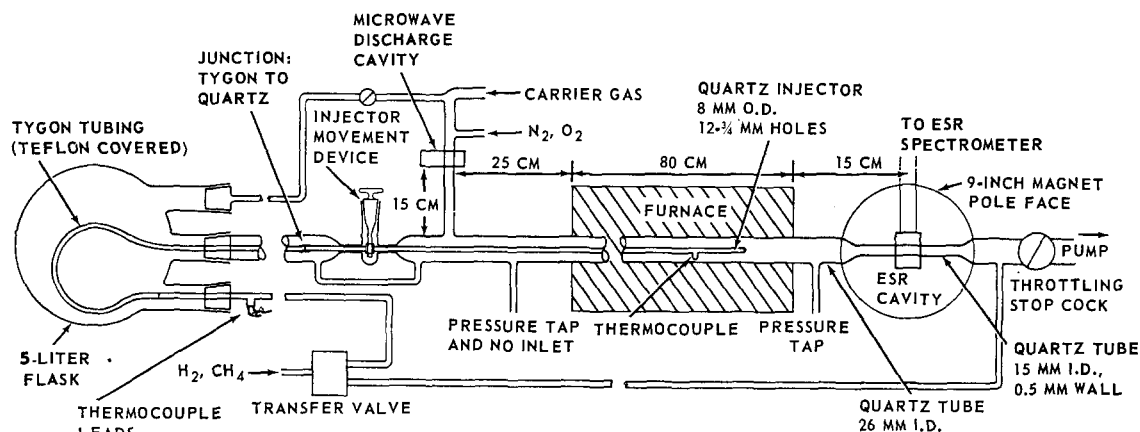


FIG. 1. Diagram of high-temperature reactor.

Subtraction of Eq. (5) from Eq. (4) gives finally

$$\ln\{[A]_{c,B=0}/[A]_c\} = k[B]t + K. \quad (6)$$

The pseudo-first-order rate constant $k[B]$ characteristic of the constant-temperature region may thus be determined from the slope of a logarithmic plot versus time of the relative atom concentration (with B "off" and "on") as measured outside of the constant-temperature region. The beauty of the method is that all atom losses other than the gas-phase reaction of interest cancel out *providing* they are first order and are independent of the presence or absence of B. Direct three-body atom recombination would thus invalidate the analysis, but it is easy to arrange conditions (low atom concentration and pressure) where this is negligible.

APPARATUS AND TECHNIQUE

Figure 1 gives a schematic diagram of the apparatus used to simulate the theoretical model discussed above. The ESR spectrometer and pumping system¹ and the cast epoxy cylindrical TE₀₁₁ cavity² have both been described previously. Movement of the cavity along the thin-walled quartz detecting section was possible but was used only for positioning purposes in these experiments. Most of the work was done with the cavity as close as possible to the heated test section, i.e., about 15 cm as indicated in Fig. 1. A strong current of air from a blower was directed at the section of flow tube between furnace and cavity so that the latter was always kept at room temperature.

The main carrier gas (Ar, He, or N₂; all 99.99% pure) was metered into the system and either mixed with a few percent of the gas to be dissociated (N₂ or O₂) or passed directly through a microwave discharge cavity operating at 2450 Mc/sec and powered by a Raytheon Microtherm unit. From the discharge the flow passed through the heated quartz section (26 mm i.d.). The furnace surrounding this section was electrically heated and consisted of a central winding and

separate windings at each end. These were adjusted so that the temperature over a 60-cm length could be maintained uniform to at least $\pm 0.5\%$. The gas in the test section could be heated to about 1000°K in this way without damage to the flow system. Linear velocities up to 5000 cm/sec could be attained in the main flow tube.

O atoms (³P) for these experiments were usually furnished by metering in NO to discharged N₂ (either pure or with Ar or He as diluent) at the inlet just upstream of the furnace. The fast reaction N + NO → N₂ + O thus provided a supply of O atoms in the absence of O₂. NO was added until the O-atom signal at the ESR cavity attained practically its maximum value, corresponding to consumption of nearly all the N atoms. A trace of air was sometimes admitted to the flow to increase dissociation of the N₂, and this was shown to have no effect on the subsequent O decay rate. In a few runs the O atoms were provided directly from discharged O₂ highly diluted with inert carrier. Additional discussion of this point is made later.

The stable reactant gas, H₂ (99.8%), CH₄ (99.0%), or C₂H₆ (99.0%), was metered into a movable injector tube coaxial with the main flow tube. The injector was an 8-mm-o.d. quartz tube having a ring of small holes at its downstream end. It could be moved along the heated section by means of a friction-drive device similar to that described by Elias and Schiff.⁶ As Fig. 1 shows, a portion of the carrier-gas flow could be routed through the 5-liter flask containing the flexible Tygon tubing attached to the injector probe and thence into the main flow tube. This was done to flush out the flask continuously and prevent any possible buildup of concentration of the added reactant by back diffusion although the flow velocities were normally much too high for this to be a problem. The stable reactant could be bypassed from the injector to the pumping line downstream of the ESR cavity when desired by means of a transfer valve. A thermocouple (Pt/Pt-10% Rh) was imbedded in the wall of the injector tube so that

the gas temperature anywhere along the main flow tube could be monitored. When the injector gas flow was bypassed, the injector tip could also be connected to a McCleod gauge for pressure measurement at any point along the flow tube. Fixed pressure taps were also provided at each end of the heated section of the flow tube. Flow velocities were often large enough to be associated with appreciable pressure drop along the reaction tube. While more sophisticated corrections for this effect were made in the early runs, it was shown that simply using the pressure at the midpoint of the measurement section to compute flow velocity and stable reactant concentration yielded essentially the same rate constant from a given set of data, and this method was used thereafter.

It was easily shown that longitudinal atom-diffusion corrections were completely negligible in these experiments. The requirement is that $k[B]D/v^2 \ll 1$, where D is the diffusion coefficient of the atoms in the carrier gas, and this condition was always fulfilled.

The experimental procedure for obtaining the data to be used in Eq. (6) was as follows: All flow conditions were allowed to become steady with the stable reactant gas B metered in at a rate at least eight to 10 times greater than that of the O atoms, the latter usually being determined by the NO flow rate when the reaction $N + NO \rightarrow N_2 + O$ was being used (or otherwise from an absolute ESR measurement¹). The injector was positioned at the $z=0$ point as far downstream in the test section as possible with the reactant B flowing through it, and the peak height of the O-atom signal at the ESR cavity was read. Reactant B was then transferred to the bypass line and the O-atom signal read again, the ratio of the two signals giving the value of $[A]_{c,B=0}/[A]_c$ in Eq. (6). The injector was then moved to a new position and the procedure repeated. A logarithmic plot of this series of ratios versus distance was made and the rate constant k determined from the slope and the known flow rates.

The main experimental difficulty sometimes encountered with this technique was a tendency for a rather sluggish response in the O-atom signal when the reactant B was switched to bypass. This was evident only when the injector was in the upstream section of the furnace, i.e., 40–60 cm from the $z=0$ position. In this region the atom signal was often observed to increase slowly by 20–30% over a period of several minutes upon bypassing the flow of B, the latter process requiring only a second or so. The sluggishness was not reversible, i.e., it was not observed when the reactant B was switched from bypass into the injector. Considerable effort was spent in trying to find and eliminate the cause of this effect. This was the main reason for flushing the 5-liter flask with part of the carrier flow, although this did not alleviate the problem. It seems likely that the sluggishness was a surface effect, particularly since it seemed to require most of the length of the reaction flow tube to become notice-

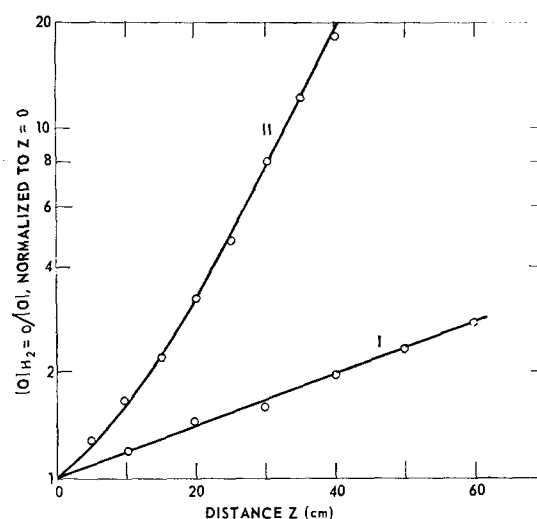
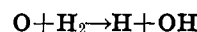


FIG. 2. Examples of O decay data in the O+H₂ reaction. Ordinate is the ratio of the O signal at the ESR cavity measured with H₂ "off" to that with H₂ "on". Curve I: $T=409^\circ\text{K}$, $P=2.36$ mm, velocity is 350 cm/sec, $[\text{H}_2]=1.39 \times 10^{-8}$ moles/cm³, argon carrier. Curve II: $T=696^\circ\text{K}$, $P=1.34$ mm, velocity is 1210 cm/sec, $[\text{H}_2]=1.61 \times 10^{-8}$ moles/cm³, argon carrier. Initial curvature in Curve II presumably due to non-steady-state [OH].

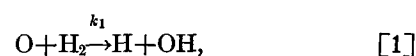
able. It is possible that some reaction product caused a greater atom wall loss when B was added than when it was bypassed, and the surface desorption process might require several minutes to accomplish. Whatever the cause, the problem was circumvented in practice by taking the $B=0$ reading quickly after switching the flow of B to the bypass line. In this way the wall-loss rate constant k_w could be kept equal for both the B "on" and "off" conditions as required in the theoretical analysis leading to Eq. (6).

RESULTS AND DISCUSSION



Examples of the data obtained are shown in Fig. 2 for the case where the injected gas B was H₂. Curve I was a relatively low-temperature run and shows good linearity as required by Eq. (6), while Curve II was taken at fairly high temperature (700°K) and has an initial curved portion up to $z \approx 15$ cm before the linear region is reached. This sort of behavior was more or less typical of the high-temperature runs, especially at the highest flow velocities. The reason is discussed later, but even when a curvature was encountered the slope of the linear section (usually extending over nearly an order of magnitude in O-atom decay) was easily obtained to calculate the rate constant.

Since O₂ was essentially absent from the system in these experiments, the only elementary reactions necessary to consider are the initial rate-determining step



followed by the very fast reaction



The mechanism has been discussed at some length by Clyne and Thrush.⁵ The reaction $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ has a rate constant⁸ at room temperature of 1.5×10^{12} which is an order of magnitude lower than that reported^{5,10} for k_2 . Both presumably have little or no activation energy, so that $\text{OH} + \text{OH}$ would not compete successfully with [2] for O removal at any temperature in these experiments. The reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ considered by Wong and Potter⁸ may also be shown to offer negligible competition to [2], since the ratio of its rate constant³ of $2.3 \times 10^{13} \exp(-5200/RT)$ to k_2 does not exceed 0.04 even at 900°K. The $[\text{H}_2]/[\text{O}]$ ratios used were kept low enough to ensure that the $\text{OH} + \text{H}_2$ reaction was unimportant.

With the fast reaction [2] following [1], a steady-state concentration of OH would be quickly set up, leading to

$$-d[\text{O}]/dt = 2k_1[\text{H}_2][\text{O}] \quad (7)$$

as the gas-phase rate equation for O-atom decay. Thus the measured rate constant should be identified with $2k_1$, and this was done in deriving the values summarized in Table I. The runs at a given temperature were carried out over a range of H_2 concentrations, pressures, and flow velocities as indicated. The fact that the measured k_1 values were independent of $[\text{H}_2]$ and pressure strongly supports the simple two-step mechanism. The data listed made use of a range of $[\text{O}]$ values with no influence on the results. The runs in N_2 carrier had O atoms furnished by adding NO to discharged N_2 as described earlier, while those in Ar or He used a few percent of O_2 in the discharge. Clearly, any residual O_2 in the flow had no effect on the data.

It seems likely that the initial curvature sometimes noted in the O-atom-decay plots at high temperatures, as in Curve II of Fig. 2, was caused by the lack of attainment of a steady-state $[\text{OH}]$ in the early stages of the reaction. The question of the approach to the steady state in this kind of a situation has been discussed by Palmer.¹¹ Strictly speaking, of course, a steady-state condition is attained only after infinite time. In the present case the governing parameter is $k_2[\text{O}]_0/k_1[\text{H}_2]$, and Palmer has shown that when this has a value greater than 100 the steady state is essentially reached after a dimensionless time $k_1[\text{H}_2]t$ of about 0.04. At the lower temperatures in these experiments the parameter was of the order of 10^3 so that a steady state was reached within a centimeter of the injector (assuming instantaneous mixing). At the higher temperatures, however, the parameter was in the range 20–100 and a time corresponding to a dis-

tance of 10–20 cm could well be required. During this time the O atom would decay at a changing (increasing) rate less than the final value determined by a steady state $[\text{OH}]$, and would exhibit the direction of curvature shown in Fig. 2.

According to Reactions [1] and [2], two H atoms are produced for every two O atoms lost, and Clyne and Thrush report⁵ some corroboration of this by their photometric-detection technique. It was originally hoped to include this kind of stoichiometric evidence in the present work, but unfortunately this was not possible. The ESR signal from H atoms generated by the reactions was easily seen, but there were wall losses present which made a quantitative comparison of H and O rates meaningless. The H-atom signal as a function of increasing injector distance did not level out corresponding to conversion of all the O to H, but passed through a maximum and then dropped off. Clearly, there was serious loss of H on the walls of the tube—much more than that of the O. Since there was no way of canceling this out by an “on-off” method such as that used for the O atoms, the rate of H appearance could not be quantitatively interpreted. That there was pronounced wall loss which seemed to be rather specific to H was further demonstrated by the fact that it was difficult to get appreciable H signals at the ESR cavity even in the usual way by a discharge in H_2 with a trace of air present, although a similar problem was not encountered when discharging either N_2 or O_2 . This difficulty requires further study, since it tends to make the measurement of H-atom reactions difficult in the present apparatus.

The results summarized in Table I shows a precision in the rate constants at a given temperature of about $\pm 10\%$. Some runs were attempted as low as 350°K but the results were erratic and not worth reporting. The practical lower limit for a rate constant to be measured with good precision in the present apparatus seems to be around 10^8 , while the upper limit is about 5×10^{14} .

The data on k_1 are plotted in simple Arrhenius form in Fig. 3, and the linearity is excellent. The data obey the expression $k_1 = 4.0 \pm 0.4 \times 10^{13} \exp(-10200/RT)$, where the $\pm 10\%$ precision has been entirely placed in the pre-exponential factor, since the data showed about this much scatter independent of temperature. The limits of error on the activation energy alone may be pessimistically put at $E_1 = 10200 \pm 500$ cal/mole based on the extreme readings of the slope.

Also plotted in Fig. 3 are the other reported data on this reaction with which significant comparisons can be made. The range of temperature over which the data were obtained is shown by the ends of the line drawn in each case. The results of Clyne and Thrush⁵ approach the present work most closely in temperature range (409°–733°K), were of about the same precision, and were done by essentially the same technique except for the method of atom detection. Their data followed

¹⁰ F. P. Del Greco and F. Kaufman, *Discussions Faraday Soc.* **33**, 128 (1962).

¹¹ H. B. Palmer, Project SQUID Rept. No. PSU-10-P, Pennsylvania State University, 1963 (to be published).

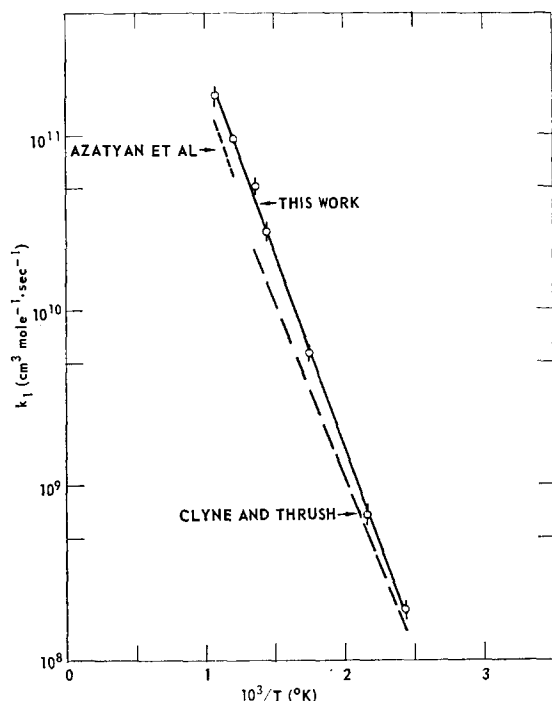
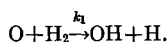
TABLE I. Summary of measurements of the rate constant k_1 for $\text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH}$.

Temperature (°K)	Carrier	Pressure (mm)	Velocity (cm/sec)	$[\text{H}_2]$ (moles/cm ³)	k_1 (cm ³ mole ⁻¹ ·sec ⁻¹)
409	Ar	2.30	480	1.27×10^{-8}	1.9×10^8
	Ar	2.40	500	2.07	1.7
	Ar	2.36	350	1.39	2.1
	Ar	2.01	470	2.07	1.6
	Ar	2.55	300	0.92	2.3
	N ₂	0.97	1300	0.59	1.9
					1.9 ± 0.2
464	N ₂	1.64	730	1.66×10^{-8}	5.9×10^8
	N ₂	2.31	460	1.55	6.2
	Ar	1.78	600	1.29	5.6
	Ar	2.32	380	0.34	7.9
	He	1.54	760	0.49	8.2
					6.8 ± 1.0
570	Ar	1.50	1110	5.21×10^{-9}	5.9×10^9
	Ar	1.73	980	5.20	5.2
	Ar	1.72	980	5.20	5.2
	Ar	1.38	1190	4.07	5.3
	Ar	2.42	650	6.23	5.9
	Ar	2.38	650	4.79	6.3
	Ar	2.38	650	4.81	5.6
					5.6 ± 0.4
699	Ar	1.96	1160	2.98×10^{-9}	2.4×10^{10}
	Ar	1.40	1630	2.13	2.6
	Ar	1.90	1180	2.23	2.9
	Ar	1.34	1210	1.61	3.2
					2.8 ± 0.3
734	N ₂	1.38	2090	1.57×10^{-9}	5.2×10^{10}
	N ₂	1.38	2050	1.04	5.9
	N ₂	1.30	2150	1.43	4.5
	N ₂	1.15	2430	1.30	4.8
					5.1 ± 0.5
830	N ₂	1.33	2250	1.02×10^{-9}	9.2×10^{10}
	N ₂	1.34	2240	1.03	9.6
	N ₂	1.08	2680	1.00	9.2
	N ₂	1.02	2840	0.95	9.7
					9.4 ± 0.2
928	Ar	1.05	2850	6.23×10^{-10}	2.0×10^{11}
	Ar	1.08	2690	4.51	1.6
	Ar	1.31	2890	4.25	1.5
					1.7 ± 0.2

$k_1 = 1.2 \times 10^{13} \exp(-9400/RT)$, so that their activation energy agrees quite closely with ours. The absolute magnitude of their k_1 values is about two-thirds ours over the whole range, however. Since no absolute atom concentrations enter the computations, one is led to suspect a discrepancy in the flow calibrations. For this reason we have repeatedly checked all of the flow metering devices (critical jeweled orifices) and must favor our higher value for k_1 . The data of Wong and Potter⁸ were obtained in a stirred-reactor experiment in the range 400°–600°K with mass-spectrometric detection, and wall losses apparently were considered negligible. While their experimental conditions may

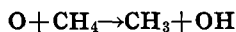
have been somewhat less well defined and their reported precision was considerably lower ($\pm 20\%$), their result $k_1 = 4.3 \times 10^{13} \exp(-10200/RT)$ agrees almost exactly with ours. Azatyan, Voevodsky, and Nalbandyan¹² used an entirely different method based on the change in the first ignition limit of $\text{CO}-\text{O}_2$ mixtures with small additions of H_2 . This is a more complicated approach and involves more assumptions than the flow method, but over a limited temperature range of 843°–933°K they obtained $k_1 = 6.7 \times 10^{13} \exp(-11700/RT)$. The

¹² V. V. Azatyan, V. V. Voevodsky, and A. B. Nalbandyan, *Kinetika i Kataliz* 2, 340 (1961).

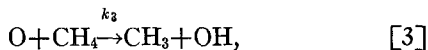
FIG. 3. Arrhenius plot of k_1 data;

○, This work; — — —, Ref. 5; - - - - -, Ref. 12. Data of Ref. 8 over the range $10^3/T = 1.67-2.50$ follow the line drawn through the data from this work.

absolute values of k_1 lie about midway between our data and those extrapolated from Clyne and Thrush.



Injection of CH_4 into a stream of O atoms produced an easily measurable reaction even at room temperature. There is little doubt that the initial step was



which is the analog of Reaction [1] in the H_2 case. As discussed presently, the measured O decay rate constant should be identified with $4k_3$, and the experimental values of k_3 on this basis are given in Table II. All runs were done in the absence of O_2 , those with Ar or He carrier having a few percent of N_2 added upstream of the discharge to provide the N for the $\text{N} + \text{NO}$ reaction. When O atoms were provided by discharging a little O_2 diluted with Ar or He the measured rate constants were significantly higher, a difference which was not observed in the $\text{O} + \text{H}_2$ case. This point is elaborated upon later. Initial curvature analogous to that shown in Fig. 2 was also observed in the $\text{O} + \text{CH}_4$ runs at the higher temperatures, presumably for the same reason.

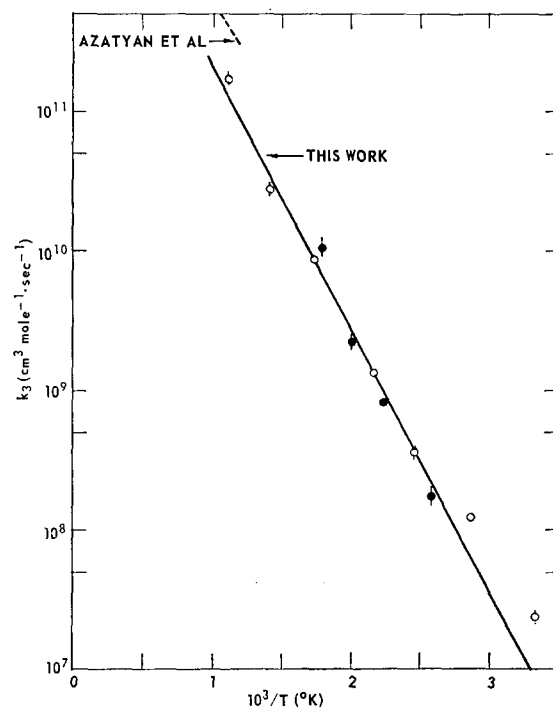
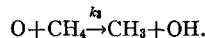
The experimental k_3 values are plotted against $1/T$ in Fig. 4 and form quite a good straight line above

about 400°K, while below that temperature the data are about a factor of 2 above the line. The linear portion obeys the relation

$$k_3 = 1.7 \pm 0.2 \times 10^{13} \exp(-8700/RT)$$

with error limits on the activation energy of about ± 700 cal/mole $^{-1}$.

Other data with which direct comparisons are possible are also shown on Fig. 4. Wong and Potter¹³ have recently determined k_3 in the absence of O_2 using their stirred-reactor technique, and the points plotted are their O decay rate constants divided by the stoichiometric factor of 4. Their points fall very close to ours, as was also the case with $\text{O} + \text{H}_2$. They fit the equation $k_3 = 9 \times 10^{13} \exp(-10\,000/RT)$ to their data giving a somewhat higher activation energy, but in view of the greater range and better precision of the present experiments our lower value of 8700 cal/mole would seem preferable. The results of Azatyan *et al.*¹⁴ were obtained from the effects of small amounts of CH_4 on the first explosion limits of H_2-O_2 and $\text{CO}-\text{O}_2$ mixtures, and their data are about a factor of 3 higher than the present measurements. It seems clear that the rather complex situation in the explosion-limit work needs additional

FIG. 4. Arrhenius plot of k_3 data;

○, This work; ●, Ref. 13; - - - -, Ref. 14.

¹³ E. L. Wong and A. E. Potter, NASA Rept. No. TN D-3371, April 1966.

¹⁴ V. V. Azatyan, A. B. Nalbandyan, and T. Meng-Yuan, *Kinetika i Kataliz* 5, 201 (1964).

TABLE II. Summary of measurements of the rate constant k_3 for $\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$.

Temperature (°K)	Carrier	Pressure (mm)	Velocity (cm/sec)	$[\text{CH}_4]$ (moles/cm ³)	k_3 (cm ³ mole ⁻¹ ·sec ⁻¹)
299	N ₂	2.01	200	2.56×10^{-8}	2.0×10^7
	N ₂	2.32	140	3.53	2.3
	N ₂	2.42	130	2.38	2.7
	N ₂	2.37	180	2.85	2.7
	N ₂	2.25	170	2.10	2.5
	N ₂	1.37	210	2.33	2.3
	N ₂	1.65	190	2.08	2.3
					2.4 ± 0.1
349	He	1.96	370	1.30×10^{-8}	1.3×10^8
	He	2.40	310	1.56	1.3
	He	2.18	320	0.74	1.3
					1.3
405	N ₂	1.42	480	8.74×10^{-9}	3.6×10^8
	N ₂	1.40	460	7.80	3.8
	N ₂	1.32	450	4.32	3.6
	N ₂	1.97	300	6.48	3.0
	Ar	1.44	470	9.04	3.8
	He	1.32	730	6.21	4.0
					3.6 ± 0.3
465	He	1.52	800	2.47×10^{-9}	1.4×10^9
	Ar	1.52	800	2.32	1.2
	Ar	1.89	640	2.89	1.4
	He	1.82	620	3.16	1.3
	He	1.78	620	1.65	1.4
	N ₂	1.56	720	2.90	1.6
					1.4 ± 0.1
573	N ₂	1.08	1120	2.33×10^{-9}	11.2×10^9
	N ₂	1.03	1120	1.13	9.1
	N ₂	1.45	1630	1.36	8.6
	N ₂	1.46	1660	2.20	9.0
	N ₂	1.01	2390	1.53	7.9
					9.1 ± 0.8
700	N ₂	1.00	2900	6.15×10^{-10}	2.6×10^{10}
	N ₂	1.26	2300	7.74	2.5
	He	1.11	2770	6.71	3.2
	He	1.03	2950	3.70	3.0
					2.8 ± 0.3
895	He	1.28	4340	3.51×10^{-10}	1.8×10^{11}
	He	1.70	4680	1.76	1.7
	He	1.51	4340	1.90	1.8
	He	1.82	5290	2.36	1.5
					1.7 ± 0.1

study. The data of Cadle and Allen¹⁵ are not included in Fig. 4 because of their large scatter. Their method apparently was a variation of that used by Elias and Schiff,⁶ and gave absolute values of k_3 (in N₂ carrier) over the temperature range 295°–533°K which are about a factor of 2 or more above the present data. They fit their data to

$$k_3 = 7.1 \pm 3.5 \times 10^{12} \exp(-7300 \pm 1500/RT).$$

For the purpose of establishing the absolute value of the rate constant k_3 of the initial step the stoichi-

ometry of the net reaction is required, i.e., the number of O atoms n reacting for each CH₄ molecule consumed. The linear portion of the Arrhenius plot in Fig. 4 implies a constant value of n over that temperature range although the corresponding activation energy of [3] may be determined without knowledge of n , of course. The detailed mechanism of the reactions subsequent to the initial reaction [3] is not needed for evaluating n either. Instead, the value of n provides evidence as to the mechanism.

The stoichiometry was determined experimentally in the following way: Under conditions where the loss of O atoms on the walls of the reactor tube is negligible

¹⁵ R. D. Cadle and E. R. Allen, J. Phys. Chem. **69**, 1611 (1965).

compared to that occurring in the gas phase by reaction with CH_4 , the change in atom concentration between the NO inlet and the ESR cavity is related to the corresponding CH_4 change simply by

$$([\text{O}]_0 - [\text{O}]_c) / ([\text{CH}_4]_0 - [\text{CH}_4]_c) = n. \quad (8)$$

If flow conditions are now arranged so that the atom concentration at the cavity $[\text{O}]_c = 0$, there will be no further change in $[\text{CH}_4]$ beyond the cavity. Analysis of the residual CH_4 may then be made at any point downstream and the result equated to $[\text{CH}_4]$. Dropping the subscript c , Eq. (8) may be written as

$$n = \frac{[\text{O}]_0}{[\text{CH}_4]_0(1 - [\text{CH}_4]/[\text{CH}_4]_0)}, \quad (9)$$

where the ratio $[\text{O}]_0/[\text{CH}_4]_0$ is obtained from the metered flow rates of NO and CH_4 , and $[\text{CH}_4]/[\text{CH}_4]_0$ is the ratio of CH_4 concentrations with the NO on and off. The latter ratio is well suited for measurement with a mass spectrometer since no calibrations are necessary.

A series of such measurements were made with the reactor in the temperature range 650°–700°K, which is well within the linear portion of the data plotted in Fig. 4. With the movable injector set as far upstream in the furnace as possible to allow maximum reaction time, the NO rate was adjusted to convert essentially all the N atoms to O atoms. The CH_4 flow was then set at a value slightly above that required to make the O signal at the ESR cavity vanish. A certain amount of trial and error with the N_2 flow, the pressure, and the NO titration procedure was necessary to get the proper combination of conditions. The CH_4 was then turned off and it was demonstrated that there was essentially no O atom loss on the walls between NO inlet and ESR cavity by proving the equality of the O mole fraction as determined from the NO flow rate and that measured absolutely by ESR using the O_2 calibration technique.¹ A trace of SF_6 in the discharged N_2 seemed to be very helpful in cleaning up the surface for this purpose, the reason being completely unknown to us.

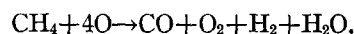
With the proper conditions established, the CH_4 was measured mass spectrometrically with the NO on and off, so that all quantities in Eq. (9) were known. During some of the runs the O_2 formed was also monitored, which permitted an independent determination of the O– O_2 stoichiometry. By the same arguments used in deriving Eq. (9), a quantity n_1 may be defined by

$$n_1 = [\text{O}]_0/[\text{O}_2], \quad (10)$$

where $[\text{O}_2]$ is that formed by the reaction, the initial O_2 being zero. Evaluation of $[\text{O}_2]$ required a mass-spectrometer calibration, of course, which was done by metering a known O_2 flow into the stream with the NO off. As discussed later, the O_2 was undoubtedly formed via Reaction [2] since none was contributed by wall

recombination. Eighteen stoichiometry runs at various NO and CH_4 flows giving $[\text{CH}_4]/[\text{CH}_4]_0$ ratios in the range 0.3–0.7 yielded an average value of $n = 3.8 \pm 0.4$, while eight runs on O_2 formation gave an average $n_1 = 3.4 \pm 0.2$. This experimental value of n is so close to 4 that the use of $n = 4$ in deriving k_3 from the observed net O decay rate constants seems amply justified, especially in view of the reasonable mechanism to be discussed. Wong and Potter¹³ found $n = 4.7$ from similar measurements on CH_4 consumption in their stirred reactor, which lends further support to the $n = 4$ assignment. They also obtained $n_1 = 4.1$ from several measurements of O_2 formation in the temperature range 400°–560°K, there being no dependence of n_1 on temperature. Our value of $n_1 = 3.4$ is somewhat lower, but all things considered it would appear quite reasonable to take $n_1 = n = 4$ as the correct value.

Some discussion of the reaction mechanism is now in order. Besides the observations noted above that four O atoms are used in the consumption of one CH_4 and the production of one O_2 molecule, the mechanism must also account for Wong and Potter's finding¹³ that the other major products obey the approximate stoichiometry



with no H_2CO formed and only a small amount of CO_2 . There seems to be little reason to doubt that the initial reaction is the slightly exothermic



followed by



both in strict analogy to the $\text{O} + \text{H}_2$ case. This simply accounts for the fact that H atoms were observed by ESR as an intermediate reaction product although, as with the $\text{O} + \text{H}_2$ experiments, excessive wall loss prevented their quantitative use. Wong and Potter also found evidence for H mass spectrometrically. It should be noted that Avramenko *et al.*¹⁶ proposed that the initiating steps are



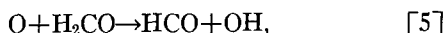
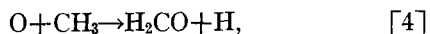
The first of these seems very unlikely because it should be spin forbidden, and there is no H_2CO formed in the absence of O_2 (the Russian work was done in the presence of much O_2 , and H_2CO was claimed as a major product). The second reaction is conceivable but we tend to prefer the simpler hydrogen abstraction reaction [3]. The reaction $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ has a rate constant¹⁷ of $2.9 \times 10^{13} \exp(-5000/RT)$ which is nearly the same as $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$, so that as mentioned in the previous section there should be

¹⁶ L. I. Avramenko, R. V. Kolesnikova, and N. L. Kuznetsova, *Izv. Akad. Nauk SSSR* **4**, 620 (1963).

¹⁷ W. E. Wilson and A. A. Westenberg, *Symp. Combust.* 11th Univ. Calif., Berkeley, Calif., 1966 (to be published).

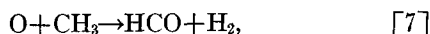
negligible competition with [2] for OH removal at the $[\text{CH}_4]/[\text{O}]$ ratios used.

The fate of the CH_3 generated in [3] is the main issue to be decided. Further hydrogen abstraction $\text{O} + \text{CH}_3 \rightarrow \text{CH}_2 + \text{OH}$ (as postulated by Wong and Potter¹⁸) may be eliminated from consideration since it is endothermic by about 13 kcal/mole and would be much too slow. The fact that no C_2H_6 is found in the products indicates that recombination of CH_3 does not occur. In the pressure range below 5 mm the recombination probably requires a third body,¹⁸ so that it is not surprising that its contribution is negligible. One conceivable sequence might be



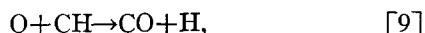
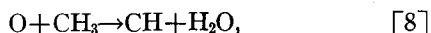
all of which are highly exothermic and spin allowed. Reaction [4] has been suggested by Fenimore and Jones¹⁹ as the key step in CO formation in $\text{CH}_4\text{-O}_2$ flames, and they have shown that the $\text{O} + \text{CH}_3$ reaction (without specifying the products) is probably very fast. There are good reasons for rejecting the mechanism [3], [2], [4], [5], [6], however. It would have $n=5$ as written, or $n=7$ if the OH radicals generated in [5] and [6] used up two more O atoms in additional occurrences of [2], while the experimental evidence is that $n=4$. Also, Wong and Potter found no H_2CO either as intermediate or final product, and our less-detailed spectrometer analyses tend to confirm this. It seems improbable that Reaction [5] would be fast enough to use up H_2CO as fast as it is formed.

Another possibility would involve



followed by [6]. The sequence [3], [2], [7], [6], without another occurrence of [2] from the OH generated in [6], would account for the fact that $n=n_1=4$, and the over-all stoichiometry observed by Wong and Potter. All of the steps subsequent to [3] would presumably be fast, and the only real drawback to this mechanism is that the OH from [6] should result in $n=5$ and $n \neq n_1$, i.e., two O_2 would be produced instead of one.

A third conceivable mechanism can be written as [3] and [2] plus

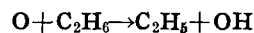


which are feasible energetically and with respect to spin. Assuming the H from [2] and [9] end up as H_2 , all of the stoichiometric requirements are nicely met

with no difficulty about $n>4$ due to OH generation other than by the initial reaction [3]. The bond rearrangement necessary for [8] seems actually no more extensive than for [7] since one triatomic and one diatomic species are formed in either case, although we have not seen [8] suggested previously. We are thus inclined to favor the latter mechanism [3], [2], [8], [9] over [3], [2], [7], [6]. Clearly, additional work on the $\text{O} + \text{CH}_3$ reaction is necessary to establish the mechanism firmly.

Incidentally, we note that if the initiating reaction $\text{O} + \text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2\text{O}$ suggested by Avramenko *et al.*¹⁶ is accepted, two sets of subsequent steps would satisfy all stoichiometric requirements. One may use $\text{O} + \text{CH}_2 \rightarrow \text{CH} + \text{OH}$ (3 kcal/mole exothermic) followed by [2] and [9], or else $\text{O} + \text{CH}_2 \rightarrow \text{HCO} + \text{H}$ (>100 kcal/mole exothermic) followed by [6] and [2]. As stated before, however, the hydrogen abstraction [3] ought to be faster and hence more probable as an initiating step.

The foregoing mechanism discussion applies to the linear portion of the data plotted in Fig. 4, but the deviation from linearity below $T \approx 400^\circ$ clearly requires $n>4$. It may be that the mechanism consisting of [3], [4], [5], [6], and three occurrences of [2] leading to $n=7$ could become important at low temperatures. Or it is possible that even without added O_2 the formation of HO_2 by $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ followed by fast $\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$ and then [2] might occur sufficiently at low temperatures to contribute to the O decay and make the effective $n>4$. The three-body rate constant for HO_2 formation has been reported²⁰ to have a value of $8 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \cdot \text{sec}^{-1}$ with $\text{M} = \text{Ar}$ at room temperature, and to be much higher with $\text{M} = \text{H}_2\text{O}$. The H and O_2 would have to come from Reaction [2], but it is conceivable that at the high pressures and slow flows required to get the main reaction to proceed measurably in the $300^\circ\text{--}400^\circ\text{K}$ range the HO_2 mechanism could be appreciable. Further speculation does not seem fruitful at this time. The pronounced increase in O decay observed when the source of O was a little O_2 discharged in Ar or He must surely have been due to a contribution by the HO_2 mechanism, as well as by the reaction $\text{CH}_3 + \text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{OH}$ and subsequent steps using up O atoms.



The reaction of C_2H_6 with O atoms was quite fast near room temperature—at least 100 times faster than CH_4 —and the highest temperature at which a good measurement could be carried out was only about 600°K . The experimental data on the $\text{O} + \text{C}_2\text{H}_6$ rate constant k_{10} are summarized in Table III. As noted below, these were obtained by identifying the measured O decay rate constant with $6k_{10}$. The data are plotted

¹⁸ R. E. Dodd and E. W. R. Steacie, Proc. Roy. Soc. (London) **A223**, 283 (1954).

¹⁹ C. P. Fenimore and G. W. Jones, J. Phys. Chem. **65**, 1532 (1961).

²⁰ M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. (London) **A275**, 559 (1963).

TABLE III. Summary of measurements of the rate constant k_{10} for $O + C_2H_6 \rightarrow C_2H_5 + OH$. All runs in N_2 carrier.

Temperature (°K)	Pressure (mm)	Velocity (cm/sec)	$[C_2H_6]$ (moles/cm ³)	k_{10} (cm ³ mole ⁻¹ sec ⁻¹)
320	1.15	680	2.46×10^{-9}	1.3×10^9
	0.95	830	2.51	1.3
				1.3
328	0.68	1000	2.08×10^{-9}	1.6×10^9
	0.61	1110	1.95	1.6
	0.63	1110	2.53	1.7
	0.64	1110	3.12	1.7
				1.6
378	1.04	1770	1.71×10^{-9}	6.0×10^9
	1.14	1900	1.74	6.3
	1.13	1850	1.39	5.0
	1.10	1880	1.45	5.0
	1.10	1900	1.79	5.3
				5.5 ± 0.5
424	0.90	1580	1.50×10^{-9}	1.2×10^{10}
	1.12	2080	0.70	1.2
	1.11	2100	0.86	1.3
				1.2
573	0.99	2420	2.57×10^{-10}	1.2×10^{11}
	1.15	2690	2.32	1.3
	1.15	2700	3.31	1.4
				1.3
589	1.08	2810	2.80×10^{-10}	1.6×10^{11}
	1.08	2780	2.47	1.5
	1.07	2800	2.82	1.8
	1.06	2820	3.51	1.5
	1.06	2810	2.01	1.4
				1.5 ± 0.1

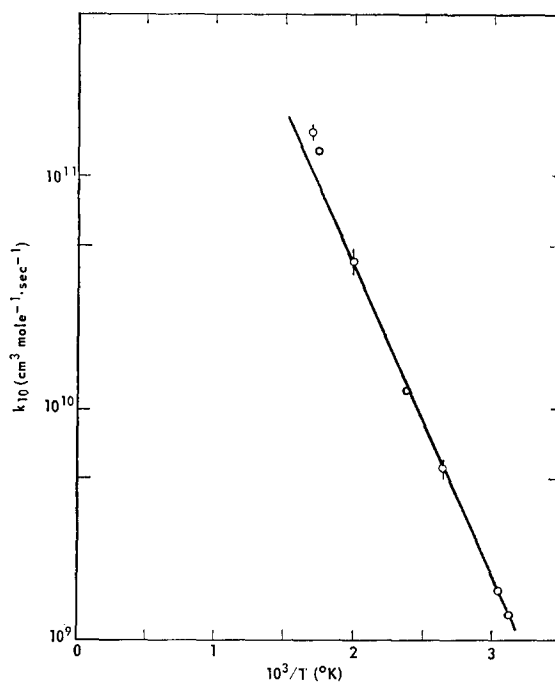
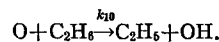
in Fig. 5, and except for the two high-temperature points, they form an excellent straight line. The linear portion gives $k_{10} = 1.8 \pm 0.2 \times 10^{13} \exp(-6100/RT)$ with error limits on the activation energy of about ± 400 cal/mole.

The stoichiometric coefficients n and n_1 for this reaction were evaluated mass spectrometrically in exactly the same way as outlined for the $O + CH_4$ reaction. The results of 16 such measurements around 500°K of the number of O atoms used per C_2H_6 molecule gave the average value $n = 6.5 \pm 0.8$, while 13 runs on the number of O atoms used per O_2 formed gave $n_1 = 3.8 \pm 0.6$. Since the tendency is for any O loss on the walls to cause a slight overestimate of n using this technique, we have chosen the whole number $n = 6$ in deriving k_{10} from the O decay rate constants. Since there is no corroborative evidence available at this time, the absolute k_{10} values of Table III are certain to the extent that n must lie between 6 and 7. The

deviation of ± 0.2 given in the k_{10} preexponential factor $1.8 \pm 0.2 \times 10^{13}$ thus reflects only the experimental precision of $\pm 10\%$.

There do not appear to be any other measurements of k_{10} with which significant comparisons can be made. Avramenko *et al.*¹⁶ give the expression $k_{10} = 5.4 \times 10^{12} \exp(-5200/RT)$ for their discharge-tube results obtained with large concentrations of O_2 present. Since it seems certain that this would cause considerable complications in interpretation, it is doubtful that a comparison with the present work done in the absence of O_2 is meaningful. The early work of Harteck and Kopsch²¹ estimated an activation energy of about 7 kcal/mole for the $O + C_2H_6$ reaction based on C_2H_6 consumption at room temperature in a discharge tube and assumptions about the collision number. The results of Saunders and Hecklen²² using Hg-photosensitized generation of O from N_2O do not give absolute values directly but only ratios of rate constants.

The mechanism of the $O + C_2H_6$ reaction is undoubtedly more complex than the $O + CH_4$ case, and there is little point in extensive discussion at this time. No attempt at a detailed product analysis was made so that the net stoichiometry is unknown. It is most likely that the initial step is the simple hydrogen

FIG. 5. Arrhenius plot of k_{10} data;

²¹ P. Harteck and U. Kopsch, Z. Physik. Chem. B12, 327 (1931).

²² D. Saunders and J. Hecklen, J. Phys. Chem. 70, 1950 (1966).

abstraction



and the OH produced would certainly undergo Reaction [2]. As in the other two reactions studied, H atom was observed by ESR as a reaction product and this is most simply explained by the sequence [10] followed by [2]. Beyond this everything is speculation but, if we may be permitted to indulge in this just a little, a possible reaction of the C_2H_5 radical might be a further hydrogen abstraction and the formation of ethylene via



which is highly exothermic (63 kcal/mole). The OH from [11] would then presumably participate in another step [2]. The reaction of O atoms with C_2H_4 is known to be very fast⁶ ($k = 7 \times 10^{11}$ at room temperature) and it has been studied in some detail by Cvetanović,²³ who showed that the O atom probably adds directly to the double bond. This energy-rich $\text{C}_2\text{H}_4\text{O}$ then decomposes to give a complex series of products, mainly CO and various aldehydes. In any case it is quite possible that the C_2H_4 from [11] could use up two more O atoms which, in addition to the sequence [10], [11], and two occurrences of [2], would give the observed stoichiometric ratio $n=6$. This would also account roughly for the measured $n_1=3.8$, although strictly such a mechanism would give $n_1=3$ if all the O_2 came from [2].

COMPARISONS

The three rate constants k_1 , k_3 , and k_{10} for the reactions $\text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH}$, $\text{O} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{OH}$, and $\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{OH}$ measured in this study offer an interesting example of an homologous series, since all are of the type $\text{O} + \text{RH} \rightarrow \text{R} + \text{OH}$. The experimental pre-exponential factors A ($\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$) and acti-

vation energies E (kcal/mole) are summarized below:

$$\begin{array}{ll} A_1 = 4.0 \times 10^{13}, & E_1 = 10.2, \\ A_3 = 1.7 \times 10^{13}, & E_3 = 8.7, \\ A_{10} = 1.8 \times 10^{13}, & E_{10} = 6.1. \end{array}$$

The A values are qualitatively as one would predict from simple collision theory, i.e., A_1 for $\text{O} + \text{H}_2$ has the highest collision number while A_3 and A_{10} have about equal collision numbers. The ratio $A_1/A_3=2.3$ is also in rough agreement with the simple collision-calculated value of 1.5. Steric factors for all three reactions are in the reasonable range 0.03–0.05 on this basis.

The activation energies are likewise in the order which might be expected. Thus the RH bond dissociation energies D_{RH} have the values (in the above order) 104.2, 101.9, and 97.6 kcal/mole. It is interesting to note that the empirical rule suggested by Otozai²⁴ for reactions of this type, namely, $E = 0.29D_{\text{RH}} - 22.2$, predicts the values $E_1=10.0$, $E_3=7.4$, and $E_{10}=6.1$ in very close agreement with experiment. The fact that the measured activation energies bear this reasonable relation to each other is additional support for the belief that the initial reaction of O atom with CH_4 and C_2H_6 should be written as simple hydrogen abstraction analogous to Reaction [1], i.e., as Reactions [3] and [10] are written, and not in the conceivable form $\text{O} + \text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2\text{O}$. Finally, the activation energy for $\text{O} + n\text{-C}_4\text{H}_{10}$ obtained by Elias and Schiff⁶ is 4.2 kcal/mole. The fact that this is appreciably lower than the 6.1 kcal/mole found for $\text{O} + \text{C}_2\text{H}_6$ in the present work may be an indication that O abstracts an H from $n\text{-C}_4\text{H}_{10}$ preferentially at one of the CH_2 groups rather than from the CH_3 end groups, since the former has a lower bond dissociation energy (≈ 94 kcal/mole).

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²³ R. J. Cvetanović, J. Chem. Phys. **23**, 1375 (1955).

²⁴ K. Otozai, Bull. Chem. Soc. Japan **24**, 218 (1951).