

KINETICS OF THE RECOMBINATION REACTION $\text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ AT LOW TEMPERATURES

R. ZELLNER, K. ERLER AND D. FIELD*

*Institut für Physikalische Chemie der Universität Göttingen, Tammannstrasse 6,
34 Göttingen, West Germany*

A discharge flow resonance fluorescence technique (for the detection of OH) was used to determine the absolute rate of the reaction (1) $\text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ for $\text{M} = \text{He}$ (in the range $T = 230\text{--}300\text{ K}$) and for $\text{M} = \text{Ar}$, N_2 and CO_2 (at 300 K). At total pressures between 3–11 torr reaction (1) is in its third-order regime, where it can be separated from the second-order (heterogeneous) recombination reaction (2) $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$. Specific rate constants k_1 at 300 K (in units of $10^{-31}\text{ cm}^6/\text{molecule}^2 \cdot \text{s}$) are: 1.5, 2.3, 4.8 and 9 for $\text{M} = \text{He}$, Ar , N_2 and CO_2 . The temperature variation of k_1 for $\text{M} = \text{He}$ can be represented by $k_1 = 4.3 \times 10^{-25} T^{-2.6}\text{ cm}^6/\text{molecule}^2 \cdot \text{s}$. The rate constant k_2 was found to be $2.7 \times 10^{-14}\text{ cm}^3/\text{molecule} \cdot \text{s}$ and independent of temperature.

A comparison of k_1 with results from high temperature flame and shock tube experiments on both reaction (1) and the reverse dissociation shows that low and high temperature data can be correlated in terms of a T^{-n} dependence, with n being 2.0–2.2. Predictions of k_1 by unimolecular rate theory of the low pressure limiting rate constant are in good agreement with our result.

Introduction

Recombination reactions of atoms and radicals are an essential source for the total energy production in combustion processes. This is obvious from the characteristics of low pressure flames, where the flame temperature is considerably smaller than that calculated from thermodynamic equilibrium conditions because radical recombination reactions are too slow under these conditions to bring the system to equilibrium.

In hydrogen-rich H_2/O_2 flames equilibration is almost entirely achieved by the mutual recombination of H atoms and by their recombination with hydroxyl radicals



In order to understand and to model flame processes, accurate rate data for reaction (1) as a function of temperature and the nature of the third body M must be known. This

has long been recognized and a great deal of experimental work has been devoted to a study of this reaction.¹ The majority of the results reported originate from flame and shock tube studies in the temperature range 1000–2500 K. However, the complexity of the systems studied does not allow a complete isolation of reaction (1) from competitive processes, i.e., partial equilibration via $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ or mutual recombination of H atoms. Moreover, in most flame studies the nature of the third body M cannot be specified accurately, and a good deal of the scatter of the available data can probably be attributed to this difficulty. Experimental work performed at low temperatures is rather scarce.^{2,3} In addition, in at least one of these studies,² complications were inferred from competitive radical-radical reactions that could not be accounted for.

In view of the uncertainties of the existing data, we have performed a direct investigation of reaction (1) at and below room temperature. It appears that the absolute rate data of reaction (1) at low temperatures is important to an assessment of results from high temperature

* Present address: School of Chemistry, University of Bristol, Bristol, England.

recombination and dissociation experiments. This has recently been demonstrated by Kaufman and coworkers⁴ for the gas phase recombination of hydrogen atoms.

The objectives of the present work were i) to determine the absolute recombination rate and its dependence on temperature as well as the relative efficiency of different collision partners M , ii) to attempt a correlation in terms of a suitable temperature dependence with high temperature recombination and dissociation data, and iii) to compare the absolute data and their variation with temperature with predictions from unimolecular rate theory.

In the present investigation, reaction (1) was studied by a discharge flow technique. As can be expected for a reaction between unlike radicals, competitive processes can not completely be excluded. In this work, however, they could be kept to a minimum largely as a result of using a resonance fluorescence technique for the detection of OH.

Experimental

A schematic drawing of the apparatus is provided in Fig. 1. It consisted of a conventional flow system, 500 mm in total length and 21 mm in diameter, the central section of which could be thermostated in the range 300–220 K. Two Wood's horns optically separated the discharge zone from the main flow tube. An additional inlet (AG) allows those inert gases (i.e. N_2 , CO_2) to be added that cannot be passed through the discharge.

Total pressures in the system ranged between 2–12 torr and were measured with a Hg manometer. Linear flow speeds in the range 25–40 m/s were achieved with a 250 m³/h rotary pump. Prior to use, the flow system was cleaned with 8% HF solution and was rinsed with distilled water. No further wall coating was used.

OH radicals were generated by injecting to a stream of excess H atoms small amounts of NO_2 ($\sim 8 \times 10^{12}$ molecules/cm³) through a moveable probe. The subsequent decay of OH was then monitored at a fixed downstream position by means of ultraviolet fluorescent scattering. Since absolute calibrations of the OH fluorescence intensity is not readily possible, OH concentrations were determined from the relation $[OH]_0 \sim [NO_2]_0$. The arrangement of the fluorescence cell was similar to the one used by other experimentalists.⁵ Briefly, it consisted of a microwave-powered OH ($A^2\Sigma^+, v' = 0 - X^2\Pi, v'' = 0$) resonance lamp connected to the flow system via a series of light traps and a quartz window. Resonance photons scattered at a right angle to the incident light beam were focussed onto a photomultiplier (EMI 9783B). A commercial interference filter (Schott, UV-IL, $\lambda_{max} = 313.5$ nm, $T_{max} = 26\%$, FWHM = 5.5 nm), tilted at 22°, served to cut out lines of high K levels and to reduce the level of stray light. The effective zone in the flow system over which OH radicals were detected is estimated to be ~ 10 mm in axial length.

OH concentrations of the order of 5×10^{12} molecules/cm³ could be detected with a sig-

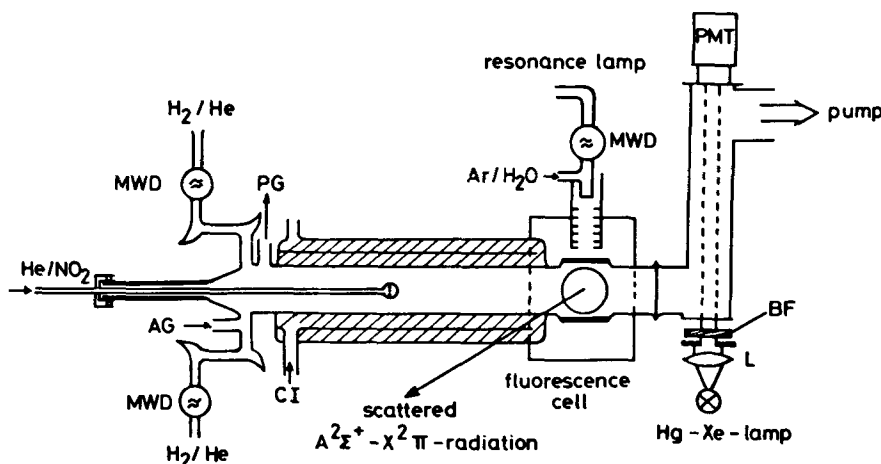


Fig. 1. Schematic diagram of flow system with resonance fluorescence detection of OH. The detection part of the fluorescence cell is omitted for clarity. MWD: microwave discharge; AG: additional gas inlet; PG: pressure gauge; CI: coolant inlet; L: lens; BF: band filter; PMT: photomultiplier.

nal-to-noise ratio of about 15. The dependence of the fluorescence intensity on the OH concentration in the flow tube was checked experimentally and was found to be linear up to at least $5 \times 10^{13} \text{ cm}^{-3}$, in agreement with what can be expected from line absorption theory for a non-reversed resonance line source.⁶

H atom concentrations in the range $5 \times 10^{14} - 5 \times 10^{15} \text{ atoms/cm}^3$ were generated by two microwave-powered discharges (100 Watts) in dilute mixtures of H_2 in He and measured by NO_2 titration. For this purpose NO_2 in excess of the H atom concentration (3–5 times) was added through the moveable injector probe placed in a central position of the usual reaction zone. The amount of NO_2 consumed was determined downstream by absorption measurements around 440 nm, using a high pressure Xe-Hg lamp (Hanovia, 901 B0011, 200 W) in combination with a bandpass filter ($T_{\text{max}} \sim 12\%$ at 447 nm; FWHM: 25 nm). The concentration of H atoms could then be calculated from the known initial NO_2 concentration ($[\text{NO}_2]_0$) using the expression

$$[\text{H}] = [\text{NO}_2]_0 \cdot S^{-1} \cdot \ln \frac{I_2}{I_1} / \ln \frac{I_0}{I_1}$$

where I_0 is the incident light intensity, and I_1 and I_2 are the transmitted intensities in the absence and presence of H atoms, respectively, and S is the stoichiometric factor ($\Delta[\text{NO}_2]/\Delta[\text{H}]$) of the reaction. An 11% correction to the NO_2 concentration for the $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ equilibrium was applied as a result of its flow rate measurement by the pressure rise in a calibrated volume. No further correction for re-association under the conditions in the flow tube was necessary.⁷ The stoichiometry (S) of the reaction was taken to be 1.5 under all conditions used in these experiments. This was not only inferred from Mulcahy and coworkers' investigation of the $\text{H} + \text{NO}_2$ stoichiometry,⁸ but was also checked by computer simulation of the full reaction scheme including wall reactions of OH and possible (additional) consumption of NO_2 , i.e., $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$. Moreover, in an experimental test in which the excess NO_2 concentration was varied over the range 1:5 – 6, the latter reaction was found not to affect the calculated H atom concentration, and therefore S , by more than 5% under all conditions. Finally, in a few experiments, absolute H was determined from the HNO^* chemiluminescence which arises upon the addition of NOCl to a stream of H atoms. The result was found to agree with the NO_2

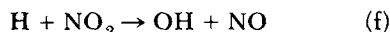
titration and an assumed stoichiometry of 1.5 to within 5%. The concentration of H atoms along the flow tube can be taken to be nearly constant^{4b} and was used in the derivation of k_1 without further correction.

In the present experiments viscous pressure drop along the flow tube was negligible,⁹ and rate data were evaluated for plug flow conditions. This is a good approximation for the lower pressures (~ 2 torr) used in our experiments.⁹ However, at higher pressures, radical diffusion becomes slower and deviations from one-dimensionality may occur. As to an assessment, either the exact solution for first-order kinetics in tubular flow reactors,¹⁰ or one of its approximations⁹ may be used. For typical "high" pressure conditions ($p = 10$ torr of He, $v = 30 \text{ m/s}$, $k_{\text{wall}} = 100 \text{ s}^{-1}$, $R = 1 \text{ cm}$) in our flow system, we calculate that the radial concentration gradient for OH will be of the order of 30%. However, such a correction does not have to be applied to the measured rate constant for two main reasons: i) the geometry of detection of OH by resonance fluorescence necessarily imposes an "integration" across the concentration profile and ii) since our flow system is short, the reaction will to a great extent proceed under the conditions of the entrance flow¹¹ where the Poiseuille profile is not fully developed. We therefore conclude that possible corrections to the rate constants imposed by flow characteristics, when He is used as a carrier gas, will be small and will be obscured by the remaining experimental scatter. However, when argon instead of helium was used as a diluent, because of the lower diffusion coefficient of OH in Ar experiments were limited to pressures below 6 Torr.^{5b}

Results and Discussion

i) The Reaction $\text{OH} + \text{H} + \text{He} \rightarrow \text{H}_2\text{O} + \text{He}$

Reaction (1) was studied by monitoring the decay of hydroxyl radicals following their formation via



in the presence of excess hydrogen atoms. The use of the resonance fluorescence detection technique allowed low initial OH concentrations, so that its kinetics could be studied under predominantly first-order conditions. A typical example of an experiment at $T = 300 \text{ K}$ and $p = 6.5 \text{ torr}$ is given in Fig. 2. Line A represents

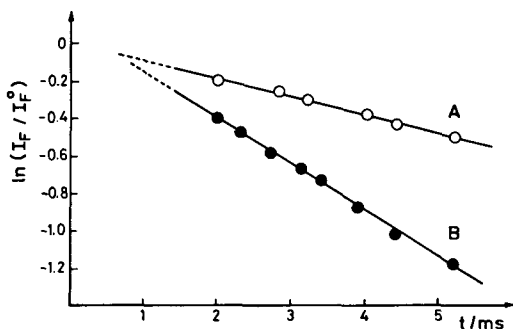
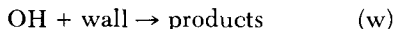
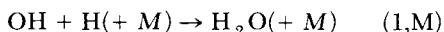


FIG. 2. Decay of OH concentration (expressed in terms of the UV fluorescence intensity I_F) with reaction time, showing predominantly first-order kinetics. $T = 300$ K, $p = 6.5$ torr of He; $[\text{OH}]_0 \sim 6 \times 10^{12}$ molecules/cm³; line A: $[\text{H}] \sim 5 \times 10^{13}$; line B: $[\text{H}] = 1.5 \times 10^{15}$ atoms/cm³.

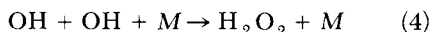
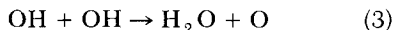
the observed OH decay at low H atom concentrations (5×10^{13} atoms/cm³), which under these conditions ($[\text{OH}] \sim 4 \times 10^{12}$ molecules/cm³ at the first point of observation) is predominantly due to heterogeneous wall removal and is therefore first order:



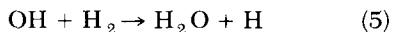
At increased H atom concentrations, e.g. 1.5×10^{15} atoms/cm³, however, an enhanced OH decay rate is observed (Fig. 2, line B) which can be attributed to additional consumption of OH in the recombination reaction



Reactions that are second order with respect to $[\text{OH}]$

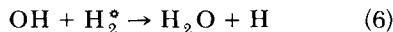


only account for a small proportion of the OH decay, particularly at higher H atom concentrations where the total decay rate is faster. In order to identify reaction (1,M) as solely responsible for the observed acceleration, one must first investigate the possibility of competitive processes. A reaction between OH and undissociated hydrogen

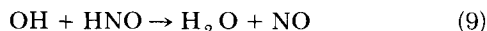


may be excluded since its contribution is small, as can be clearly determined from the known flow of total H_2 and a well established rate

constant $k_5^{1,12}$. However, microwave discharges of hydrogen (even in dilution with He) are known to produce vibrationally excited H_2^* (H_2^*)^{13,14} and this may remove OH via



more extensively at high than at low discharge power levels. Although the residence time of discharge products upstream of the OH generation point is of the order of 3 ms and hence H_2^* may to a great extent be relaxed either by collision with the walls or by reaction with H atoms,¹³ it appeared important to perform an experimental test. In this experiment a clean Pt wire mesh, which effectively destroys H atoms but leaves H_2^* virtually unaltered,¹⁴ was inserted into the side arms of the flow system immediately downstream of the discharge. In this case the OH decay rate was small and could be completely attributed to reactions (w) and (5). An additional source of OH removal via the reaction sequence



may be evaluated by setting the HNO concentration as quasistationary. Although the rate constants k_8 and k_9 are not very well established,¹⁵ a maximum $[\text{HNO}]_{qs}$, calculated with a lower limit for k_8 and an upper limit for both k_7 and k_9 ,¹⁵ leads to an overall contribution of less than 20% by reaction (9) to OH decay.

The occurrence of reaction (1,M) is confirmed by an investigation of its dependence on both $[\text{H}]$ and $[\text{M}]$. Figure 3 shows the resulting dependence of the first-order OH decay constant k_{1st} upon the H atom concentration for two different pressures at room temperature. At H atom concentrations up to 5×10^{15} atoms/cm³, k_{1st} increases proportionally to $[\text{H}]$

$$k_{1st} = -\Delta \ln [\text{OH}] / \Delta t - k_w = k_{1,M} [\text{H}]$$

confirming that OH, apart from reaction (w), is removed by a reaction with hydrogen atoms (Here, $k_{1,M}$ represents the rate constant for reaction (1,M) at a given total $[\text{M}]$). The dependence of the second-order rate constant, $k_{1,M}$, upon M can be represented by (Fig. 4)

$$k_{1,M} = k_1 [\text{M}] + k_2$$

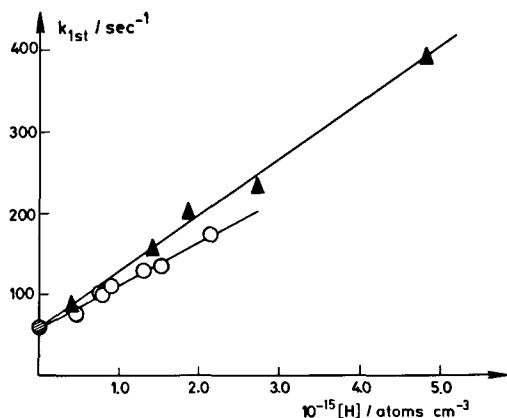


FIG. 3. Dependence of the first-order rate constant on H atom concentration; $T = 300$ K, $p = 8.6$ torr (\blacktriangle) and 5.0 torr (\circ) of He; \bullet represents the wall rate constant k_w .

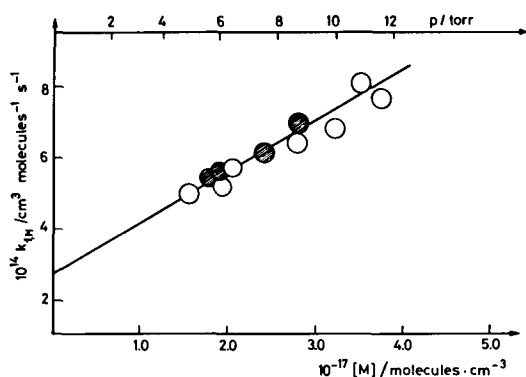
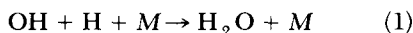


FIG. 4. Dependence of the second-order rate constant on total $[M]$ for $M = \text{He}$. $T = 300$ K. Open circles refer to one experiment each, whereas closed circles refer to several (at least 4) experiments in which the H atom concentration was varied at a given constant pressure (cf. Fig. 3).

indicating both third-order (homogeneous)



and second-order recombination kinetics



The rate constants at $T = 300$ K were derived from the data in Fig. 4:

$$k_1 = (1.5 \pm 0.4) \times 10^{-31} \text{ cm}^6 / \text{molecule}^2 \cdot \text{s};$$

$$M = \text{He}$$

$$k_2 = (2.7 \pm 0.6) \times 10^{-14} \text{ cm}^3 / \text{molecule} \cdot \text{s}$$

One of the objectives of the present work was to study the variation of k_1 with temperature. Since in our experiments k_1 can only be derived from plots such as in Fig. 4, the dependence of $k_{2\text{nd}}$ on $[M]$ had to be determined at different temperatures. The results of an investigation in the range $T = 230$ – 300 K are summarized in Table I. Rate constants k_1 and k_2 , as derived for different temperatures, are given in the last two columns. Reaction (1) has a fairly strong negative temperature dependence, reflecting its third-order character. The variation of k_1 with temperature can be represented by

$$k_1 = (4.3 \pm 3) \times 10^{-25} T^{-(2.6 \pm 0.2)} \text{ cm}^6 / \text{molecule}^2 \cdot \text{s}; \quad M = \text{He}$$

In Arrhenius form this corresponds to an apparent negative activation energy of 5.4 ± 1.2 kJ/mol. The dependence of k_2 on temperature cannot be clearly determined from our experiments. Within the error limits of extrapolation of $k_{1,M}$ to $[M] = 0$ the rate constant k_2 remains nearly constant $k_2 = 2.7 \pm 0.6 \times 10^{-14} \text{ cm}^3 / \text{molecule} \cdot \text{s}$ for all temperatures. Our measurements provide a rather direct determination of the rate constant k_1 . The data of Oldenberg et al.² have been criticized¹ because OH was generated by an electrical discharge through water vapor. Using Oldenberg's data, Black and Porter³ normalized their total decay rate constants, which contained contributions from (4) $\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$. From similar experimental work¹⁶ on reaction (4) it has been inferred¹ that Black and Porter's absolute data are too low by a considerable factor. Their relative rate constants, however, show good agreement with our results (see below).

Under the conditions of the present experiments ($p \leq 11$ torr), reaction (1) was found to be in its third-order regime. This is to be expected for a 3-atom molecule with about 490 kJ/mol excitation. An extension of the experimentally accessible range to pressures where the reaction is in the "fall-off" regime or even in the high pressure limit is difficult to envisage. However, Margitan et al.¹⁷ have recently investigated the isotopic exchange reaction $D + \text{OH} \rightarrow \text{OD} + \text{H}$. The rate of this reaction equals the rate of the formation of the excited DOH^* molecule, and, including a small correction for the isotope effect, can be identified with the high pressure limiting rate for reaction (1). Using Slater's method to construct a "fall-off" curve from known low

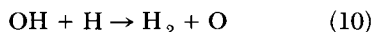
TABLE I
Experimental conditions and rate data for the reaction $\text{OH} + \text{H} (+M) \rightarrow \text{H}_2\text{O} (+M)$, $M = \text{He}$

T (K)	P (torr)	$10^{-15} [\text{H}]$ (atoms/cm ³)	$10^{14} k_{2\text{nd}}$ (cm ³ /molecule · s)	$10^{14} k_2$	$10^{31} k_1$ (cm ⁶ /molecule ² s)
300	4.9	0.7	5.1		
	5.6	var. ⁺	5.4		
	5.8	var.	5.7		
	6.0	1.5	5.3		
	6.6	1.8	5.7		
	7.3	var.	6.2		
	8.6	var.	7.0		
	8.7	1.4	6.4		
	10.1	2.1	6.9		
	10.8	1.0	8.2		
	11.5	1.6	7.8	2.7 ± 0.6	1.5 ± 0.4
263	5.6	1.3	7.1		
	8.2	1.4	10.2		
	8.2	1.4	8.9		
	6.8	1.3	8.0		
	10.7	1.2	11.6	2.7 ± 0.6	2.4 ± 0.7
247	6.0	1.8	9.7		2.9 ± 0.8
233	6.0	1.9	9.7		
	8.1	0.8	15.7		
	9.7	1.4	17.7	2.7 ± 0.6	3.2 ± 1.0

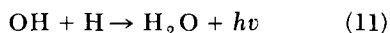
var. ⁺: In these cases the H atom concentration was varied in at least 4 different experiments at constant total pressure.

and high pressure limiting rate constants, we estimate that reaction (1) will effectively be third-order at pressures of He up to ~ 3 atm.

Our result for reaction (2) allows some conclusions to be drawn as to the nature of this process. Among possible homogeneous processes only a reaction



or radiative recombination



would explain second-order kinetics. Reaction (10) can be ruled out because of its low rate constant.¹ Moreover, from the probability of radiation¹⁸ during one vibrational period in an electronically excited H_2O molecule, it can be estimated that reaction (11) will also be too slow to account for a rate constant of 3×10^{-14} cm³/molecule · s. Therefore, the observed second-order reaction should be ascribed preferably to a heterogeneous recombination of OH with H atoms (reaction 2).

The existence of such a reaction was first inferred by McKenzie et al.⁸ They attributed a rate constant of $k_2 = 3.3 \times 10^{-14}$ cm³/molecule · s to this reaction in good agreement with our result. The authors conclude further that reaction (2) shows both first- and zero-order dependence on the hydrogen atom concentration. This, at first view, seems to contradict our result, where (2) is always first-order in [H]. It must be noted, however, that in the notation of this work a wall recombination which is zero order in [H] will be included in reaction (_w), which was observed when $[\text{H}]_0 \sim 5 \times 10^{13}$ atoms/cm³ (cf. Fig. 3). Finally it should be noted that the second-order dependence of reaction (2) as well as its temperature independence cannot be explained by simple Langmuir kinetics. Similar experimental observations of second-order heterogeneous processes, however, have been reported before.^{5b,8}

ii) *The Reaction* $\text{OH} + \text{H} + M \rightarrow \text{H}_2\text{O} + M$; $M = \text{Ar}, \text{N}_2, \text{CO}_2$

Reaction (1) was also studied at room temperature in Ar, N_2 and CO_2 . Since possible deviations from one-dimensional flow profiles may affect the derived rate constants, the total pressures in these experiments were kept below 6 torr, where the reaction was assumed to be third-order. Moreover, in evaluating the data, the wall rate constant k_2 was taken to be invariant with M (i.e. $k_2 = 2.7 \times 10^{-14} \text{ cm}^3/\text{molecule} \cdot \text{s}$), in agreement with the result of Anderson et al.^{5b} Since N_2 and CO_2 could not be passed through the discharge, they had to be added at some position downstream. Rate data for the reaction in pure N_2 (CO_2) were derived from extrapolations of plots of k_1 vs. mole fraction. The maximum percentage of M in He (80% for $M = \text{N}_2$, 20% for $M = \text{CO}_2$) was primarily determined by their quenching efficiency for $\text{OH A}^2\Sigma^+$. Whereas N_2 is only moderately efficient, CO_2 mole fractions of only 0.2 decrease the observed fluorescence intensity to 1/3 of its value in pure He.⁷ Table II summarizes our data together with the only other determination of relative efficiencies at room temperature, obtained by Black and Porter.³ There is good agreement between the data for He, Ar and CO_2 . For N_2 , however, our data is slightly smaller which appears to be realistic on the basis of the predicted dependence¹⁹ of collisional transition probabilities upon the number of atoms in M .

iii) Comparison with High Temperature Dissociation and Recombination Data

Fig. 5 summarizes some data on reaction (1) and the reverse dissociation for the third bodies He, Ar and N_2 . The data points presented here have been selected according to the evaluation of Baulch et al.,¹ who recommend the rate expressions $k_1 = 2.3 \times 10^{-26} T^{-2} \text{ cm}^6/\text{molecule}^2 \cdot \text{s}$ and $6.0 \times 10^{-26} T^{-2} \text{ cm}^6/\text{molecule}^2 \cdot \text{s}$ in the range 1000–3000 K for $M = \text{Ar}$ and N_2 , respectively. These expressions give a good fit with our data at $T = 300 \text{ K}$ for both Ar and N_2 . The temperature dependence, however, determined by us in the

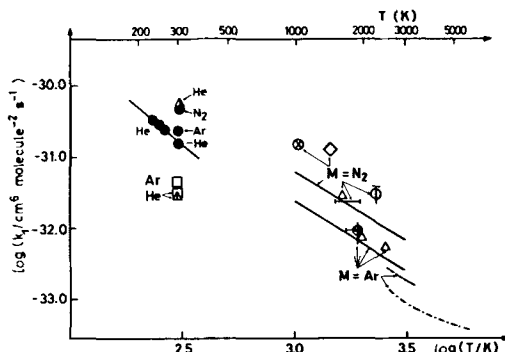


FIG. 5. Plot of $\log k_1$ versus $\log T$ for $\text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$. This is not a complete summarization of all available results. The data presented here are selected according to Baulch et al.'s¹ recommendation. Moreover, some of the authors have also reported rate constants for other M 's, which have been omitted here for clarity. Δ : Frost and Oldenberg;^{2a} \blacktriangle : Oldenberg and Rieke;^{2b} \square : Black and Porter;³ —: recommended expressions by Baulch et al.¹ for $M = \text{N}_2$ and Ar; \otimes : Dixon-Lewis et al.²⁰ \diamond : Rosenfeld and Sugden,²¹ Φ : Zeegers and Alkemade;²² \triangle : Gay and Pratt;²³ \dashv : Getzinger and Blair;²⁴ Φ : Halstead and Jenkins;²⁵ —: Homer and Hurle²⁶ (from measurements of k_{-1}) - - - - Olschewski et al.²⁷ (from measurements of k_{-1}); \bullet : this work for $M = \text{He}$, Ar and N_2 .

range $T = 230\text{--}300 \text{ K}$ for $M = \text{He}$ ($T^{-2.6}$) is stronger than that used for the correlations for Ar and N_2 .

Further information on k_1 at high temperatures is available from dissociation studies.^{26,27} Of these, the value of Homer and Hurle²⁶ for $M = \text{Ar}$ is close to Baulch et al.'s¹ expression. The data of Olschewski et al.,²⁷ however, are lower by a factor of 2 and, in combination with the $M = \text{Ar}$ result obtained here, would suggest a temperature coefficient of $n \approx 2.2$ over the whole range $T = 300\text{--}3000 \text{ K}$ in closer proximity to $n = 2.6$, as derived from our $M = \text{He}$ data for $T = 230\text{--}300 \text{ K}$. However, it must be borne in mind that the attempt to correlate low and high temperature data in terms of one single temperature coefficient is only a first approximation. The difference in temperature exponents at low and high temperatures may be genuine. Therefore, a T^{-n} expression with n varying from ~ 2.6 around room temperature to 2.0–2.2 at 3000 K seems most appropriate as long as no further experimental information is available in the intermediate temperature range.

An inspection of Fig. 5 reveals that some of the important data^{20–22} in the range $T =$

TABLE II
Relative third body efficiencies at 300 K.

M	He	Ar	N_2	CO_2	H_2O	Ref.
1	1.5	4.7	6	25		Black, Porter ³
1	1.5	3.2 ± 0.3	6 ± 1	—		this work

1000–2500 K are considerably higher than those predicted by Baulch et al.'s¹ expression. In an assessment of these data it must be taken into account that they were derived from experiments in which considerable amounts of water (among other collision partners) were present, and that an attempt to derive a rate constant in pure N₂ or Ar is not without complications. However, since there is sufficient evidence that H₂O is a particularly efficient third body^{3,26} these data can be brought into satisfactory agreement with all other results. Taking the collision efficiency of H₂O relative to He to be 25^[3] and normalizing the He data with the result obtained here, a rate coefficient at 300 K of $k_1 \sim 3.7 \times 10^{-30}$ cm⁶/molecule² · s for $M = \text{H}_2\text{O}$ is predicted. From this, a T^{-2} extrapolation yields rate coefficients above 1000 K that are close²¹ or slightly above^{20,22} the observed data, and also correlates well with a rate constant predicted for $M = \text{H}_2\text{O}$ from Homer and Hurle's²⁶ absolute data in Ar and a relative efficiency H₂O/Ar of 20.

iv) Comparison with Predictions from Unimolecular Rate Theory

The experimental data obtained here may be compared with predictions based on a theoretical treatment of unimolecular rate processes.^{28,29} We calculated the low pressure rate constant for the recombination of OH and H in the strong collision limit ($k^{s.c.}$) following the expression and notation of Troe²⁹

$$k^{s.c.} = \frac{1}{K} [M] \cdot Z_{LJ} \cdot \frac{\rho_{vib,h}(E_o) \cdot RT}{Q_{vib}} \cdot F_{vib} \cdot F_{anh} \cdot F_{rot} \cdot \exp(-E_o/RT)$$

With the collision number Z_{LJ} calculated with a Lennard-Jones parameter of 0.8 at 300 K,³⁰ the density of states ($\rho_{vib,h}(E_o)$), vibrational partition function (Q_{vib}) and F_{vib} ³⁰ derived with frequencies from Herzberg,³¹ $F_{anh} = 1.7$,²⁹ $E_o = 493$ kJ/mol, and the rotational correction factor (F_{rot}) estimated using an expression by Waage and Rabinovitch,³² one obtains $k_1^{s.c.} = 4.2 \times 10^{-31}$ cm⁶/molecule² · s. If the measured rate constant is identified with the "weak collision rate constant," then we can derive a collision efficiency factor, defined²⁹ as $k_1 = k_1^{s.c.} \cdot \beta_c$, of $\beta_c \sim 0.33$ for $M = \text{He}$ at 300 K. This agrees very well with observed values from other systems where a direct comparison

of experiment and theory has been possible.^{19,33}

Further, in order to derive an approximate expression for the temperature variation of β_c , we calculated $k_1^{s.c.}$ in the range 1000–4000 K, where experimental data on k_1 exist for comparison. Using k_1 from Baulch et al.'s¹ expression we obtain $\beta_c \sim 0.07$ at 1000 K and ~ 0.02 at 4000 K and, with the value at 300 K derived above and corrected for $M = \text{Ar}$, $\beta_c \sim T^{-1.3}$ for $M = \text{Ar}$ over the whole range. This is consistent with what has been found in other systems^{19,33} and with the theoretical T^{-2} limit.³⁴

Acknowledgement

We are grateful to Prof. H. Gg. Wagner for sustained interest in this work and for valuable discussions and advice. One of us (R. Z.) thanks NATO for a research grant to enable cooperation with Dr. I. W. M. Smith, to whom we are grateful for useful discussions. D. F. thanks ICI for a post-doctoral fellowship.

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COMMENTS

T. Fujiwara, Nagoya University, Japan. I would like to ask you whether you established a reaction-controlled regime in your reaction chamber in connection with the surface destruction of OH/H. The radial diffusion characteristic time R^2/D for your experimental condition turns out to be ~ 0.1 sec, which may be longer than the characteristic time of surface OH destruction. If that is the case, you are observing simply the diffusion rate of OH/H which is limiting the whole process, and the reported surface destruction rate should be higher.

Authors' Reply. The first order rate constant (k_w) for the removal of OH in the absence of large excess H atom concentrations, which we have determined prior to each run on reaction (1), does not show a systematic variation with pressure in the range 4–11 Torr of He. It does, however, depend on the nature and the history of the wall coating. From this it may be concluded that wall destruction of OH is reaction-controlled. A change-over with in-

creasing pressure from reaction to diffusion control does not seem to occur under the conditions of our experiments. The effects observed for wall destruction of OH only should be expected to hold also for the wall recombination of OH and H (reaction (2)). The lack of importance of radial concentration gradients in tubular flow reactors at pressures of a few Torr of He is treated quantitatively in Ref. 9, 10, and is discussed further in the main text of the present paper.

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Daniel W. Trainor and C. W. von Rosenberg, Jr., Avco Everett Research Laboratory, Inc. USA. In your presentation, you showed that the theory of Troe (Ref. 28) gave a theoretical prediction that was in good agreement with your experimental value for the reaction $\text{H} + \text{OH} + \text{M}$. Have you applied that calculation to the other recombination permutations involving these radicals and/or would you feel the

theory would predict the relative magnitudes of the measured experimental values (i.e., $\text{H} + \text{OH} + \text{N}_2 \rightarrow \text{H}_2\text{O} + \text{N}_2$, $4.8 \times 10^{-31} \text{ cm}^6/\text{sec}$, this work; $\text{OH} + \text{OH} + \text{N}_2 \rightarrow \text{H}_2\text{O}_2 + \text{N}_2$, $2.4 \times 10^{-31} \text{ cm}^6/\text{sec}$, Trainor and vonRosenberg, J. Chem. Phys. 61, 1010 (1974); and $\text{H} + \text{H} + \text{N}_2 \rightarrow \text{H}_2 + \text{N}_2$, $9.1 \times 10^{-33} \text{ cm}^6/\text{sec}$ (Ref. 4)?

Authors' Reply. We have so far not applied the full theoretical expression (Troe, Ref. 29) to calculate the absolute rate constant for the reaction (4) $\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$ in the low pressure regime. From a first estimate of the relative rate constants, however, it appears that k_4 may be larger than k_1 (the rate constant for (1) $\text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$) by a factor of 5-10, predicting rate constants for k_4 in marked discrepancy with your own data but in closer proximity to Baulch et al.'s (Ref. 1) evaluation for reaction (4). Unfortunately, the theory of Troe can not be applied in the given form to the recombination of atoms, and therefore a theoretical cross-check of the experimental data on k_1 (this work) and on $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$ (Ref. 4) is not readily possible.

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Carleton J. Howard, NOAA, USA. I would like to know what evidence you have that the calorimetric probe you use selectively removes H atoms and not any vibrationally excited H_2 as well. In general calorimetric probes lack specificity for either atomic or vibrationally excited species. For example, Morgan et al.¹ report that both N atoms and excited N_2 are converted to ground state N_2 with very high efficiencies by the probe surface. The observation of Trainor et al.² that H atoms are recombined into ground state H_2 on the probe surface and the known chemical activity of platinum to hydrogen make it

surprising to me that vibrationally excited H_2 escapes the probe unscathed.

I wouldn't expect vibrationally excited H_2 to be a problem in your measurements because of efficient deactivation by H and collisions with the tube walls.³

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Authors' Reply. We have no direct evidence of any specificity for either atomic or vibrationally excited species of our Pt wire mesh. The test on $\text{H}_2(v=1)$ was performed following a similar experimental procedure of Stedman et al. (Ref. 14 in the paper) and the only quantitative test thus far reported of a catalytic probe in which $\text{H}_2(v=1)$ was followed directly (Heidner¹). The latter author observed similar, although small, quantities of $\text{H}_2(v=1)$ in mixtures of H/H_2 (from a microwave discharge) upstream as well as downstream of the probe.

Concerning our experiments on reaction (1) we can only reiterate what we have said in the main text in agreement with your last statement: Vibrationally excited H_2 will be relaxed by collisions with H atoms or with the wall (Ref. 13) prior to our observation of the OH decay.

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