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Radical Reactions in an Electron Spin Resonance Cavity Homogeneous Reactor

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Experiments are described using a homogeneous reactor entirely contained within the detection cavity of an esr spectrometer. This permits atom and radical concentrations in the homogeneous reaction zone to be directly measured. The effective reactor volume was calibrated using the room temperature $O + C_2H_2$ reaction as a known "standard" rate constant, and the volume obtained was very close to the geometric volume. Direct measurements on the reaction $O + OH \rightarrow O_2 + H$ (k_4) were then carried out with the reactor operated at temperatures in the range 228–340°K. The results gave $k_4 = 2.0 \pm 0.3 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ independent of temperature, in good agreement with previously reported values. Attempts to measure $OH + OH \rightarrow H_2O + O$ were unsuccessful, for reasons which are discussed.

Introduction

The idea of a homogeneous ("well-stirred") reactor was apparently first developed by Denbigh¹ as a means of measuring reaction rates in liquids, and the basic principles were later summarized by Denbigh and Page.² After a number of engineering applications of this concept to the determination of overall rates in combustion reactions,³ the well-known work of Kistiakowsky and Volpi⁴ appears to be the first use of a homogeneous reactor for the determination of rate coefficients of elementary gas reactions. A few other studies by this technique have been reported subsequently.^{5,6}

Electron spin resonance (esr) spectroscopy has now been developed into a practical and rather versatile method for the quantitative measurement of gas-phase atom and radical concentrations, and a number of applications to kinetics have been made.^{7–10} All of these studies utilized esr as a detector in a linear (one-dimensional) fast-flow system. The work of Mulcahy, *et al.*,⁶ is the only previous report of the use of esr with a homogeneous reactor, where esr was used to monitor inlet and outlet atom concentrations in a double cavity arrangement. All previous esr work in both linear and

homogeneous reactors has been concerned with measurements of atom-molecule reaction rates, except for the study of $OH + OH \rightarrow H_2O + O$ in this laboratory.¹¹ It seemed that the use of a homogeneous reactor *entirely contained within an esr detection cavity* might offer

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- (1) K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944).
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- (4) G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.*, **27**, 1141 (1957).
- (5) E. L. Wong and A. E. Potter, *ibid.*, **43**, 3371 (1965); *Can. J. Chem.*, **45**, 367 (1967).
- (6) M. F. R. Mulcahy, J. R. Steven, and J. C. Ward, *J. Phys. Chem.*, **71**, 2124 (1967).
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some possibilities in the difficult area of atom-radical and radical-radical rate measurements.

The work on the OH + OH reaction¹¹ was done in a linear reactor with movement of the entire esr cavity (and associated magnet) to establish the time (spatial) dependence of the OH decay. This was not only tedious and difficult, but would be practically impossible at other than room temperature. Another important consideration when attempting to deal with extremely fast atom-radical reactions ($k > 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$) is the difficulty of separating mixing time from reaction time in a linear flow system before concentrations drop too low for adequate measurement, a particularly vexing problem using esr, where spatial resolution ($\sim 2 \text{ cm}$) is not especially good. The present paper outlines the principles for operating an esr cavity as a homogeneous reactor and gives some results with such a system.

Reactor Theory

The basic idea of the homogeneous reactor is very simple and may be briefly reviewed. Assume that two reactants A and B are separately introduced to a reactor of volume V where they react with a rate constant k . Mixing is assumed to be so rapid that the concentrations of all species (as well as temperature and pressure) are uniform everywhere in the volume—hence the name homogeneous reactor. The inlet flows of A and B are steady, and they are diluted with a large excess of inert gas so that the total volumetric flow rate \dot{V} in and out of the reactor is essentially constant. (The latter is not an essential requirement but makes the interpretation somewhat easier.) The concentrations (A) and (B) in the reactor are the same as those leaving it, so that the governing equation is easily derived by equating the difference between inlet and outlet flow rates of a given species to the rate at which it is being consumed by reaction in the volume V , *i.e.*

$$[(A)_0 - (A)]\dot{V} = k(A)(B)V \quad (1)$$

where \dot{V} and the molar concentrations are evaluated at the pressure and temperature existing in the reactor. Measurement of the ratio $(A)_0/(A)$ and the absolute (B) allows k to be determined. The ratio $(A)_0/(A)$ is determined in this technique by the relative esr signal due to A with the reactant B turned off and on. This has the advantage of measuring A as it actually exists inside the reactor, but it has the distinct disadvantage (compared to a movable source linear reactor) that loss of A on the walls of the reactor is not canceled out, since with any wall loss the measurement of $(A)_0$ with (B) = 0 is not the concentration entering the reactor. If independent knowledge of the $(A)_0$ entering the reactor is available, then a measure of A with and without B would allow a first-order wall loss of A to be canceled, but this is not ordinarily feasible. Thus, it is important that

wall losses be negligible compared to the homogeneous gas phase contribution to k .

The key assumption clearly is that of "instantaneous" mixing which, if valid, allows the condition of homogeneity to obtain in the reactor. As noted in ref 4, this limit may be approached in practice if conditions are such that the average time t_D required for any species to diffuse to the walls is small compared to its average residence time t_R in the reactor; *i.e.*, the requirement for homogeneity is

$$t_D/t_R \ll 1 \quad (2)$$

If r is some characteristic distance to the wall, the average diffusion time $t_D \sim r^2/2D$, where D is the diffusion coefficient of a given species in the mixture. The average residence time may be approximated by $t_R \sim V/\dot{V}$, although this is an upper limit since reactants are partially consumed in the reaction. Equation 2 thus becomes

$$r^2\dot{V}/2DV \ll 1$$

or since $D \propto D_1/P$ and $\dot{V} \propto \dot{V}_1/P$, where D_1 and \dot{V}_1 refer to some reference pressure

$$r^2\dot{V}_1/2D_1V \ll 1 \quad (3)$$

The rapid mixing criterion is thus independent of the pressure in the reactor. It is somewhat temperature dependent, however, since D_1 and \dot{V}_1 are different functions of temperature ($\dot{V}_1 \propto T$, while D_1 is roughly proportional to $T^{0.7}$). Once the geometry of a reactor has been fixed, eq 3 governs the maximum total flow rate \dot{V}_1 allowable for a given D_1 . The geometry will be determined by a compromise between practical convenience, the size of the esr cavity itself, and the rate of the reaction to be measured *via* a relation like eq 1.

Experimental Section

The cavity was essentially the same as that used in a previous investigation,⁷ being a large access hole cavity modeled after one described by Carrington, *et al.*¹² A diagram of the cavity is shown in Figure 1. This particular version had a modulation section constructed of slotted brass (silver plated) to allow penetration of the 100-kc modulation field. Operation was in the TE₀₁₂ mode, and the indicated orientation of the microwave electric and magnetic field vectors allowed both electric and magnetic dipole transitions to be observed when the cavity was placed with its axis perpendicular to the external field. The spectrometer was a Varian Model 4502 with 9-in. magnet.

A reactor was constructed to fit closely within this cavity ($\sim 1\text{-mm}$ clearance). Figure 2 illustrates the reactor schematically. It was made entirely of quartz, the walls being etched down to about 0.8 mm for minimum cavity loading. Even so, the necessary large

(12) A. Carrington, P. N. Dyer, and D. H. Levy, *J. Chem. Phys.*, **47**, 1756 (1967).

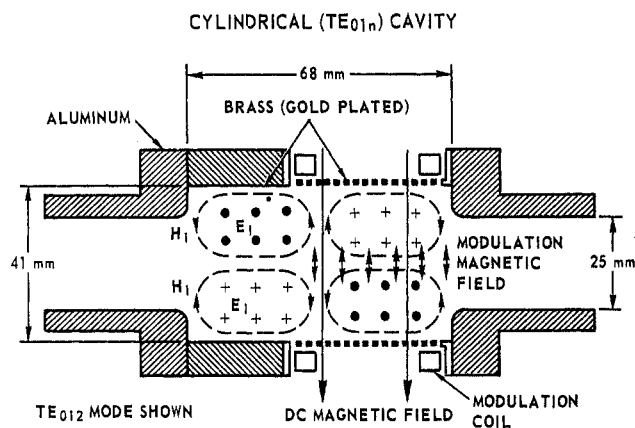


Figure 1. Schematic diagram of cylindrical TE_{01n} cavity showing orientation of various field vectors.

amount of quartz resulted in a loaded Q of only about 1500. The geometric reactor volume (excluding the small volume taken up by the injector) was 67 cm^3 from inlet hole to outlet hole.

Atoms were furnished to the main inlet flow in the usual way by a microwave discharge in a few per cent of the parent diatomic molecule diluted with helium, while various stable reactants could be fed to the simple four-hole injector near the center of the reactor. All metering was done by means of jewelled, critical orifices, except for NO_2 which was throttled through a Granville-Phillips leak. The NO_2 was calibrated each time by transferring the flow into a known volume and timing the pressure rise on an oil (Kel-F) manometer. This method is to be preferred over the alternative of metering NO_2 out of a known volume, since corrections for N_2O_4 - NO_2 equilibrium may be avoided entirely by keeping the final calibration pressure very low. All gases used were best commercial grade taken directly from the tanks.

The reactor was provided with a Pyrex-enclosed thermocouple which could be moved along the axis for temperature measurement, or entirely removed from the reactor to a position downstream while esr measurements were being taken. Pressure in the reactor was measured by connecting the injector to a McLeod gauge after transferring the gas flow normally fed through the injector to the main flow upstream of the reactor. In this way, any additional pressure contributed by the stable reactant flow (a small fraction of the total at most) was maintained during pressure measurement.

For operation above or below room temperature, the entire cavity was encapsulated in styrofoam molded in place. A stream of dry nitrogen gas, either cooled by passage through liquid nitrogen or heated by a water bath, was fed to the inside of the cavity (but outside the reactor, of course) and allowed to pass around the main inlet tube for some distance upstream before escaping to the room. The reactor wall temperature was continuously monitored by a thermocouple, while

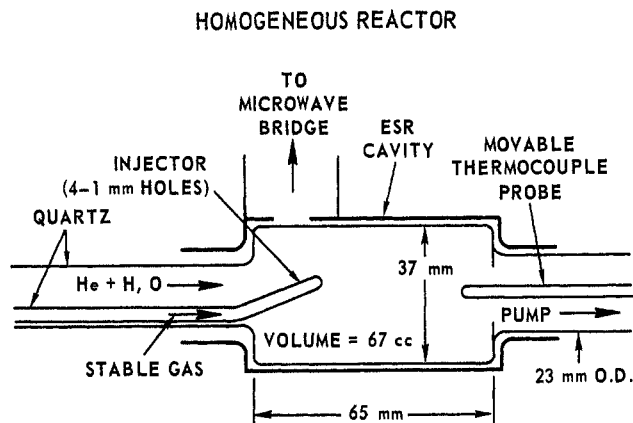


Figure 2. Schematic diagram of homogeneous reactor contained in TE_{01n} cylindrical cavity.

the actual gas temperature in the reactor was measured with the movable thermocouple mentioned above. The temperature profile from inlet to outlet end of the reactor could be kept fairly uniform by this arrangement (within $\sim 10^\circ\text{K}$), and long term stability after attainment of lowest (225°K) or highest (340°K) temperature was good (within $\sim 2^\circ\text{K}$). For the low activation energy reactions of interest, this degree of spatial homogeneity in the reactor was adequate.

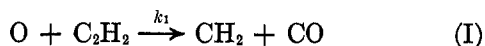
The geometry of the reactor was such that the characteristic dimension r in eq 3 was about 2 cm. Since rapid mixing is promoted by making D_1 as large as possible, the use of helium as an inert carrier gas was clearly indicated. For most species a binary diffusion coefficient in helium at 300°K and 1 atm pressure of about $0.5 \text{ cm}^2/\text{sec}$ is a reasonable estimate (H atoms having a larger D_1 , of course). Thus, for a reactor volume V of 67 cm^3 , the homogeneity criterion of eq 3 required that the total flow rate \dot{V}_1 (at 300°K and 1 atm) be kept less than about $1.5 \text{ cm}^3/\text{sec}$ ($r^2\dot{V}_1/2D_1V \leq 0.1$).

Reactor Calibration Results

It is clear that the validity of the homogeneous reactor model needed testing in some way, even though the criterion given by eq 3 is met. A direct check on the homogeneity of the concentrations during reaction would be highly desirable, but this was practically impossible in the present case (nor has it really been done satisfactorily in any previous work, although some evidence has been offered⁶). The esr measurements simply record spatial averages of concentration over a rather ill-defined volume determined by the microwave and modulation fields in the cavity. It is also not exactly obvious what volume should be used in equations like (1), since the influence of inlet and outlet end effects, possible aerodynamic effects, etc., make the geometric volume of the reactor subject to some uncertainty.

Under the circumstances it seemed that the most significant test of the system we could perform would be to compare a rate constant measured in the reactor

with a known value from other independent experiments. While such a comparison would not have been very meaningful a few years ago, we feel that in certain cases kinetic data have now been refined enough to rely on for such a purpose. After examining a number of candidates for the role of "calibrating reaction," it was decided that the reaction



would be the most favorable. Besides being of a suitable magnitude for our reactor at room temperature, it is a fairly simple and clean reaction with rather good references. There have been six recent absolute room temperature measurements of k_1 for the $\text{O} + \text{C}_2\text{H}_2$ primary reaction. These were all fast-flow, linear reactor experiments using a variety of detection methods and reaction conditions. Five of these studies were discussed in the paper from this laboratory.¹³ Our own value¹³ obtained under pseudo-first-order conditions, *i.e.*, with $(\text{C}_2\text{H}_2) \gg (\text{O})$, was $k_1 = 8.9 \pm 0.3 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, using esr detection. The other determinations discussed in that paper gave the values 9.2 ± 0.4 ,⁸ 8.4 ,¹⁴ 9.0 ± 1.8 ,¹⁵ and 9.6 ($\times 10^{10}$). Since then one other measurement has appeared¹⁷ giving 8.0 ± 1.2 . This rather impressive unanimity lends considerable confidence that the value $k_1 = 8.9 \times 10^{10}$ at room temperature should be reliable at least to $\pm 10\%$.

A test of the homogeneous reactor actually requires only the value nk_1 , where n is the stoichiometric coefficient for the number of O atoms consumed per C_2H_2 molecule. nk_1 is the directly determined O-decay rate under excess C_2H_2 conditions in our previous experiments,¹³ the data giving $nk_1 = 17.8 \times 10^{10}$. The value $n = 2$, measured by mass spectrometry, then led to the value $k_1 = 8.9 \times 10^{10}$ quoted above, and this stoichiometry has also been independently verified.¹³

Thus eq 1 was employed with $\text{B} = \text{C}_2\text{H}_2$, under large excess C_2H_2 conditions so that (C_2H_2) was constant, *i.e.*

$$nk_1V = \frac{\dot{V}}{(\text{C}_2\text{H}_2)} \left[\frac{(\text{O})_0}{(\text{O})} - 1 \right] \quad (4)$$

\dot{V} and (C_2H_2) were evaluated from the metered flow rates at the pressure in the reactor, and $(\text{O})_0/(\text{O})$ was a direct esr peak height ratio with the C_2H_2 off and on. The reactor walls were uncoated for these experiments.

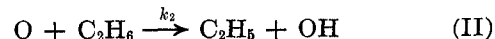
Results of 16 such calibration runs on k_1 are given in Table I. The ranges of pressure, flow rates, and degree of reaction were about as great as could be covered in the apparatus while retaining good precision. The actual O atom concentration entering the reactor was considerably less than indicated by the inlet O_2 rate (to the discharge) due to incomplete dissociation and losses up to the reactor. The data showed the desired independence of all variables except for a slight variation with the C_2H_2 inlet rate (all else being constant),

Table I: Summary of Calibration Runs on the Homogeneous Reactor Using the $\text{O} + \text{C}_2\text{H}_2$ Reaction (k_1) at Room Temperature. Helium Carrier. Geometric Volume = 62 cm^3

Pressure, mm	Inlet flow rates, $\text{cm}^3 \text{ atm sec}^{-1}$			$(\text{O})_0/(\text{O})$	nk_1V , $\text{cm}^6 \text{ mol}^{-1} \text{ sec}^{-1}$
	C_2H_2	O_2	Total		
0.26	0.024	0.009	1.20	2.00	1.28×10^{13}
0.26	0.059	0.009	1.24	3.47	1.31
0.26	0.130	0.009	1.31	6.36	1.36
0.35	0.040	0.010	1.38	3.28	1.22
0.35	0.115	0.010	1.45	8.30	1.41
0.37	0.026	0.003	1.32	2.40	0.99
0.37	0.026	0.010	1.33	2.47	1.05
0.37	0.026	0.014	1.33	2.30	0.93
0.38	0.026	0.009	2.35	1.54	1.10
0.38	0.065	0.009	2.38	2.30	1.07
0.38	0.130	0.009	2.45	3.67	1.13
0.54	0.039	0.010	1.38	6.32	1.23
0.54	0.069	0.010	1.41	11.1	1.35
0.59	0.022	0.008	2.14	2.42	1.19
0.59	0.022	0.008	2.86	1.67	1.00
0.72	0.069	0.010	2.10	8.61	1.30
Av					$1.18 \pm 0.13 \times 10^{13}$

increasing C_2H_2 usually giving slightly increasing nk_1V . The reason for this is not clear, and in any case it was not serious. In some cases the total flow rate was deliberately increased to values somewhat greater than the $1.5 \text{ cm}^3/\text{sec}$ required by eq 3, which was only a rough upper limit anyway. No variation in the measured result up to $\dot{V}_1 \sim 2.8$ could be detected. Several runs using an argon carrier (in which the diffusion coefficients would be 3–4 times lower than in helium) did give different results (higher nk_1V), however, indicating that the homogeneity criterion was probably not being fulfilled. The average of all the values in Table I is $\langle nk_1V \rangle = 1.18 \pm 0.13 \times 10^{13} \text{ cm}^6 \text{ mol}^{-1} \text{ sec}^{-1}$, and using the independent value $nk_1 = 17.8 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ gives a calibration value for the reactor volume of 66 cm^3 . This is remarkably close to the measured geometric volume of 62 cm^3 . (This work was done on an earlier version of the reactor having a slightly smaller volume than the 67 cm^3 shown in Figure 1.)

Similar calibration runs were made using two other reactions with rather mixed results. Eight runs on



gave $\langle nk_2V \rangle = 4.4 \pm 0.4 \times 10^{11}$. These were re-

(13) A. A. Westenberg and N. deHaas, *J. Phys. Chem.*, **73**, 1181 (1969).

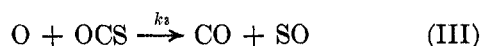
(14) C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *J. Chem. Phys.*, **43**, 525 (1965).

(15) J. O. Sullivan and P. Warneck, *J. Phys. Chem.*, **69**, 1749 (1965).

(16) K. Hoyeremann, H. G. Wagner, and J. Wolfrum, *Z. Phys. Chem. (Frankfurt am Main)*, **55**, 72 (1967).

(17) G. S. James and G. P. Glass, *J. Chem. Phys.*, **50**, 2268 (1969).

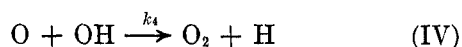
stricted to conditions giving $(O)_0/(O) < 3$, since for higher values there was a definite increase in the nk_2V value measured. This is, of course, a reaction with much more complex stoichiometry ($n \sim 6$), and there is much less information on it than on reaction I. The most recent data obtained in our laboratory¹⁸ give $nk_2 = 5.1 \times 10^9$, which yields a volume $V = 86 \text{ cm}^3$, or about 30% larger than the 66 cm^3 derived from the $O + C_2H_2$ results. Similar measurements on



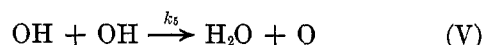
gave $\langle nk_3V \rangle = 7.9 \pm 0.4 \times 10^{11}$ for six runs, again restricted to $(O)_0/(O) < 3$ because of an increasing trend beyond this. Using our value⁷ $nk_3 = 8.5 \times 10^9$ one obtains $V = 93 \text{ cm}^3$, or about 40% above the $O + C_2H_2$ result. In the $O + OCS$ case there may be serious wall losses, since SO is a product of the primary reaction, and there could be loss of O due to $O + SO$ reaction on the walls of the reactor, which would give too high a measured nk_3V . Although both k_2 and k_3 results gave values of V larger than the geometric volume, it is felt that they are less reliable than the very well established reaction I. Therefore, the validity of the homogeneous reactor model and the use of its geometric volume seems at least partially verified.

Results for Radical-Radical Reactions

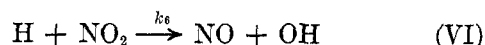
The use of the homogeneous reactor for radical-radical reactions may be illustrated by new results for



There have been three previous fairly direct measurements of k_4 at room temperature. Clyne¹⁹ measured the decay of O atoms generated from



in a linear flow system, the OH radicals being generated by the reaction



The O decay was monitored by its well-known chemiluminescence with NO, absolute (O) being determined by NO_2 titration. Assuming a steady state of (O) at any point between reactions IV and V, Clyne was able to show that the O decay rate was directly related to k_4 , and obtained $k_4 = 3 \pm 1 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ at 265 and 293°K. Kaufman and Del Greco²⁰ used a double discharge linear flow system, producing OH from reaction VI in the presence of O from $N + NO \rightarrow N_2 + O$. Since (VI) is much faster than the $O + NO_2$ reaction, it is possible to cause the NO_2 to react nearly exclusively with H even when O is present, a fact utilized in our own experiments to be described shortly. By monitoring OH decays by uv absorption with and without added O, and using a rather complex graphical method of data analysis, Kaufman and Del Greco

estimated $k_4 \sim 1 \times 10^{13}$ at room temperature. In later work,²¹ Kaufman reinvestigated k_4 in the OH decay system without adding extra O, apparently in a manner similar to Clyne's employing steady state (O), but measuring both OH and O decays. Few details were given, but Kaufman's revised value for k_4 is $3 \pm 1 \times 10^{13}$ at 300°K, in excellent agreement with Clyne's value. Very recently, Breen and Glass²² have reported a value $k_4 = 2.6 \pm 0.8 \times 10^{13}$ from a linear reactor with esr detection, using the steady-state assumption for (O). This was an experiment similar to ref 11 on k_5 , but employing a movable NO_2 source for OH and a fixed cavity, while ref 11 used a fixed source and movable cavity. The value of k_4 determined by Breen and Glass relies directly on their measurement of the product k_5 (OH) as well as absolute (O) at steady state, so that it probably is not as reliable, but their reported value agrees well with the others.

The homogeneous reactor offered a particularly simple and direct approach to the measurement of k_4 . Small amounts of both H_2 and O_2 diluted in helium were passed through the discharge so that H and O entered the reactor through the main inlet in low concentration (1–2%). This inlet esr signal for O atom was $(O)_0$, with $(H)_0 > (O)_0$. NO_2 was then metered into the central injector, and since the rate constant for $H + NO_2$ is at least 10 times larger than that for $O + NO_2$, the former reaction occurred practically to the exclusion of the latter, as was noted earlier. The OH generated in reaction VI then reacted homogeneously with the O present by reaction IV (and with itself to a slight extent by reaction V) giving esr readings (O) and (OH). The governing relation for O loss in the reactor was then

$$[(O)_0 - (O)]\dot{V} = [k_4(O)(OH) - k_5(OH)^2]V$$

so that

$$k_4 = \left[\frac{(O)_0}{(O)} - 1 \right] \frac{\dot{V}}{(OH)V} + \frac{k_5(OH)}{(O)} \quad (5)$$

In practice the second term above was completely negligible compared to the first, so that k_4 could be determined by relative measurements of the O signal with the NO_2 off and on, and an absolute esr measure of (OH) when the NO_2 was flowing. (The absolute OH required the NO calibration procedure which has been described,²³ and the details for carrying this out at other than room temperature are given in the Appendix.) Knowledge of k_5 was thus not required for

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(20) F. Kaufman and F. P. Del Greco, *ibid.*, p 659.

(21) F. Kaufman, *Ann. Geophys.*, **20**, 106 (1964).

(22) J. E. Breen and G. P. Glass, *J. Chem. Phys.*, **52**, 1082 (1970).

(23) A. A. Westenberg, *ibid.*, **43**, 1544 (1965).

Table II: Summary of Measurements of k_4 for $O + OH \rightarrow H_2 + H$ in the Homogeneous Reactor. Helium Carrier. $V = 67 \text{ cm}^3$

Temp, °K	Pressure, mm	Inlet flow rates, $\text{cm}^3 \text{ atm sec}^{-1}$				$(O)_0/(O)$	$(OH),$ mol/cm^3	$k_4,$ $\text{cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$
		H_2	O_2	NO_2	Total			
228 ± 2	0.71	0.080	0.024	0.047	1.41	2.12	0.67×10^{-12}	2.9×10^{13}
	0.70	0.080	0.024	0.062	1.43	9.00	5.88	2.4
	0.70	0.100	0.034	0.094	2.29	8.26	8.88	2.3
	0.70	0.100	0.034	0.094	2.29	12.5	14.2	2.3
298	0.55	0.070	0.014	0.034	1.27	3.30	2.85	2.3
	0.56	0.070	0.021	0.043	1.29	4.29	4.78	1.9
	0.60	0.068	0.025	0.065	1.32	4.29	4.25	2.0
	0.63	0.072	0.020	0.043	1.88	5.42	9.63	1.7
	0.63	0.072	0.020	0.046	1.88	7.58	16.9	1.4
	0.63	0.090	0.029	0.049	1.38	2.92	3.03	1.6
	0.64	0.072	0.020	...	1.37	16.9	20.7	2.0
	0.64	0.072	0.020	...	1.37	6.59	6.96	2.1
	0.68	0.081	0.032	0.045	1.33	2.70	2.08	1.8
	0.76	0.105	0.027	0.055	1.43	6.95	6.01	2.1
	0.88	0.069	0.027	0.051	2.02	11.2	13.5	2.1
	0.88	0.069	0.027	0.044	2.01	3.61	3.45	2.1
340 ± 4	0.40	0.082	0.023	0.016	1.63	1.88	1.90	2.4
	0.63	0.082	0.023	0.024	1.64	2.28	2.48	1.7
	0.63	0.082	0.023	0.029	1.64	3.72	4.17	2.2
	0.70	0.079	0.025	0.038	0.92	6.26	5.68	1.6
	0.71	0.079	0.025	0.045	0.93	10.7	10.8	1.6
								$\text{Av } 2.0 \pm 0.3$ $\times 10^{13}$

the measurement of k_4 , which is a very desirable feature of this method.

A summary of the runs made at three temperatures over a modest range is given in Table II. The range of flow variables and pressure was rather restricted, mostly because of the necessity of retaining sufficient OH signal for a good integrated intensity measurement. But within the accessible ranges, the results for k_4 are rather uniform and show no significant temperature dependence. Averaging the runs at all temperatures together gives $k_4 = 2.0 \pm 0.3 \times 10^{13}$, in good agreement with the results of Clyne¹⁹ and Kaufman²¹ discussed earlier. The lack of temperature dependence found by Clyne is also verified over a somewhat larger range. An essentially zero activation energy would be expected for such a fast reaction.

The value for k_4 derived^{24,25} from the extensively studied reverse reaction and the equilibrium constant is 1.3×10^{13} with zero activation energy. This is not too significant a comparison, however, since the compilation for k_{-4} itself depends heavily on the data of Clyne and Kaufman for k_4 and the equilibrium constant at the low temperature end. Our present data for k_4 thus confirm that the $H + O_2$ composite rate constant $k_{-4} = 2.2 \times 10^{14} \exp(-16,800/RT)$ derived using this low-temperature k_4 anchor is probably valid.

Attempts to measure k_5 and its temperature dependence were not successful. Two different methods were used which should have worked in principle, but

there were difficulties which will be noted. With H_2 in the discharge with helium, the main inlet flow contained only H in this experiment. NO_2 was then metered into the central injector, generating OH by reaction VI, followed by reactions V and IV. Assuming these are the only reactions occurring and that all rates are finite, the homogeneous reactor equation for NO_2 is

$$[(NO_2)_0 - (NO_2)]\dot{V} = [\dot{V}_{NO_2}N/\dot{V} - (NO_2)]\dot{V} = k_6(H)(NO_2)V \quad (6)$$

where $N = P/RT$ is the total molar concentration. The equation for H atom (with steady-state O atom) is

$$[(H)_0 - (H)]\dot{V} = [k_6(H)(NO_2) - k_5(OH)^2]V \quad (7)$$

Since there is no OH in the inlet flow, its equation is

$$-(OH)\dot{V} = [-k_6(H)(NO_2) + 3k_5(OH)^2]V \quad (8)$$

Method I. Addition of eq 6 and 8 gives

$$k_5 = \frac{[\dot{V}_{NO_2}N/\dot{V} - (NO_2) - (OH)]\dot{V}}{3(OH)^2V} \quad (9)$$

which is the correct form when OH generation by (VI) is assumed to be not infinitely fast. When k_6 is as-

(24) R. M. Fristrom and A. A. Westenberg, "Flame Structure," McGraw-Hill Book Co., New York, N. Y., 1965, p 361.

(25) D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, High Temperature Reaction Rate Data Report No. 3, Department of Physical Chemistry, The University of Leeds, England, April 1969.

Table III: Summary of Measurements of k_5 for $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ at Room Temperature in the Homogeneous Reactor. Helium Carrier. $V = 67 \text{ cm}^3$

Method I							
Pressure, mm	Inlet flow rates, $\text{cm}^3 \text{ atm sec}^{-1}$			$(\text{OH})_0$, mol/cm^3	k_5 , $\text{cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$		
	H_2	NO_2	Total				
0.26	0.09	0.021	0.61	52×10^{-12}		1.5×10^{12}	
0.30	0.06	0.039	1.47	59		2.1	
0.30	0.09	0.025	0.61	37		3.9	
0.34	0.08	0.034	1.72	56		2.0	
0.39	0.09	0.078	1.20	115		1.2	
0.56	0.07	0.061	0.68	63		3.3	
0.58	0.07	0.091	1.88	106		1.6	
0.58	0.07	0.099	1.11	93		2.4	
0.63	0.09	0.053	0.84	59		2.4	
0.67	0.09	0.076	0.86	78		2.1	
0.68	0.09	0.098	2.27	118		1.4	
0.70	0.09	0.094	1.23	100		2.0	
0.73	0.07	0.065	1.08	66		3.2	
0.75	0.07	0.088	2.00	107		1.6	
0.75	0.07	0.090	2.75	107		1.6	

Method II							
Pressure, mm	Inlet flow rates, $\text{cm}^3 \text{ atm sec}^{-1}$			$(\text{H})_0$, mol/cm^3	$(\text{H})/(\text{H})_0$	$(\text{OH})_0$, mol/cm^3	k_5 , $\text{cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$
	H_2	NO_2	Total				
0.41	0.12	0.048	1.22	10×10^{-10}	0.57	87×10^{-12}	0.77×10^{12}
0.41	0.12	0.063	1.23	17	0.29	86	2.7
0.43	0.10	0.037	1.22	10	0.67	56	1.5
0.55	0.10	0.065	1.23	21	0.32	70	3.5
0.55	0.10	0.065	1.23	33	0.32	93	3.2
0.66	0.11	0.048	1.56	23	0.59	89	1.4
0.67	0.11	0.047	1.55	16	0.56	88	1.0
0.67	0.11	0.068	1.58	11	0.35	90	1.1
0.88	0.11	0.037	1.13	15	0.47	37	4.1

sumed to be infinite, $(\text{NO}_2) = 0$ (providing it is not added in excess), and the term $\dot{V}_{\text{NO}_2}N/\dot{V}$ is simply equivalent to an inlet $(\text{OH})_0$.

Since it was not possible to measure the residual (NO_2) in this experiment, a direct test of this assumption could not be made. A large number of experiments were performed at room temperature with (NO_2) taken to be zero, however, so that k_5 could be evaluated simply from the metered flow rate of NO_2 and \dot{V} , together with an esr measurement of (OH) . The results were not very satisfactory, as shown in Table III. The values of k_5 tend to be higher than our earlier value¹¹ of 1.5×10^{12} and to increase with decreasing \dot{V}_{NO_2} . This is the behavior to be expected when neglect of the (NO_2) in eq 9 is not justified; *i.e.*, a residual (NO_2) would be more significant at low values of \dot{V}_{NO_2} so that its neglect would lead to a relatively larger apparent k_5 . In other words, the effect of finite k_6 combined with appreciable mixing time for the entering NO_2 means that the frequent practice of computing initial $(\text{OH})_0$ from the inlet NO_2 rate may tend to overestimate the effective $(\text{OH})_0$. In

the present experiments this leads to a high apparent k_5 , while in linear reactor experiments an overestimate of $(\text{OH})_0$ would tend to underestimate k_5 for a given measured $(\text{OH})^{-1}$ slope. The latter point had been noted earlier¹¹ in attempting to understand the discrepancy between our value of k_5 obtained in a linear reactor and the lower values of Kaufman and Del Greco.²⁰ The overestimate of $(\text{OH})_0$ by the NO_2 rate has also been noted by Breen and Glass.²²

Another possible cause of the difficulty might be loss of OH on the walls, particularly due to the deposit formation which is known to occur with the $\text{H} + \text{NO}_2$ system. This deposit (presumably NH_4NO_3) was noted previously¹¹ in this laboratory and elsewhere, and was again apparent in the present work. It tended to concentrate around the central injector. Since the deposit is known to accentuate OH loss, it may have been a contributor to the high values of k_5 measured. Breen and Glass²² have also invoked a wall loss in the analysis of their linear reactor data, which gave a k_5 lower than either ref 20 or 11.

Method II. Addition of eq 7 and 8 gives

$$k_5 = \frac{[(H)_0 - (H) - (OH)]\dot{V}}{2(OH)^2V} \quad (10)$$

which is an alternate form not requiring a value for initial $(OH)_0$. The initial $(H)_0$ was obtained by esr with the NO_2 off, while (H) and (OH) were obtained with NO_2 on. No assumption was necessary about the rapidity of reaction VI, since this term cancels out. This method was also unsatisfactory, giving erratic values of k_5 depending on \dot{V}_{NO_2} (see Table III). It seems most likely that deposit formation and serious wall loss of OH were largely responsible for this behavior.

Thus, the homogeneous reactor is suitable only for radical-radical reactions which are fast enough in the gas phase so that wall losses are negligible. Establishing this in a given case is difficult, and lacking independent evidence, perhaps the best indication that wall losses are not important would be a set of results consistent with an analytical model derived for zero wall loss which are independent of flow variables over as wide a range as possible. In some cases finite wall losses can be canceled out, as noted earlier.

Appendix

For operation of the reactor at other than room temperature, in the case of reaction IV the temperature dependence of the calibration relation for determining absolute (OH) is required. The general procedure for calibrating electric dipole species such as OH against NO has been described in detail.²³ The integrated esr intensity is given by

$$\int_0^\infty \chi''_{ij} dH = \frac{(OH)h\nu_0|\langle\mu_r\rangle_{ij}|^2}{k\beta g_{eff}} \frac{\exp(-E_i/kT)}{TZ} \quad (11)$$

where the terms have been defined previously.²³ The last factor in eq 11 contains all of the temperature-dependent quantities.

The OH lines best suited for practical intensity measurements are those for the lowest rotational level $J = 3/2$ of the $2\pi_{3/2}$ ground state, for which the Boltzmann factor is unity. The total partition function Z for OH as function of T was derived from the appropriate thermodynamic tables²⁶ and is given in Table IV. For present purposes the single OH line $M_J = 1/2 \rightarrow 3/2$, $M_I = 1/2$, ($J = 3/2$, $2\pi_{3/2}$ state) of the $+\rightarrow -\Delta$ doubling transition was more convenient than the composite OH lines (lines A and B in the notation of ref 23) used previously. This is the lowest field line (7926

Table IV: Total Partition Functions for OH and NO as Functions of Temperature

Temp, °K	Z_{OH}	Z_{NO}
100	28.4	292
200	54.2	704
300	82.8	1160
400	113	1632
500	143	2124
600	175	2630
700	206	3154
800	236	3702
900	268	4284
1000	296	5103

G at 8765 Mc) of the set of six $+\rightarrow -$ transitions for $J = 3/2$, $2\pi_{3/2}$. Let us designate it as line C. For this line $|\langle\mu_r\rangle_{ij}|^2 = 0.634$ and $g_{eff} = 0.935$, so that eq 11 gives

$$(OH) = 1.47 \left(\frac{k\beta}{h\nu_0} \right) T_{OH} Z_{OH} \int_0^\infty \chi'' (OH, \text{line C}) dH \quad (12)$$

In a similar manner, the relation for line "a" of NO may be derived (line "a" is the lowest field line of the nine-line $J = 3/2$, $2\pi_{3/2}$ set of NO transitions,²³ lying at 7944 G for $\nu_0 = 8765$ Mc). The Boltzmann factor for the desired level is not unity in this case,²³ so the result is

$$(NO) = 64.5 \left(\frac{k\beta}{h\nu_0} \right) T_{NO} Z_{NO} \exp(-180/T_{NO}) \times \int_0^\infty \chi'' (NO, \text{line a}) dH \quad (13)$$

Normally the NO calibration is carried out with pure NO in the reactor at a pressure P_{NO} , and the calibration temperature T_{NO} may be different than the temperature T_{OH} at which OH is measured. Combining eq 12 and 13 gives the working relation

$$(OH) = [0.0228] \left[\frac{P_{NO}}{RT_{NO}} \right] \left[\frac{T_{OH}}{T_{NO}} \right] \left[\frac{Z_{OH}}{Z_{NO}} \right] \times \left[\exp\left(\frac{-180}{T_{NO}} \right) \right] \frac{\int_0^\infty \chi'' (OH, \text{line C}) dH}{\int_0^\infty \chi'' (NO, \text{line a}) dH} \quad (14)$$

(26) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1960.