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VALÉRIE NAUDET, SANDRA JAVOY and
CLAUDE-ETIENNE PAILLARD[*]

*Laboratoire de Combustion et Systèmes Réactifs (LCSR), UPR 421 du CNRS,
1 C, avenue de la Recherche Scientifique 45071 ORLÉANS cedex 2, France*

The OH radical dissociation has been studied behind shock waves in the temperature range of 2950–3700 K at total pressures of about 220–310 kPa by Atomic Resonance Absorption Spectroscopy using mixtures of H_2 and O_2 highly diluted in Ar. The OH decomposition was followed by monitoring the time dependent O concentration in the post shock reaction zone. In our experimental conditions this reaction is very sensitive to O-atom profiles. The rate constant k_{-2} of the termolecular recombination reaction between H, O and Ar as collision partner was calculated from OH dissociation rate constant k_2 measurements and the equilibrium constant. The results expressed in the simple Arrhenius form are:

$$k_2 = 1.2 \times 10^{15} \exp(-48100/T) \ cm^3 \ mol^{-1} \ s^{-1}$$

$$k_{-2} = 6.75 \times 10^{18} T^{-1} \ cm^6 \ mol^{-2} \ s^{-1}$$

with an uncertainty of ± 30 %, which are in good agreement with the estimate of Tsang and Hampson in 1986. No experimental results were reported by earlier investigators.

Keywords: shock tube; chemical kinetics; ARAS; high temperature

INTRODUCTION

High Mach number flight required for the scramjet propulsion can lead to very high temperatures in the combustor yielding high densities of radical and atomic

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* e-mail: paillard@admin.cnrs-orleans.fr

species. The high internal velocities in a hypersonic engine result in very short residence times (millisecond time range). Consequently the engine efficiency depends strongly on the rate of the radical and / or atom recombination reactions in the nozzle (Jachimowski, 1992). It exists a few experimental data on the rate constants of the reactions in the form X+Y+M = XY+M with X,Y = H, O or OH.

The purpose of this study was to examine and revalue the rate constants of the direct and inverse reactions:

$$OH + Ar = O + H + Ar \quad (R_2/R_{-2})$$

There are no direct measurements of the R_2 and R_{-2} reaction rates. The rate constant values are given in the literature with an error of one order of magnitude. Thus, there is need for experimental data in order to validate the estimates found by Tsang and Hampson (1986). Atomic Resonance Absorption Spectrophotometry (ARAS) has been used to measure the O-concentration profile behind reflected shock waves. This technique is very sensitive and allows the use of very diluted reactants mixtures. It is very important if we want to be able to neglect secondary reactions. The atomic resonance absorption method has been used by numerous authors for kinetics studies of elementary reactions in the past (Myerson and Watt in 1969, Frank and Just in 1985, Natarajan and Roth in 1987 for example).

Oxygen atoms concentration was deduced from the calibration curve. The ARAS system newly developed in the laboratory was validated from the comparison between our O_2 dissociation rate constant measurements (Naudet et al., 1999) and previous experimental published results for dissociation in oxygen-argon mixtures. We noted a good agreement between our results and the values recommended by Warnatz in 1984 and confirmed by other groups.

EXPERIMENTAL TECHNIQUE

The Shock Tube

The apparatus is a 78-mm internal diameter stainless steel, pressure driven shock tube with a 4-m long driven section and a 0.9-m driver section. All gaskets used were of Viton. No greased O-rings were in contact with the driver and the driven sections. The driven section was evacuated using a 0.2 m^3 s^{-1} diffusion pump (PAD Alcatel Crystal 62) backed by a two-stage mechanical pump (Alcatel 2020 AC) equipped with a zeolite molecular sieve to reduce contamination from oil back-streaming. The inner of the driven section was honed to a smooth finish. The driver section filled with He was vacuumed using a two-stage mechanical

pump (Alcatel 2012 A). The oil diffusion pump was connected to the shock tube via a water-cooled baffle and a liquid nitrogen trap. The whole tube could be heated up to 100°C to limit the amount of water vapor adsorbed by wall. The pressure and leak rate were monitored with a pressure controller type Micro-Pascal. The driven section could be evacuated to 10^{-5} Pa. The typical leak-plus-outgassing rates were of the order of 8×10^{-7} Pa s^{-1} or less. Figure 1 shows schematically the shock tube and associated equipment.
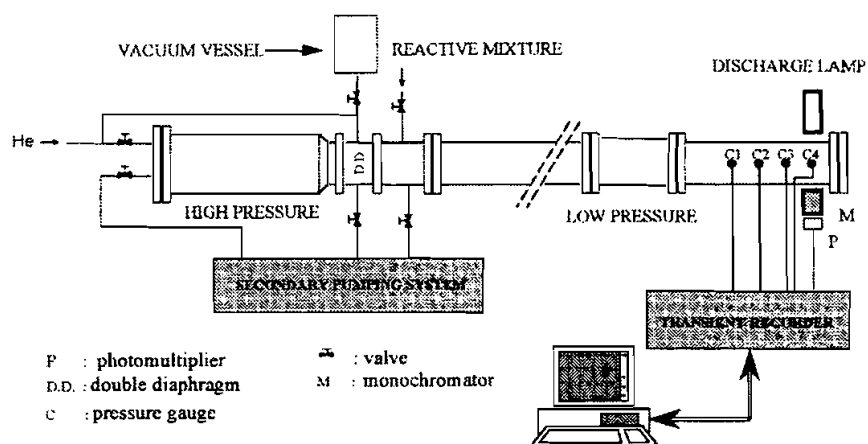

FIGURE 1 Experimental setup

The driver section was separated from the driven section by Mylar films of various thicknesses (from 18 to 50 μm). The temperature and pressure behind the reflected shock waves were computed from the incident shock speed, which was measured by four piezo-electric pressure gauges, placed along the test section. An uncertainty less than 1 % was estimated on temperature and 2 % on pressure. One dimensional shock equations assuming complete vibrational equilibrium were used. The shock tube was equipped with two thin opposite MgF_2 windows 10 mm in diameter, 5 mm thick were mounted flush on both shock tube walls. The absorption was registered behind the reflected shock, 10 mm from the end flange of the shock tube.

Optical detection technique

The optical detection technique for measuring O-atom concentration was an emission-line absorption method. The arrangement consists of a microwave

excited discharge lamp, a monochromator and a photomultiplier. The discharge which constituted our light source is composed of three parts: a generator, a cavity (or antenna) and a quartz tube. The generator type GMP 03 KE/SM is a 2.45 GHz microwave generator (SAIREM) with a power that could be varied from 0 to 300 W. It was air-cooled. The plasma was created in a 15-mm o.d., 2-mm thick quartz tube crossing the downstream source. The quartz tube contained a flowing high quality grade mixture of 1 % O_2 in Helium (Air Liquide) for the emission of the OI triplet at 130.2, 130.5, 130.6 nm ($^3P_{2,1,0} - {}^3S_1$). The operating conditions were chosen to minimize noise and reflected power without significant loss of signal strength. The lamp was connected directly to the shock tube with a plane MgF_2 window fit as flush to the inner surface of the tube. The lamp gas mixture pressure was controlled with two needle valves; the pressure was measured with an Edwards 0–100 Torr pressure gauge. The downstream source was water-cooled. The whole system generated a neutral plasma which characteristics depend on pressure in the lamp, gas type and microwave power. Since plasma density and ion recombination are affected by pressure and system geometry, the nature of the species arriving at the treatment area is also dependent on these factors. Bell and Kwong presented a model on the kinetics of molecular oxygen dissociation in a microwave discharge in 1973. The 1 % O_2/He flow was maintained at a pressure of 400 Pa. The operating power level of the resonance lamp was 40 W. The OI triplet was selected by a vacuum-ultraviolet monochromator (Jobin-Yvon LHT30) before detection. It is pumped down to 10^{-4} Pa or lower by a turbomolecular pump (Alcatel ISO EAU). The associated mechanical pump (Alcatel 2004) was equipped with a zeolite molecular sieve. The radiation transmitted through the shock-heated gases is measured with a Hamamatsu solar blind UV photomutiplier model R972 with a spectral range varying from 50 to 300 nm. It was powered with a 0–3000 Volts high voltage power supply. The operating conditions in our case were: V= –2000 V, 2-mm monochromator entrance and exit slits. The rise time of the detection system was about 13 μs with a R_{load} of 47 kΩ

Test gas mixture preparation

The different gas mixtures were prepared by partial pressure measurements employing two calibrated MKS baratron pressure gauges (model 122B 0–10 and 0–1000 Torr), in two glass bulbs. A turbomolecular pump pumped the glass system down to 10^{-5} Pa. Because of the high sensitivity of ARAS technique, all gases used were of ultra high purity. They were supplied by Air Liquide and certified to be of the purity: Ar = 99.9999 %, O_2 = 99.998 %, N_2O = 99.998 % and H_2 = 99.9999 %. The residue of evaporation of H_2O was inferior to 0.0003 %.

Prior to each run the shock tube was swept by argon and evacuated to a pressure of 4.10^{-5} Pa or lower. Initial pressures in the test section were in the range of 700–5000 Pa.

O-ATOM ARAS SYSTEM CALIBRATION

The spectral shape of the line is not known in detail, there is no simple relation between the absorption and the concentration. Hence precise calibration measurements were necessary to relate the measured resonance absorption to the corresponding atom concentration. The lineshape was a function of the optical depth of the plasma and unexcited layers. Thus the calibration can be varied through the adjustable parameters that determine the optical depth. These parameters included lamp power, pressure in the lamp, O_2/He mixture dilution and cavity location. The ARAS diagnostic sensitivity depends on the lamp design which may allow access to different ranges of O-atom concentrations in shock tube experiments. A two-layer model has been applied by Just (1981) to describe the ARAS lamp emission profile. In this model the excited zone (plasma) emits and absorbs, whereas an adjacent unexcited layer, in front of the plasma, only absorbs. The effect of the absorption in the plasma is to broaden the emission lineshape; the second layer results in self-absorption (self-reversal). By increasing lamp temperature (through increased power level), or optical depth (through increased lamp pressure, O concentration and greater cavity-shock tube separation) the emission lineshape can be made more broad and self-reversed. This results in a greater fraction of the lamp emission away from the line-center and thus lower resultant cross section in the shock-heated gases. Then it is necessary to perform separate calibration experiments to determine the absorption cross section. Just (1981) mentioned that, at temperature above 2200 K the dissociation of a few ppms of N_2O is so fast that a steady state concentration of O atoms is achieved. Subsequent reactions like $O+N_2O \rightarrow N_2+O_2$ or 2NO are known to be slow and are unimportant at low N_2O concentrations. Recombination of O-atoms can be neglected in the typical time scale of 400 to 600 μs. Different gas mixtures of N_2O/Ar were shock heated to temperatures in the range 2490–4600 K and pressure between 100 and 300 kPa. Mixtures containing 11 to 26.5 ppm of N_2O in Argon were used. An overall uncertainty of ± 1.5 or 2 % is estimated in the concentration behind reflected shock waves in function of the number of dilution and the MKS baratron pressure gauge accuracy. The useful temperature range for each investigated mixture was limited at low temperature side by the detection limit, and at high temperature end by absorption, which had to be less than 90 %. The calibration curve is presented in figure 2.
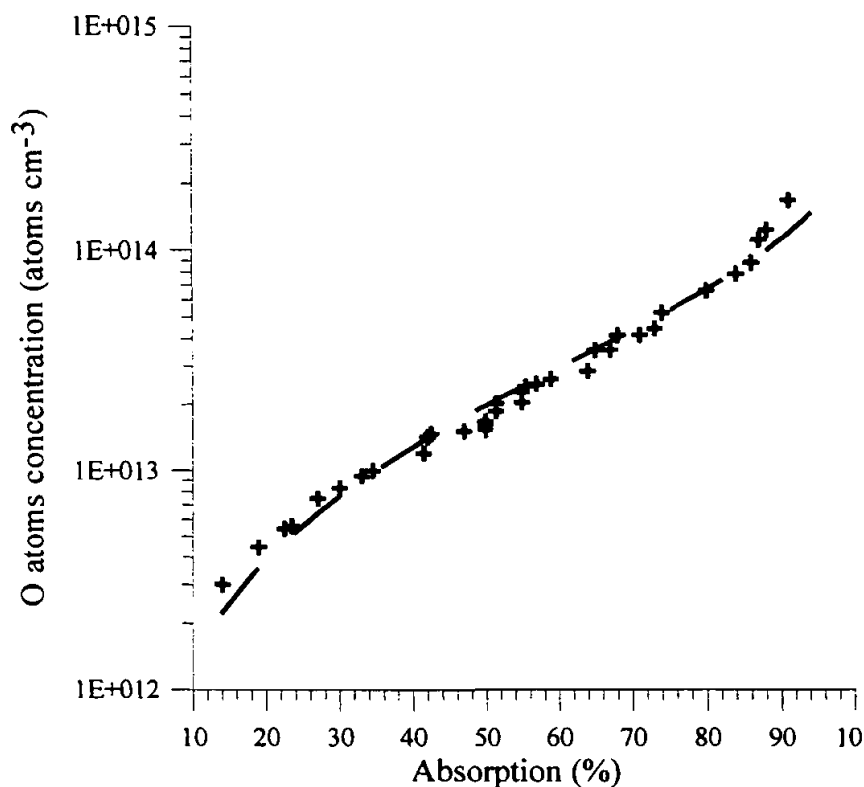
FIGURE 2 Calibration curve for O atoms

Assuming Beer's law to be valid, the absorption cross section was calculated from oscilloscope trace and the relation 1:

$$I/Io = \exp(-\kappa\ell[O]) \tag{1}$$

where κ is the absorption cross section in $cm^2 \ mole^{-1}$, [O] the concentration of oxygen atoms in moles cm^{-3}, and ℓ the shock tube width in cm.

We showed no dependence of the cross section in function of temperature too. The calibration experiments can be approximated by the following modified Beer-Lambert expression (2):

$$A = 1 - \exp(-1.88 \times 10^{-11}[O]^{0.7}\ell) \tag{2}$$

Where the numerical constant is given in $cm^{1.1} \ mol^{-0.7}$. We note a good agreement between the experimental results and this expression. The modified Lambert-Beer law (with an exponent of 0.7 on the O-atom concentration) is used to

increase the concentration range. A table with different modified Beer's law used by different authors was presented in Naudet et al. (1999).

RESULTS

OH+Ar = H+O+Ar determination

The experiments were conducted in rich $H_2/O_2/Ar$ mixtures. The temperature ranged between 2940 and 3700 K, the pressure between 220 and 310 kPa and the O-atom concentration between 2×10^{12} and 10^{14} atoms cm^{-3}. O-atoms produced by the OH radical dissociation were monitored behind reflected shock waves.

TABLE I Reduced mechanism deduced from sensitivity analysis

	Reactions	A	n	E/R (K)	Δk/k	References
1	$H_2+Ar \rightarrow 2H+Ar$	2.23×10^{14}	0	48350	± 0.3	Baulch et al.
2	$OH+Ar \rightarrow O+H+Ar$	1.2×10^{15}	0	48100	± 0.3	this work
3	$H+O_2 = OH+O$	1.99×10^{14}	0	8460	± 0.2	Baulch et al.
4	$H_2O+H = OH+H_2$	4.52×10^8	1.	9720	± 0.3	Baulch et al.
5	$O+H_2 = OH+H$	9.25×10^{14}	0	9740	± 0.3	Javoy et al.
6	$H_2O+Ar \rightarrow H+OH+Ar$	1.26×10^{14}	0	50323	± 0.8	Bopp et al.
7	$O_2+Ar \rightarrow 2O+Ar$	3.41×10^{14}	0	55700	± 0.3	Naudet al.

A in $cm^3 \, mol^{-1} \, s^{-1}$

The experimental conditions have been deduced from sensitivity analysis (29 elementary reactions) presented in figure 3. It showed that in rich H_2-O_2 mixtures highly diluted in Ar (210 $<x_{H2}$ (ppmv) < 400 and $30 < x_{O2}$ (ppmv) < 45) and in the 2940–3700 K temperature and 220–310 kPa pressure ranges the absorption profiles are primarily sensitive to the rate of the dihydrogen dissociation reaction.

The more sensitive reactions are presented in order of decreasing sensitivity in table I with the rate constant expression for each reaction.

Rate constant choice for $H_2+Ar \rightarrow 2H+Ar$ (R_1)

Many authors have studied the thermal dissociation of dihydrogen. For example, Breshears and Bird measured postshock density gradient profiles (1972) and Myerson and Watt (1968) or Lissianski et al. (1997) used the ARAS technique. Baulch et al. (1992) recommended a dissociation rate constant with an error of ±
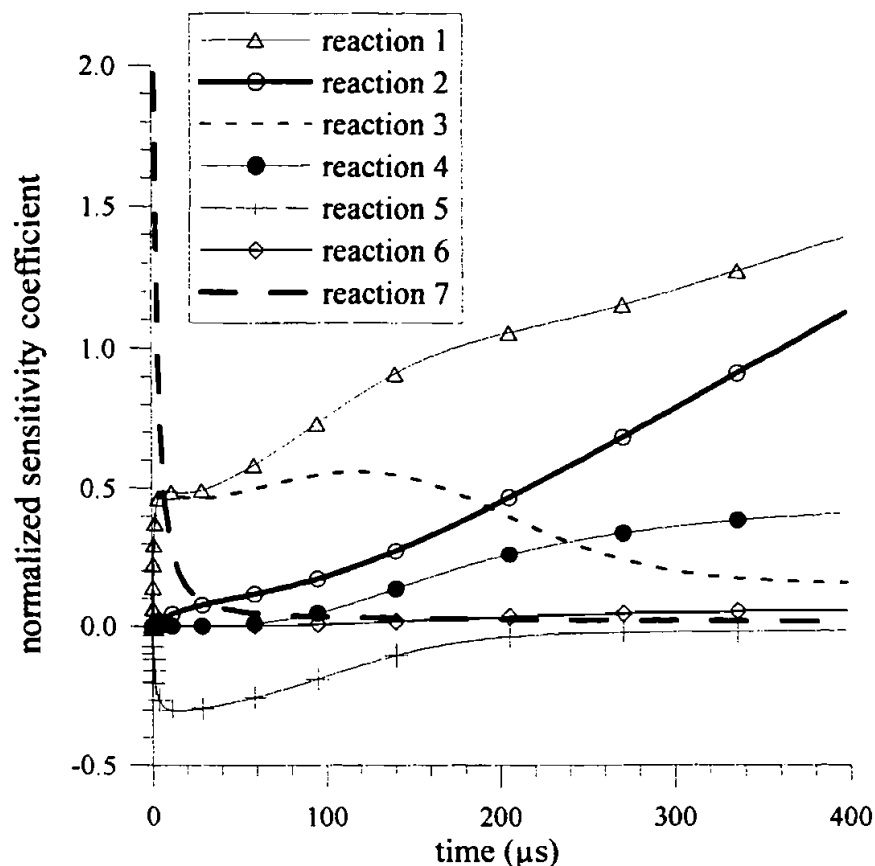
FIGURE 3 Result of the sensitivity analysis. T= 3500 K, P= 300 kPa, x_{O2}= 30 ppm and x_{H2}= 200 ppm

30 % on a large temperature range. Thus, reaction R_1 rate constant can be considered as well known.

Rate constants choice for $H+O_2 \rightarrow OH+O$ and $H_2O+H = OH+H_2$ (R_3) and (R_4/R_{-4})

Even if Yuan et al. (1991) published a rate constant with an uncertainty of ± 5 % for R_3, we chose the value recommended by Baulch et al. (1992) as it gave best fits between experimental and calculated O-atom profiles. For (R_4/R_{-4}) we chose the last recommended values by Baulch et al. (1992).

We have measured the rate of reactions 5 and 6 in the temperature range 2700–3300 K in a recent study. We shock-heated several $N_2O/H_2/Ar$ (R_5) or H_2O/Ar

(R_6) highly diluted mixtures and monitored the O-atoms concentration in the reaction zone behind reflected shock waves.

Rate constant choice for $O+H_2 \rightarrow OH+H$ (R_5)

The rate constant for the reaction R_5 has been the subject of numerous high temperature studies. Pamidimukkala and Skinner (1982 and 1985) used the shock-tube technique and followed the O-atom profiles successively in $H_2/N_2O/Ar$ mixtures (1900–2800 K) and in $H_2/O_2/Ar$ mixtures (1000–2500 K). They deduced a higher pre-exponential factor in their second study. Then, the ARAS method was used by Frank and Just in 1985 (1700–2500 K), Sutherland et al. in 1986 (880–2495 K), Natarajan and Roth in 1987 and Davidson and Hanson in 1990.

The present experimental result (Javoy et al., 2000) is compared to the results from the earlier studies in figure 4. We found:

$$k_5 = 9.25 \times 10^{14} \exp(-9740/T) \text{ with a standard deviation of } \pm 8\%.$$

We note a good agreement with the study of Natarajan and Roth (1987) and this of Davidson and Hanson (1990) by ARAS.

Rate constant choice for $H_2O+Ar \rightarrow OH+H+Ar$ (R_6)

Several authors have already published experimental results on the H_2O dissociation for temperatures up to 2700 K and higher. All used the shock-tube technique. In 1967 Olschewski et al. monitored the absorption of H_2O and OH. They suggested an Arrhenius expression with Ar as diluent between 2700 and 6000 K.

Browne et al. in 1969 deduced the H_2O dissociation rate constant from the recombination rate measurements. The density field behind shock waves in H_2-O_2, H_2-N_2-O_2, and H_2-CO-CO_2 mixtures highly diluted with argon was measured by optical interferometry. They recommended a non-Arrhenius expression with a −0.31 exponent on the temperature. They used a detailed mechanism for the $H_2/CO/O_2/N_2$ system (28 reactions). One year later, Homer and Hurle (1970) deduced two Arrhenius expressions from OH absorption measurements. They gave a relative collision efficiency of 20 between H_2O and Ar. Bopp et al. presented a very high temperature (3600 K-4800 K) study using the shock-tube technique and the D_2O infrared emission in 1978.

In the present study, four mixtures of water vapor highly diluted in argon 1000 ppm, 3000 ppm, 4000 ppm and 6000 ppm, were shock heated between 2700 K and 3200 K and in the 210–250 kPa pressure range. The sensitivity analysis showed that 5 reactions were necessary to reproduce O-atom profiles in the first 300 μs (R_1, R_2, R_3 and R_6 presented in table I). The fifth reaction was $2H_2O \rightarrow H+OH+H_2O$. A relative collision efficiency of 18 was chosen compared to the
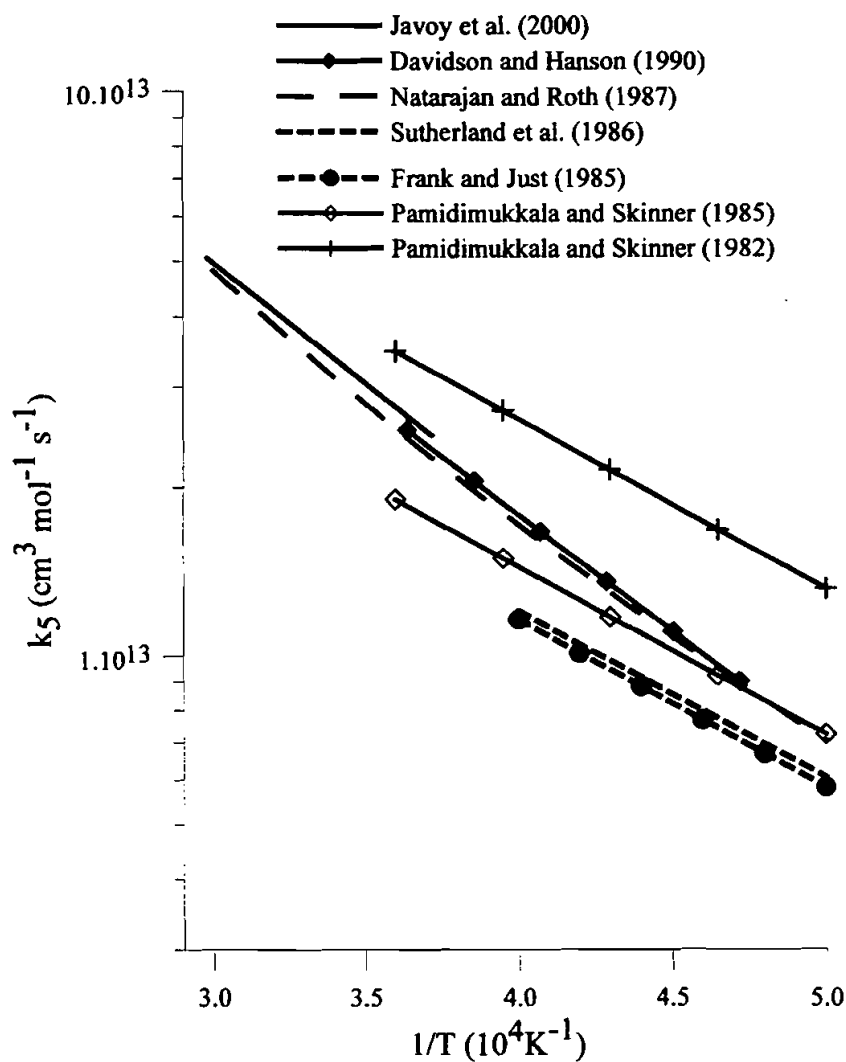
FIGURE 4 Comparison between our k_5 rate constant determination and the values found in the literature

water vapor dissociation in Ar. It gave the best fit between the O-atom experimental and calculated profiles. It was difficult to deduce an Arrhenius expression for R_6 from our experiments in H_2O/Ar mixtures because of the problems due to the steam presence. The percentage of vapor water adsorbed at the wall during the mixture introduction was difficult to estimate. Nevertheless we were able to choose between the Baulch et al. (1992) recommended value and the Arrhenius

expression given by Bopp et al. (1978). Figure 5 shows our experimental data compared to these authors' results. Thus, we decided to choose the expression published by Bopp et al. (1978) for the water dissociation and we fixed a factor of 18 between the rate constant with argon and water as collision partner.
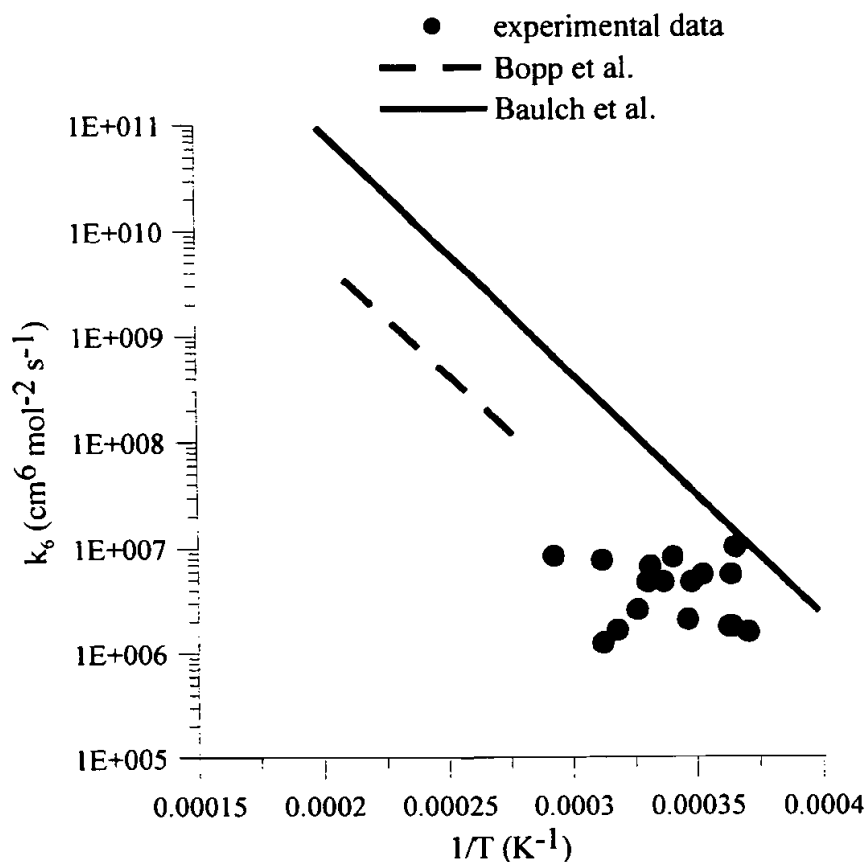

FIGURE 5 Comparison between our k_6 rate constant determination and the values found in the literature

Rate constant choice for $O_2+Ar \rightarrow 2O+Ar$ (R_7)

We chose the rate constant value deduced from ARAS measurements in our laboratory. (Naudet at al., 1999). This value is very closed to the one recommended by Warnatz et al. (1984).

The rate constant for the OH dissociation can be adjusted to match experimental concentration profiles. Figure 6 presents a comparison between simulated and experimental profiles at 3113 K and 305 kPa.
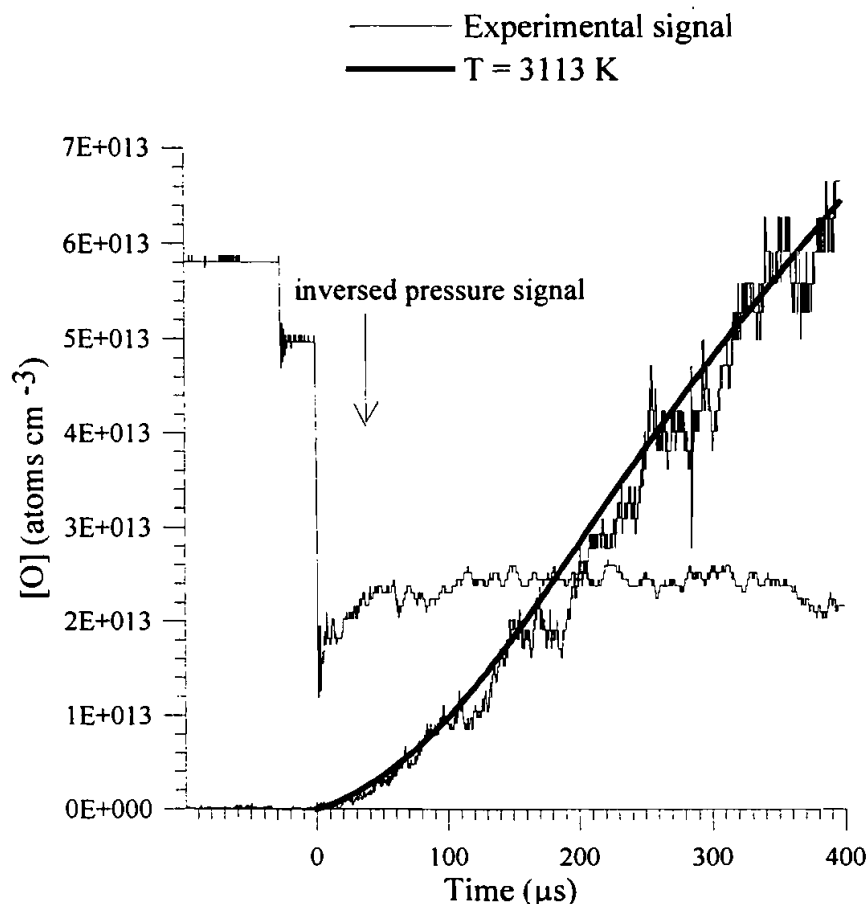
FIGURE 6 Experimental and simulated [O] profiles for an experiment at T=3113 K and P=305 kPa, x_{H_2} = 213.9 ppm , x_{O_2} = 33.3 ppm . Bath gas is Ar

The recombination rate constant k_{-2} was calculated from the equilibrium constant. The Arrhenius expressions derived are:

$$k_2 = 1.2 \times 10^{15} \exp(-48100/T) \ \text{cm}^3 \ \text{mol}^{-1} \ \text{s}^{-1}$$

$$k_{-2} = 6.75 \times 10^{18} T^{-1} \ \text{cm}^6 \ \text{mol}^{-2} \ \text{s}^{-1}$$

with an average statistical deviation of ± 10 %. The figures 7 and 8 show the Arrhenius diagrams for the direct and inverse rate constants respectively. We found an activation energy 14.5 % lower than the OH dissociation energy given in JANAF tables (Chase et al., 1985).
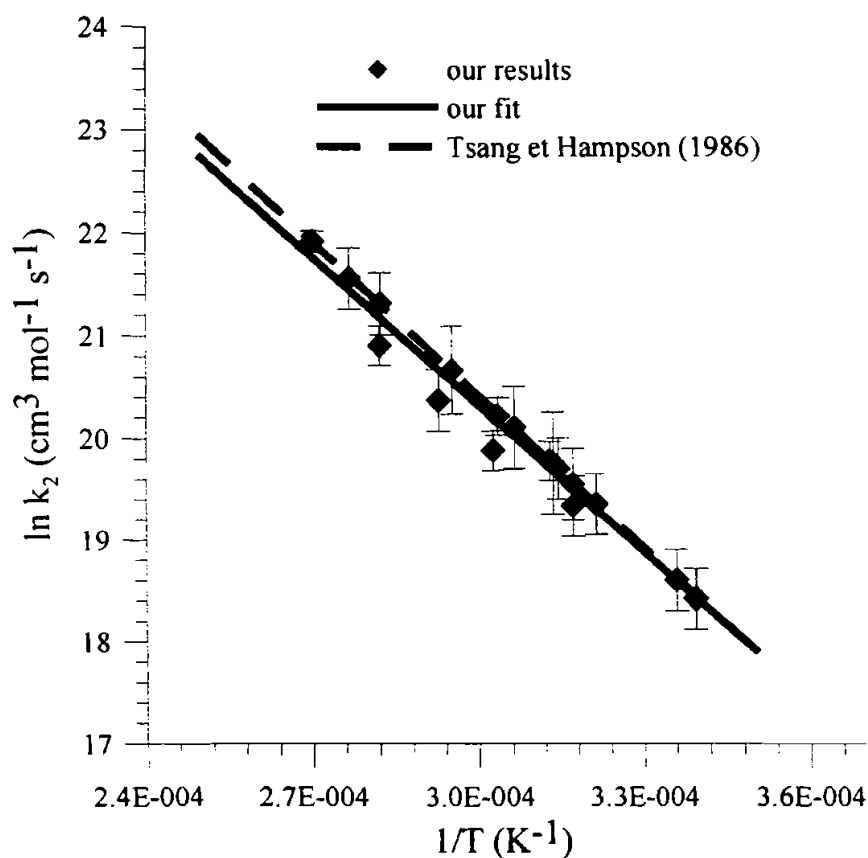
FIGURE 7 Arrhenius diagram for the OH dissociation reaction rate constant for temperatures between 2950 and 3700 K. Comparison between our results and Tsang and Hampson estimate

DISCUSSION

The actual results are in a good agreement with Tsang and Hampson recommended values (1986):

$$k_2 = 2.41 \times 10^{15} \exp(-50000/T) \ cm^3 \ mol^{-1} \ s^{-1}$$

$$k_{-2} = 4.71 \times 10^{18} T^{-1} \ cm^6 \ mol^{-2} \ s^{-1}$$

We found rate constants for R_2 and R_{-2} with an experimental uncertainty of $\pm$ 30 %. However it would be interesting to evaluate the influence of the different reactions uncertainties given in table I ($\Delta k/k$) on k_2 and k_{-2} determination.
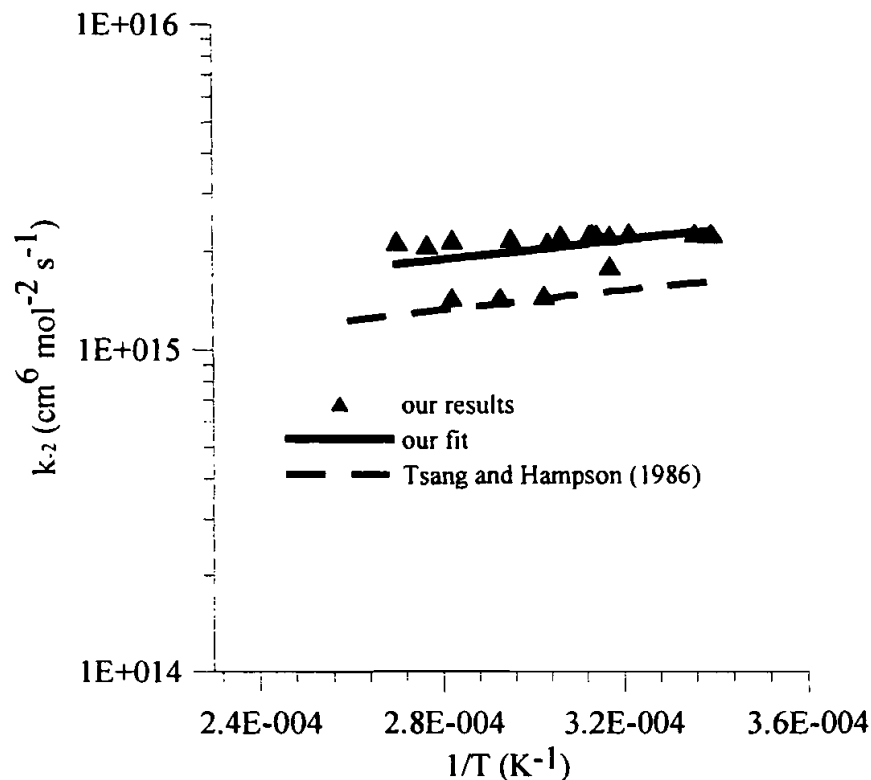
FIGURE 8 Arrhenius diagram for the H+O+Ar → OH+Ar reaction for temperatures between 2950 and 3700 K. Comparison between our results and Tsang and Hampson estimate

The first reaction presented in table 1 was the most sensitive. The compilation of Baulch et al. (1992) gave an Arrhenius expression with a percentage error of ± 30 %. Recent ab initio calculations by Schwenke (1990) gave a good agreement with experimental results. It is important to note that an error of ± 30 % on the H_2 dissociation rate constant resulted on an error of ± 50 % on our determination of k_2 and k_{-2}.

If we took into account the uncertainty of ± 20 % on k_3, it resulted on an error of ± 30 % on our determination of k_2 and k_{-2}.

Reaction R_4 and R_6 rate constant errors (± 30 % and ± 80 %) had very small influence on the O-atom profiles even if we considered the presence of additional H_2O impurities.

Reaction R_5 was revalue in our laboratory. The uncertainty of ± 30 % on this reaction resulted in very small influence on the R_2 rate constant determination.

Reaction R_7 was revalue in a previous study by Naudet et al. (1999). The estimated error on the experimental rate constant was $\pm$ 30 % and did not change the error on k_2.

CONCLUSION

The first experimental results for the OH dissociation reaction (R_2) have been presented for the temperature range of 2950–3700 K by monitoring O-atom concentrations by ARAS in the $H_2/O_2/Ar$ reaction system. The inverse reaction rate constant has been calculated from the equilibrium constant. The measured (k_2) and calculated (k_{-2}) rate coefficients showed an Arrhenius behavior over the temperature range of this study. The experimental results presented here are in excellent agreement with the estimate of Tsang and Hampson (1986). We propose our own Arrhenius expressions:

$$k_2 = 1.2 \times 10^{15} \exp(-48100/T) \; cm^3 \; mol^{-1} \; s^{-1}$$

$$k_{-2} = 6.75 \times 10^{18} \; T^{-1} \; cm^6 \; mol^{-2} \; s^{-1}$$

The experimental accuracy of the values of k_2 and k_{-2} is estimated to be $\pm$ 30 %. The standard deviation is $\pm$ 10 %.

References

Baulch, D., Cobos, C., Cox, R., Esser, C., Frank, P., Just, Th., Kerr, J., Pilling, M., Troe, J., Walker, R. and Warnatz, J. (1992) Evaluated Kinetic Data for Combustion Modeling, *J. Phys. Chem. Ref. Data* 21.

Bopp, J.M., Kern, R.D. and Niki, T. (1978) Decomposition of Water behind reflected Shock Waves, *J. Phys. Chem.*, 82, p. 1343.

Bell, A.T. and Kwong, K. (1973) A Model for the Kinetics of Oxygen Dissociation in a Microwave Discharge. *Ind. Eng. Chem. Funda.*, 12: 1, pp. 90–94.

Breshears, W.D. and Bird, P.F. (1972) Precise Measurements of diatomic Dissociation Rates in Shock Waves. *Symp. Int. Combust. Proc.*, 14, p. 211.

Browne, W.G., White, D.R. and Smookler, G.R. (1969) A Study of the chemical Kinetics of Shock heated $H_2/CO/O_2$ Mixtures, *Symp. Int. Combust. Proc.*, 12, pp. 557–567.

Chase, M.W. Jr., Davies, C.A., Downey, J.R. Jr., Frurip D.J., Mc Donald R.A. and Syverud, A.N. (1985) Janaf Thermochemical Tables Third Edition Part I, Al-Co Part II, Cr-Zr, *J. of Phys. Chem. Ref. Data*, 14, p. 1248.

Davidson D.F. and Hanson R.K. (1990) A Direct Comparison of Shock Tube Photolysis and Pyrolysis Methods in the Determination of the Rate Coefficient for $O+H_2 \rightarrow OH+H$, *Combust. Flame*, 82, pp. 445–447.

Frank, P. and Just, Th. (1985) High Temperature Reaction Rate for $H+O_2=OH+H$ and $OH+H_2=H_2O+H$, *Ber. Bunsenges. Phys. Chem.*, 89, pp. 181–187.

Homer J.B., Hurle, I.R. (1970) The Dissociation of Water Vapour behind Shock Waves, *Proc. R. Soc. London A*: 314, pp. 585–598.

Jachimowsky, C.J. (1992) Chemical Kinetic Research related to Combustion in high-Speed Flows. *In major Research Topics in Combustion* (Hussaini M.Y., Kumar A and Voigt R.G., eds), Springer Verlag, pp. 339–355.

Javoy, S., Naudet, V., Abid, S. and Paillard, C.E. (2000) Rate Constant for the Reaction of O with H_2 at high Temperature by Resonance Absorption Measurements *Int. J. Chem. Kinet.*, **32**, pp. 643–666.

Just, Th. (1981) Atomic Resonance Absorption Spectrometry in Shock Tubes. *Shock Waves in Chemistry*, by Lifshitz A., Mr. Dekker Edition, p. 390.

Lissianski, V.V., Gardiner, W.C. Jr., Fujii, N. and Murayama, S. (1997) Shock Tube Study of Hydrogen thermal Dissociation. *Symp. Int. Shock Waves.*, **21**, paper 8200.

Myerson, A.L. and Watt, W.S. (1968) Atom-Formation Rates behind Shock Waves in Hydrogen and the Effect of added Oxygen. *J. Chem. Phys.*, **49**, pp. 425–433.

Natarajan, K. and Roth, P. (1987) High Temperature Rate Coefficient for the Reaction of $O(^3P)$ with H_2 obtained by the Resonance Absorption of O and H Atoms, *Combust. Flame* **70**, pp. 267–279.

Naudet, V., Abid, S. and Paillard, C.E. (1999) A high Temperature Chemical Kinetic Study of the O_2 Dissociation and the O Atoms Recombination by ARAS. *J. Chim. Phys.*, **96**, pp. 1123–1145.

Olschewski, H.A., Troe, J. and Wagner, H.Gg. (1967) Studies of unimolecular Reactions of triatomic Molecules, *Symp. Int. Combust. Proc.* 11, p. 155.

Pamidimukkala, K.M. and Skinner, G.B. (1982) Resonance Absorption Measurements of Atom Concentrations in Reacting Gas Mixtures. VIII. Rate Constants for $O+H_2 \rightarrow OH+H$ and $O+D_2 \rightarrow OD+D$ from Measurements of O Atoms in Oxidation of H_2 and D_2 by N_2O, *J. Chem. Phys.*, 76:1, pp. 311–315.

Pamidimukkala, K.M. and Skinner, G.B. (1985) Resonance Absorption Measurement of Atom Concentration in Reacting Gas Mixture. Measurements of O atoms in Oxidation of H_2 and D_2, *Proceedings of the 13th International Symposium on Shock Tubes and Waves*, pp. 585–592.

Sutherland, J.W., Michael, J.V., Pirraglia, A.N., Nesbitt, F.L. and Klemm, R.B. (1986) Rate Constant for the Reaction of $O(^3P)$ with H_2 by the Flash Photolysis-Shock Tube and Flash Photolysis-Resonance Fluorescence Techniques 504 K≤T≤2495 K", *21st Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, pp. 929–941.

Schwenke, D.W. (1990) Theoretical Prediction of Hydrogen Molecule Dissociation-Recombination Rates including an accurate Treatment of internal Sate Non-equilibrium Effects, *J. Chem. Phys.*, **92**, N° 12, pp. 7267–7282.

Tsang, W. and Hampson, R.F. (1986) Chemical Kinetic Data Base for Combustion Chemistry. Part I. Methane and related Compounds., *J. Phys. Chem.* 15, p. 1087.

Warnatz, J. (1984) Rate Coefficients. in the C/H/O System. *In Combustion Chemistry* (Gardiner WC Jr, ed), Springer Verlag, p. 197.

Yuan, T., Wang, C., Yu, C.L. and Frenklach, M. (1991) Determination of the Rate Coefficient for the Reaction $H+O_2 \rightarrow OH+O$ by a Shock Tube/Laser Absorption/detailed Modeling Study, *J. Phys. Chem.*, **95**, pp. 1258–1265.