BRIEF COMMUNICATION

A Direct Comparison of Shock Tube Photolysis and Pyrolysis Methods in the Determination of the Rate Coefficient for $O + H_2 \rightarrow OH + H$

D. F. DAVIDSON and R. K. HANSON

High Temperature Gasdynamics Laboratory, Department of Mechanical Engineering, Stanford University, Stanford, CA 94305

Mixtures of NO, N_2O, and H_2 in Ar were shock-heated and photolyzed with an ArF excimer laser. Measurements of O-atom profiles using atomic resonance absorption spectroscopy (ARAS) permitted the determination of the rate coefficient for the reaction, $O + H_2 \rightarrow OH + H$, by two methods under near-identical conditions. The first used the pyrolysis of N_2O as an O-atom source, and the second used the photolysis of NO as the O-atom source. The rate coefficients determined by the two methods are indistinguishable and are well represented in the temperature range 2120 to 2750 K by the expression $8.13(\pm 10\%) \times 10^{14} \exp\{9540[\pm 800/T \text{ (in K)}]\} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This rate coefficient agrees well with those previously reported in the literature.

There has been some discussion [1] about possible complications with using photolysis methods in the determination of chemical reaction rate coefficients. These complications stem primarily from the nonthermal distributions of products that may occur when only certain discrete states of a species are photolyzed and only certain states are produced. If these distributions are not thermalized rapidly, that is, in times shorter than the time of the measurements, then it is likely that the rate coefficient measured will be that of some intermediate distribution of states and not that of the thermal distribution.

The following experiment should demonstrate that, at least in the case of the reaction

$$O + H_2 = OH + H, \qquad (1)$$

the source of the O atoms, either from the pyrolysis of N_2O or from the excimer laser photolysis of NO, does not affect the determination of the rate coefficient, k_1.

Gas mixtures composed of 2000 ppm NO, 5 ppm N_2O, and 200 ppm H_2, diluted in Ar, were shock heated, and the absorption at 130.5 nm by O atoms was measured. The temperature (above 2100 K) and the pressure range (approximately 0.5 atm) of this experiment are such that immediately after the onset of the reflect shock, O atoms are produced by the pyrolysis of trace amounts of N_2O in the driven gas. Except for the two lower-temperature experiments (below 2200 K), this decomposition is rapid enough to provide an effectively instantaneous source of O atoms. (In the two lower-temperature experiments, O atoms were still being formed by the slower N_2O decomposition, and the simple first-order data reduction scheme given below does not accurately return the rate coefficient). Under the conditions of this experiment, the reactant H_2 was vibrationally equilibrated within several microseconds of the transit of the reflected shock [2].

In the same shockwave experiment approximately 500 μs after the pyrolysis of the N_2O and the subsequent decay of the O atoms by their

reaction with H_2, O atoms are again produced, in this case by photolysis of NO. The photolysis production path for O atoms is

$$NO(X^2\Pi)(v > 0) + h\nu_{193\,nm} \rightarrow N(^4S)$$
$$+ O(^3P). \quad (2)$$
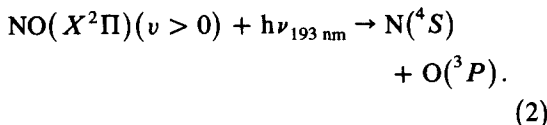
The 193-nm absorption cross section is a result of the electronic transition of vibrationally excited $NO(X^2\Pi)$ $(v > 0)$ to the $D(^2\Sigma^+)$ state. This D state, upon collision with argon, is converted to the predissociating $C(^2\Pi)$ state with unit efficiency [3].

The O atoms, as well as the N atoms, are created in their electronic ground state with little excess translational energy. Because of the oxygen–argon mass ratio however, they are expected to be rapidly thermalized to the reflected-shock temperature. The initial N atoms subsequently react rapidly (typically is less than 25 μs) with the mother species NO to produce more $O(^3P)$ atoms; essentially half the total O atoms produced come from this reaction. All of the photolytically generated O atoms then decay by reaction with the H_2.

The shock tube in this experiment has been described previously [4]. The constant temperature level behind the reflected shock was confirmed using the OH narrowline laser scanning technique of Chang et al. [5]. The pressure profiles were measured using piezo electric transducers. During the 1 ms that the data were collected, both the reflected-shock pressure and temperature were found to vary no more than the experimental uncertainty of 1.5%. Shock speed attenuation was typically less than 1%/m.

The 193.3-nm radiation pulse was produced by an ArF excimer laser. The excimer pulse is approximately 15 ns long, short enough to be considered instantaneous in the present chemical kinetic study. The excimer radiation entered the shock tube through the endwall. The intensity profile was approximately Gaussian in the vertical dimension, and tophat-shaped across the diameter of the shock tube. A similar photolysis optical scheme for the shock tube is described in Kohse-Höinghaus et al. [6].
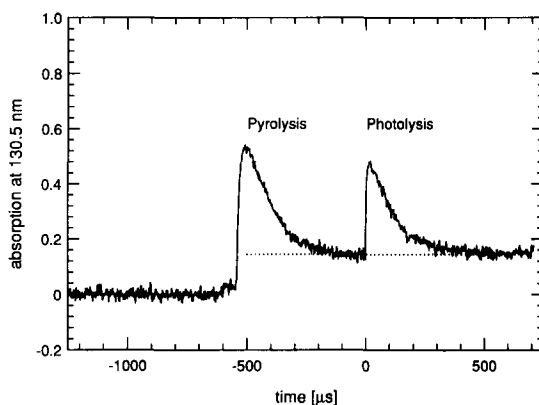

Fig. 1. O atom ARAS: example data. The reflected shock conditions were 2580 K, 0.53 atm, 1998 ppm NO, 212 ppm H_2, 5 ppm N_2O, and 3 ppm N/O yield by photolysis. The change in baseline at -540 μs, the onset of the reflected shock, is due to absorption by NO at 130.5 nm.

O atom ARAS at 130.5 nm has been used extensively in shock tubes in conjunction with flashlamp photolysis [7, 8]. In those studies, the first 150 μs of test time after the photolysis pulse was unusable, primarily because of emission oscillations in the flashlamp. In the present experiment this early time regime was accessible, as electrical interference to the oscilloscopes from the excimer laser was eliminated by optically isolating the triggering circuits, and saturation of the PMT/amplifier by the excimer pulse was eliminated by using a monochromator. The ARAS diagnostic beam was 6 mm tall and 15 mm wide and coincided with the uniform (within $\pm 10\%$) illumination region formed by the excimer radiation.

It should be noted that an absolute calibration of the O atom ARAS diagnostic is unnecessary in a first-order kinetics analysis. It is necessary in the present analysis, however, to verify that the Beer–Lambert law describes the lamp emission absorption. This has been borne out in calibration experiments, where it has been demonstrated that, for fractional absorptions as large as 70%, the simple Beer–Lambert law accurately predicts the O atom concentrations for our ARAS system.

An example of a typical O atom profile produced by this sequence of pyrolysis of N_2O and then photolysis of NO is shown in Fig. 1. The

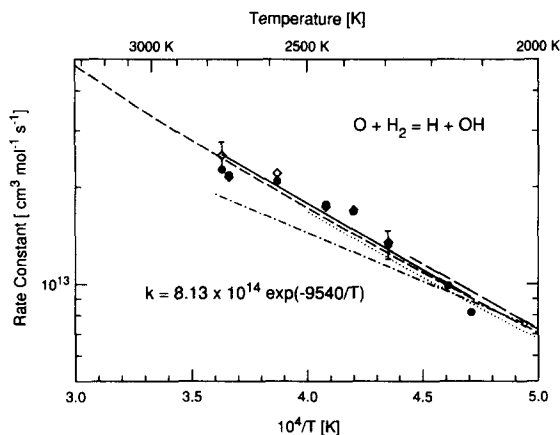Fig. 2. Arrhenius diagram: $O + H_2 \rightarrow OH + H$. Filled circles—data derived from photolysis method. Open diamonds—data derived from pyrolysis method. Error bars represent $\pm 10\%$. Solid line—best fit to present data. Dotted line—Sutherland et al. [8]. Dashed line—Nataranjan and Roth [9]. Dot-dashed line—Pamidimukkala and Skinner [10]. Long-dashed line—Shin et al. [11].

offset in the baseline occurring at -500 μs, resulting from the absorption of the diagnostic beam by the NO in the gas mixture is constant because of the overwhelmingly large concentration of NO existing compared to any perturbations in this concentration caused by the photolysis or chemistry. A small fraction of this plateau, representing less than 3% of the peak absorption is due to the equilibrium O atoms from Reaction 1. The competing reaction, $O + NO \rightarrow O_2 + N$, has a contribution to the O atom profile that is typically two orders of magnitude lower than that of the measured reaction. This ensures that the O atom chemistry is dominated by the first-order kinetics of Reaction 1 after the formation of the O atom peak.

k_1 is directly determined from the data in the following manner. The quantity, $\ln(I_0/I)$, is directly proportional to the concentration of O atoms, [O]. The absolute value of the rate of change of the ln of this quantity with time is equal to k_1 [H_2]. The rate coefficients derived in this manner are shown in Fig. 2. It is evident that there is no distinguishable difference between the data points derived from the pyrolysis or photolysis cases.

The best fit to the present data is 8.13 ($\pm 10\%$) $\times 10^{14} \exp\{-9540[\pm 800)/T(\text{in K})]\}$ cm^3

mol^{-1} s^{-1}. A complete discussion of the available data from 504 to 2495 K is given by Sutherland et al. [8]. Above this temperature it is useful to consider the work of Natarajan and Roth [9] and Pamidimukkala and Skinner [10]. The results of Pamidimukkala and Skinner begin to diverge from the fit of Sutherland et al. above 2300 K. The small scatter in the present work supports the high-temperature representation of this rate coefficient by Natarajan and Roth, and the simple extension to higher temperatures of the fit given by Sutherland et al. Recent measurements of this rate coefficient by Shin et al. using a method other than ARAS (OH laser absorption spectroscopy) are also consistent with our measurement [11].

REFERENCES

1. Davidson, D. F. Chang, A. Y., and Hanson, R. K. *Twenty-Second Symposium (International) Combustion*, The Combustion Institute, Pittsburgh, (1988), p. 1877.
2. Zellner, R., in *Combustion Chemistry*, ed. (W. C. Gardiner Jr., ed. Springer-Verlag, New York, (1984), Chap. 3.
3. Callear, A. B., and Pilling, M. J., *Trans. Farad. Soc.* 66:1618, 1886, (1970).
4. Davidson, D. F., Chang, A. Y., Kohse-Höinghaus, K., and Hanson, R. K., *J. Quant. Spectrosc. Radiat. Trans.* 42:267 (1989).
5. Chang, A. Y., and Rea Jr., E, and Hanson, R. K., *Appl. Opt.*, 26:885 (1987).
6. Kohse-Höinghaus, K., Davidson, D. F., Chang, A. Y., and Hanson, R. K., *J. Quant. Spectrosc. Radiat. Trans.* 42:1 (1989).
7. Sutherland, J. W., Michael, J. V., and Klemm, R. B., *J. Phys. Chem.* 90:5941 (1986).
8. Sutherland, J. W., Michael, J. V., Pirraglia, A. N., Nesbitt, F. L., and Klemm, R. B., *Twenty-First Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1986, p.929.
9. Natarajan, K., and Roth, P., *Combust. Flame* 70:267 (1987).
10. Pamidimukkala, K. M., and Skinner, G. B., *J. Chem. Phys.* 76:311 (1982).
11. Shin, K. S., Fujii, N., and Gardiner, W. C. Jr., *Chem. Phys. Lett.*, 161:219 (1989).