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Atom-Formation Rates behind Shock Waves in Hydrogen and the Effect of Added Oxygen*

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A direct isothermal measurement has been made of the rate of formation of atomic hydrogen behind shock waves in hydrogen–argon mixtures. This has been accomplished by using atomic resonance absorption spectrophotometry at the Lyman-α line of both ^{1}H and ^{2}H. The observations were made in an ultrahigh-purity shock tube. Absorption coefficients for the atoms were determined experimentally. The hydrogen–argon dissociation rate is given by the expression $k_{\text{H}_2-\text{Ar}} = 2.23 \times 10^{12} T^{1/2} \exp(-92\,600/RT)$ cm^{3}mole^{-1}·sec^{-1} over the temperature range 2290°–3790°K. The hydrogen molecule was found to be five times more effective than argon as a collision partner. Because of the sensitivity of the technique, it was also possible to determine quantitatively the catalytic effect of the addition of small amounts of oxygen. From these observations an expression $k_{\text{H}-\text{O}_2} = 6.0 \times 10^{12} T^{1/2} \exp(-17\,750/RT)$ cm^3 mole^{-1}·sec^{-1} was obtained for the reaction H+O$_2$=OH+O over the temperature range 1700°–2700°K.

INTRODUCTION

This paper describes a measurement of the rate of dissociation of molecular hydrogen made by following directly the concentration of atomic hydrogen as it is formed behind a shock wave. Hydrogen-atom production was monitored by the attenuation of resonance radiation from hydrogen (^{1}H) and deuterium (^{2}H) light sources. Because of the control exercised on the gaseous composition, it was also possible to study the effect of small amounts of oxygen on the rate of formation of hydrogen atoms and hence to determine the rate of the reaction H+O$_2$→OH+O.

The rate of dissociation of hydrogen behind shock waves has been studied previously[1-6] by a number of techniques. The rate constants obtained, however, are in disagreement by as much as one-half to one order of magnitude for a given collision partner. The present study, for which the feasibility was established in a preliminary account,[7,8] was initiated with the intent of resolving the existing discrepancies by incorporating four basic features in the method of attack. The first of these was the directness of the approach, in that the parameter measured was the concentration of the product itself. This is in contrast to previous studies which measured the density of the gas behind the shock,[1-3] the absorption by molecular hydrogen,[4] the vibrational temperature,[5] or the infrared emission from a trace

additive.[6] The second basic feature was the creation of an ultrahigh-purity shock tube whose leak rate, outgassing rate, and ultimate vacuum were such that the impurities in the driven gas at the time of shock arrival could be controlled to within a few parts per million. This represents a significant departure from the preliminary observations,[7,8] where it was shown that with the sensitivity of this type of experiment it is necessary to eliminate all sources of foreign gases (especially oxygen) such as leakage and outgassing. The third feature lay in the relatively minor sensitivity of atomic absorption coefficients to temperature and pressure (e.g., compared with the sensitivity of molecular spectra to these parameters). The use of a hydrogen (^{1}H) light source allows an added advantage in that the atomic absorption coefficient is so large that very small amounts of dissociation can be detected, and extremely dilute mixtures of hydrogen in argon can be used to determine the efficiency of the rare-gas collision partner without a contribution from other species. In addition, this small amount of dissociation ensures that isothermal conditions are maintained behind the shock and that reverse reactions are unimportant.

With the deuterium (^{2}H) light source, absorption no longer occurs at the line center, but in the wings of the line. Here, as a result of the lower absorption coefficient, extremely dilute mixtures of hydrogen in argon can no longer be used. Furthermore, the dissociation required for measurable attenuation of the light source causes a slight temperature drop behind the shock wave. However, the use of more concentrated mixtures allows the collision efficiency of molecular hydrogen to be determined.

The use of atomic resonance absorption spectrophotometry (hereafter aras) as a direct means of determining absolute atom concentrations was not exploited to any significant degree or used quantitatively until Vidale[9] showed that accurate measurements could be

[1] W. C. Gardiner, Jr., and G. B. Kistiakowsky, J. Chem. Phys. **35**, 1765 (1961).
[2] E. A. Sutton, J. Chem. Phys. **36**, 2923 (1962).
[3] J. P. Rink, J. Chem. Phys. **36**, 262 (1962).
[4] R. W. Patch, J. Chem. Phys. **36**, 1919 (1962).
[5] I. R. Hurle, Symp. Combust. 11th Berkeley, Calif., 1966, 827 (1967).
[6] T. A. Jacobs, R. R. Giedt, and N. Cohen, J. Chem. Phys. **47**, 54 (1967).
[7] A. L. Myerson, H. M. Thompson, and P. J. Joseph, J. Chem. Phys. **42**, 3331 (1965).
[8] A. L. Myerson, H. M. Thompson, and P. J. Joseph, "Resonance Absorption Spectrophotometry of the Hydrogen Atom Behind Shock Waves," Cornell Aeronautical Lab. Rept. No. AD-1689-A-3, 1964.
[9] G. Vidale, "Measurement of the Absorption of Resonance Lines," General Electric Missile and Space Vehicle Dept. TIS Rept. R60SD330, 1960, *et seq.*
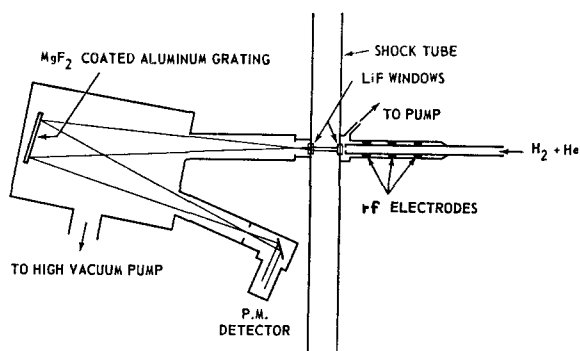
FIG. 1. Apparatus for determining hydrogen-atom-formation rates behind shock waves.

made of minute partial pressures of atomic Na, Si, et al., existing over refractories in high-temperature furnaces. The important point established there was that the measurements are best made with a thin-line source, i.e., one at low pressure and temperature, and with broad-line absorbing atoms, i.e., at high temperature and pressure. It was then shown that errors introduced in calculating the absolute absorption coefficient were small. While it has not been possible here to provide a source line sufficiently thin to rely on this calculation, the basic principles established by Vidale have been applied to the present study. Thus, these observations were made with a low-pressure, low-temperature, radio-frequency-excited source, while the absorption-line profile of the hydrogen atoms was broadened by the high temperature and pressure behind the shock front. The details of the experiment and calculations will be described in the following sections.

It should be pointed out that our use of aras differs from its use in analytical flame determinations in which indirect calibrations of the concentration are applied. This is in contrast to the direct experimental calibration used here, in which the attenuation of the light source is measured for a known concentration of hydrogen atoms. This calibration is then used to determine the rate of appearance of hydrogen atoms. The earliest use of aras to measure hydrogen-atom concentrations was apparently that of Preston,[10] who observed, qualitatively and at room temperature, hydrogen atoms which had been produced in a discharge but recombined on a surface rather than in the gas phase. More recently, aras has been used[11–13] to observe static partial pressures of hydrogen atoms which were at essentially the same low pressure and temperature as the source.

[10] W. M. Preston, Phys. Rev. **57**, 1074 (1940).
[11] F. A. Morse and F. Kaufman, J. Chem. Phys. **42**, 1785 (1965).
[12] E. A. McLennan and L. Goldstein, "Atomic Density Measurements in Nitrogen Oxygen and Hydrogen Afterglow Plasmas," Univ. of Illinois Gaseous Electronics Lab., Scientific Rept. No. 3, 1966.
[13] J. V. Michael and R. E. Weston, Jr., J. Chem. Phys. **45**, 3632 (1966).

The developments which were essential, then, to the present study were the intense low-temperature and low-pressure source of Lyman-α radiation and a shock tube capable of maintaining gaseous systems in the realm of ultrahigh purity. With these techniques, the initial rates of dissociation of the hydrogen molecule in argon and the effect of oxygen on these rates have been determined. In addition, the rate in pure hydrogen has been obtained.

EXPERIMENTAL

A schematic diagram of the apparatus is shown in Fig. 1. The experiments were performed by observing the attenuation of Lyman-α radiation by hydrogen atoms formed behind a shock wave. The undispersed light passed through the shock tube, after which the Lyman-α wavelength was selected by a vacuum-ultra-violet monochromator before detection.

The most important changes in the apparatus from that described in the preliminary Note[7] were the use of a newly developed high-purity shock tube, which could be considered chemically clean, and an improvement in the intensity of the Lyman-α signal. The tube itself was constructed from one 24-ft length of seamless, 316 stainless steel. The internal dimensions were $1\frac{1}{2} \times 2\frac{1}{2}$ in. with rounded corners of $\frac{1}{2}$-in. radius. The few gaskets in close contact with the test gases were of high-purity aluminum, so that no organic materials were directly exposed. The other gaskets used were of vacuum-baked Viton or Teflon; these were ungreased and not in direct contact with the test gas. The three gauges which measured the shock arrival consisted of flush-mounted thin-film resistance thermometers (platinum on Pyrex) and were completely free of organic matter. One of these gauges was located at the same position in the shock tube as the windows; the others were 2 ft upstream and 2 ft downstream from this point.

The vacuum port was located centrally with respect to the tube, which was separated from the pumping system by a special 2-in. all-metal, high-pressure high-vacuum valve and a commercial 2-in. bakeable ultra-high vacuum valve. The pumping source was a 4-in. diffusion pump followed by a water-cooled baffle and a Cryosorb liquid-nitrogen trap which together were designed to reduce backstreaming to a negligible amount. This system made it consistently possible to attain vacua in the 10^{-7}–10^{-8} mm Hg range, with effective leakage limited essentially to outgassing rates, e.g., 1–5 μ/1000 min. The tube was provided with facilities for baking, but these have proved unnecessary thus far because of the apparent effectiveness of the repeated shocks in outgassing the stainless steel. By restricting the gases that entered the tube under any circumstances to H_2, Ar, and He, subsequent pump down and outgassing became routinely rapid and thorough.
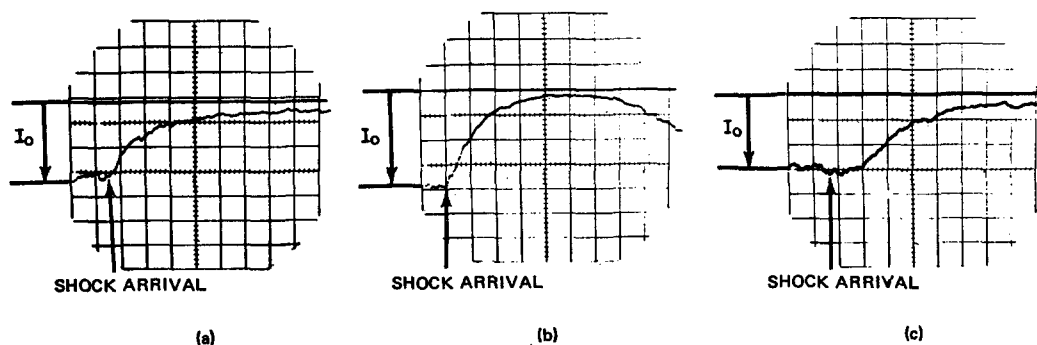
FIG. 2. Oscilloscope records showing the time history of absorption behind shock waves. Time scale: 1 division = 50 μsec. (a) 1% hydrogen in argon, $p_1 = 21$ mm Hg, $T_2 = 2490°$K; (b) 10% hydrogen in argon, $p_1 = 8$ mm Hg, $T_2 = 3440°$K; (c) 1% hydrogen in argon with 1000 ppm O_2, $p_1 = 13$ mm Hg, $T_2 = 1975°$K; an induction period of ~ 70 μsec is clearly indicated.

The driver was constructed of the same seamless, stainless-steel tubing. Scored stainless-steel diaphragms were punctured in it by an electromagnetically driven plunger. Helium was used as the driver gas.

The Lyman-α light source was developed specifically for this research and is shown schematically in Fig. 1. It was designed to emit continuously radiation of sufficient intensity to follow the rapid transients involved. The source was kept cool (near room temperature) and at low pressures by using 200 W of 30-MHz radio-frequency excitation and a very fast flow system with external air cooling. The conditions under which the lamp operated were selected[8] to maximize Lyman α and minimize the adjacent bands which were due mostly to molecular hydrogen.

The constant intensity was achieved, without the use of the line-broadening environments of arcs or spark discharges, by means of a differentially pumped source as shown in Fig. 1. The rf discharge was maintained by two external band electrodes around a quartz tube through which flowed a mixture of 10% hydrogen in helium. The tube ended in an open slit 1 mm wide and 12 mm high. The gas was drawn through the slit into the expansion chamber, which was continuously evacuated by a large mechanical pump. With this differentially pumped source, the intensity was three orders of magnitude greater than that obtained from our first, conventional, closed source with LiF windows. This large gain in intensity is known not to be due to elimination of opaque LiF windows. While the signal output was high for a continuously operating vacuum-ultraviolet light source, it was found preferable to increase the signal-to-noise level by insertion of a load resistance into the RC circuit of the scope–cable network and then to correct for the filtering process ($\tau_{RC} = 25$ μsec). The method used is described in Appendix A of Ref. 8.

In our initial experiments[7,8] complete attenuation of the Lyman-α signal was observed. However, as the research progressed and purer shock-tube conditions

were attained, it was noticed that complete attenuation could no longer be achieved. A series of experiments revealed that a small percentage (approximately 15%) of the signal picked up by the photomultiplier was due to radiation other than Lyman-α (^{1}H). The source of this stray radiation was not positively identified, but it was found to be absorbed when small amounts of water vapor were present in the test gas. Since water is known to have sharp absorption bands on either side of Lyman α,[14] these observations support our assumption that this extraneous radiation is due to the molecular hydrogen bands which lie within the 16-Å spectral bandpass used. It was found that the amount of this stray radiation was constant [see Figs. 2(a) and 2(c)], so that all data were reduced with allowance for it. In the experiments where the deuterium (^{2}H) source was used, this stray radiation was less important and amounted to only 5% of the total intensity. This is shown in Fig. 2(b).

The 1215.7-Å radiation passed through LiF windows masked by disks with 1×12-mm slits mounted in the shock tube and then immediately entered the monochromator. A mirror chamber previously used[8] was eliminated, resulting in a considerable gain in light intensity. The signal, after leaving the monochromator, was focused on a sodium salicylate-coated aluminum mirror which then emitted its fluorescence in the direction of an uncoated EMI 9558C photomultiplier which was cooled to dry-ice temperatures. The output was observed on an oscilloscope which was triggered, with varying delays, by the upstream time-of-arrival gauge and which produced traces such as those in Fig. 2.

All gases used were obtained commercially and of "ultrahigh purity." Analyses by the supplier's laboratory showed that nitrogen was the major impurity in the mixtures (10–15 ppm), while other impurities to-

[14] J. O. Sullivan and A. C. Holland, "Planetary Physics IX: A Congeries of Absorption Cross Sections For Wavelengths Less Than 3000 Å. II," Geophysics Corp. of America Tech. Rept. No. 64-20-N, 1964.

taled less than 5 ppm. It was possible to place the levels of H_2 and O_2 as impurities in the carrier gases at less than ~ 0.5 and 1.5 ppm, respectively, by the use of our aras technique.

RESULTS AND DISCUSSION

The rates measured herein are for the dissociation of hydrogen in argon,

$$H_2 + M' \rightarrow H + H + M', \qquad (1)$$
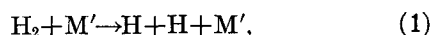
through direct observation of the increasing concentration of atomic hydrogen behind a shock wave. Thus, for $[M] = [M'] + [H_2]$,

$$-d[H_2]/dt = k_d[H_2][M] = \tfrac{1}{2}(d[H]/dt). \qquad (2)$$

For the case of a thin-line source and shock-broadened absorbing medium, which we have described previously, the concentration of hydrogen atoms in the shock-tube width l can be calculated from

$$I/I_0 = \exp(-\kappa_{\nu_0} l). \qquad (3)$$

Here κ_{ν_0} is the absorption coefficient of the appropriate spectral transition at its line center (frequency ν_0), which can be closely calculated[15] when the appropriate broadening mechanisms in the absorber are taken into account. This simple approach is inaccurate, since it is difficult to produce a thin-line atomic resonance light source of sufficient intensity for transient measurements. To eliminate this difficulty, the resonance light source described above was calibrated against known atom concentrations and the results then used to measure the rate of hydrogen-atom formation behind incident shock waves.

Two different series of measurements were made, using slightly different spectroscopic techniques. In the first an ^1H or protium light source was used to measure the rate of formation of ^1H, and in the second an ^2H or deuterium light source was used also to measure the rate of formation of ^1H. These two investigations will be described in detail in the succeeding sections.

Measurement of the Rate of Hydrogen-Atom Formation with a Protium Light Source

The concentration of hydrogen atoms which results in $\sim 50\%$ attenuation of the Lyman-α line is approximately 6×10^{-12} mole cm^{-3} for an absorption length equal to the shock-tube width. This atomic density can be produced by fully dissociating a few torr of a mixture of ~ 5-ppm hydrogen in argon. Although such a procedure is feasible, it was not attempted here, since organic compounds or water vapor present as impurities would contribute spuriously to hydrogen-atom formation behind the shock.

To carry out the calibration, deuterium was substituted for hydrogen in both the light-source gas mixture and test gas. By this procedure the problem of hydrogen-bearing impurities was avoided, since deuterium-containing compounds are not normally found except in the small ratio of the naturally occurring abundances. For a few parts per million deuterium in argon, temperatures over 4000°K were required to completely dissociate the deuterium within the available test time. The absorption resulting from this known atom concentration was then used to characterize the source emission and to calculate its linewidth.

The profile of the emission from the resonance source was not resolved, but was assumed to be broadened by self-absorption. In other hydrogen-atom resonance absorption studies[11,13] using sources similar to ours, a Doppler-emission profile was assumed. Michael and Weston[13] considered self-absorption in the source in reducing their data, but found this did not improve their results. Here it was assumed that the emission from the source could be approximated by a Doppler profile, but with a larger half-width than would be expected from the local thermal environment in the source.

For Doppler-broadened emission and absorption profiles, where the emission linewidth is not thin compared with the absorption linewidth, the measured light absorption is related to the absorber concentration by

$$1 - \frac{I}{I_0} = \int_{-\infty}^{\infty} \exp\left(-\frac{\omega}{\alpha}\right)^2 \{1 - \exp[-\kappa_{\nu_0} l \exp(-\omega^2)]\} d\omega \left[\int_{-\infty}^{\infty} \exp\left(-\frac{\omega}{\alpha}\right)^2 d\omega\right]^{-1}. \qquad (4)$$

Here, $\omega = [2(\nu - \nu_0)/\Delta\nu_D](\ln 2)^{1/2}$ and α is the ratio of the emission linewidth to the absorption linewidth. In these experiments, the linewidth of the absorbing species of the shock tube was predominantly Doppler broadened. Thus, κ_{ν_0}, the line-center (ν_0) absorption

coefficient calculated from

$$\kappa_{\nu_0} = 8.51 \times 10^{15} (f m^{1/2}/\nu_0 T^{3/2}), \qquad (5)$$

was used along with the measured attenuation to yield a value for α. For the calculation of κ_{ν_0}, the Lyman-α doublet for deuterium was taken to be a single line with an oscillator strength $f = 0.4162$, since the doublet separation (0.37 cm^{-1}) is much less than the linewidth in the shock tube. The linewidth of the resonance light

[15] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, England, 1961).

source was then obtained by multiplying α by the Doppler linewidth $\Delta\nu_D$, corresponding to the shocked-gas conditions. This is given by

$$\Delta\nu_D = [2(2R\ln 2)^{1/2}/c]\nu_0(T/m)^{1/2}. \tag{6}$$

The results obtained for the light-source calibration are given in Table I. From these data, α is seen to be 1.3 ± 0.2 for these experimental conditions, and since $\Delta\nu_D$ is calculated to be 2.78 cm^{-1}, the half-width obtained from the deuterium-atom source is 3.61 cm^{-1}.

Now, for the rate measurements, hydrogen replaces deuterium in both the resonance light source and test gas. This causes the Doppler linewidth of the atoms in the shocked gas to be greater by the square root of the ratio of the atomic mass of deuterium to that of hydrogen. The effect on the light-source equivalent linewidth is less obvious. If the resonance source were predominantly Doppler broadened and optically thin, then it too would be similarly affected by the substitution of hydrogen for deuterium, and α would be independent of the atomic species. However, the breadth of the source is not merely the result of Doppler broadening, since for these sources a temperature of 600°K is normally accepted.[11] Thus, only $\sim$1.04 cm^{-1} of the deuterium-source width of 3.61 cm^{-1} can be attributed to Doppler broadening of the deuterium atoms. In the absence of significant collisional broadening, the difference in source width must be largely the result of self-absorption broadening.

When deuterium is replaced by hydrogen in the source, all other source parameters are unchanged. Thus, since both gases have essentially the same dissociation energy, it has been assumed that the atom concentration in the source is essentially the same for hydrogen as for deuterium.

Substituting hydrogen atoms for deuterium atoms in the source increases the linewidth attributable to Doppler broadening from 1.04 to 1.47 cm^{-1} (i.e., $1.04\sqrt{2}$). However, the effect of self-absorption broadening is in the other direction, since hydrogen atoms absorb ^{1}H resonance radiation less strongly than deuterium atoms absorb ^{2}H resonance radiation. The broadening due to self-absorption is proportional to $(\kappa_\nu l)^{1/2}$. Thus for equal atomic concentrations, broadening by this effect is less for hydrogen atoms than for deuterium atoms by the ratio of the square roots of the appropriate absorption coefficients $[\kappa_{\nu_0}(^1H)/\kappa_{\nu_0}(^2H)]^{1/2}$. This ratio is given by the fourth root of the ratio of the atomic masses $[m(^1H)/m(^2H)]^{1/4}$. Hence, if 2.56 cm^{-1} is attributed to self-absorption broadening in the deuterium source, then substituting hydrogen (^{1}H) for deuterium (^{2}H) would reduce broadening by this effect to $\sim$2.17 cm^{-1}. The net result is that the hydrogen source has essentially the same linewidth as that measured for the deuterium source. Thus, it has been assumed here that these linewidths are equal. It should be noted that the calculated linewidth of ^{1}H is insensi-

TABLE I. Calibration of Lyman-α light source.

T (°K)	p_1 (torr)	[H²] (mole cm^{-3})	I/I_0	κ_{ν_0} calc (cm² mole^{-1})	α calc
4460	5	1.04×10^{-11}	0.278	7.26×10^{10}	1.2_2
4470	6	1.21×10^{-11}	0.263	7.26×10^{10}	1.5_0
4460	6	1.21×10^{-11}	0.214	7.26×10^{10}	1.1_8

tive, for present purposes, to the temperature assumed for the ^{2}H light source.

Whereas the source linewidth is constant, the linewidth of the absorbing species is determined by the shocked-gas temperature and pressure. Hence, α is not constant throughout the temperature range over which measurements were made. At the highest temperature used, 3790°K, Doppler broadening far outweighs collision broadening, and here $\Delta\nu_D=3.59$ cm^{-1}. Thus, for this temperature, α is given by $\Delta\nu_{source}/\Delta\nu_D=3.61/3.59=$ 1.0 for all practical purposes.

At the other end of the temperature scale, rate measurements were made at 2290°K. Here $\Delta\nu_D=2.81$ cm^{-1}, but there is now a nonnegligible contribution from collision broadening which, if one assumes a temperature-independent collision cross section of 70 Å², gives $\Delta\nu_L=0.35$ cm^{-1}. These two broadening processes result in a Voigt profile[16] whose half-width is 3.01 cm^{-1} and whose line-center absorption coefficient is slightly less than that calculated for Doppler broadening only. Taking this linewidth for the shocked gas, one then obtains $\alpha=1.2$ for the experiments around 2300°K. Hence, the range of α for the present experiments was 1.0–1.2.

The effect of the source linewidth being comparable to the absorption linewidth is that a higher atom concentration is required to produce a given amount of absorption than would be predicted by using the calculated line-center absorption coefficient in Eq. (3).

In reducing the data to obtain the rate constants, the following procedure was adopted. Equation (3) and the calculated line-center absorption coefficient were used to obtain the hydrogen-atom concentration required for 50% absorption. This along with the initial concentrations and the time to reach 50% absorption gives a rate constant directly by using Eq. (2). However, as we have noted, this procedure is inaccurate for calculating the hydrogen-atom concentration, and hence the rate of dissociation, when the source is not thin compared to the absorber. In particular, when $\alpha=1.0$ the concentration of hydrogen atoms required for 50% absorption, as given by Eq. (4), is 43% higher than that given by Eq. (3). Similarly, when $\alpha=1.2$ an atom density 71% higher than that given by Eq. (3) is required for 50% absorption. Thus, corrections of 43% and 71% were added to the rates obtained thru Eq.

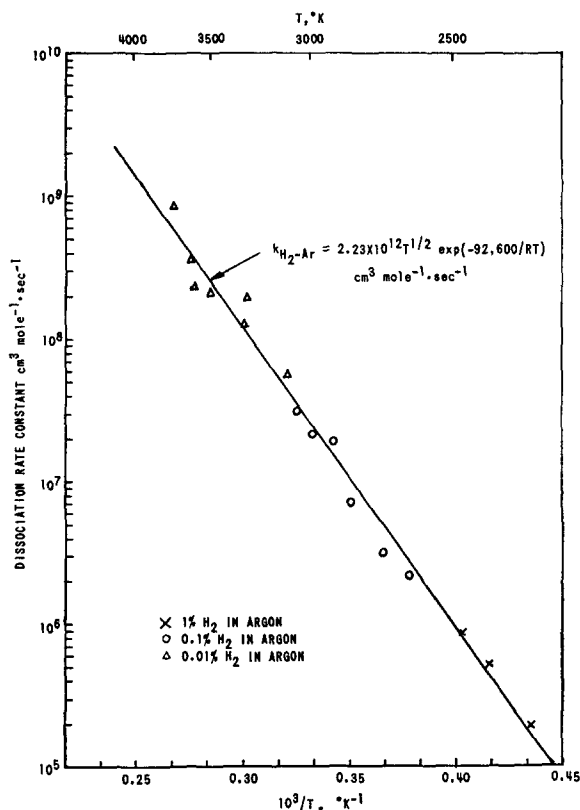[16] J. T. Davies and J. M. Vaughan, Astrophy. J. **137**, 1302 (1963).

FIG. 3. Arrhenius plot of the experimental data for the dissociation rate constant (k_d) for 1%, 0.1%, and 0.01% H_2 in Ar using an ^1H light source.

(3) for the highest and lowest temperature. Rather than solving Eq. (4) for each intermediate experimental condition, interpolated corrections between 43% and 71% were applied.

Experiments were carried out for a number of hydrogen-argon mixtures at reaction pressures of approximately 0.2–1.0 atm at temperatures in the range 2290°–3790°K. The rate constant data obtained are given in Fig. 3, and the rate of dissociation is best described by an Arrhenius equation of the form

$$k_{H_2-Ar} = 2.23 \times 10^{12} T^{1/2} \exp(-92\ 600/RT)$$

$$cm^3\ mole^{-1} \cdot sec^{-1}. \quad (8)$$

The activation energy for the reaction is 94 kcal, which is ~9 kcal less than the spectroscopic dissociation energy, and the calculated pre-exponential factor is approximately 15% of the hard-sphere collision frequency at 2500°K, assuming a collision diameter of 3 Å. Comparing this result with previous determinations, it can be seen in Fig. 4 that these data lie between the values given by Patch[4] and by Sutton[2] and are in excellent agreement with these results. These other two determinations lie within ±10% of the present data. The data of Jacobs et al.[6] and Rink[3] are approximately 35% and 100% higher, respectively, than the present results.

Classical simple collision theory gives

$$k_{dissoc} = PZ(D/RT)^S(S!)^{-1} \exp(-D/RT), \quad (9)$$

where P is the collision efficiency, Z is the collision frequency, D is the spectroscopic dissociation energy, and S is half the number of square terms of internal energy, other than those of translational energy along the line of centers, which contribute to dissociation. Expressing our results in this form, we find

$$k_{H_2-Ar} = 1.3 \times 10^{-2} Z(D/RT)^{3/2} \exp(-D/RT). \quad (10)$$

This implies the participation of three square terms, which is less than the number available. The apparent collision efficiency is then ~2×10^{-2}. A similar value of $S = 1.5$ was found previously[17] for the dissociation of oxygen in argon. The over-all pre-exponential temperature of T^{-1} in Eq. (10) (when allowing for $T^{1/2}$ included in Z) agrees with the results of Sutton,[2] Rink,[3] Patch,[4] and Jacobs.[6]

Measurements of the Rate of Hydrogen-Atom Formation with a Deuterium Light Source

In these experiments the same apparatus and experimental conditions were used as before. However, both the calibration experiments and the rate measurements
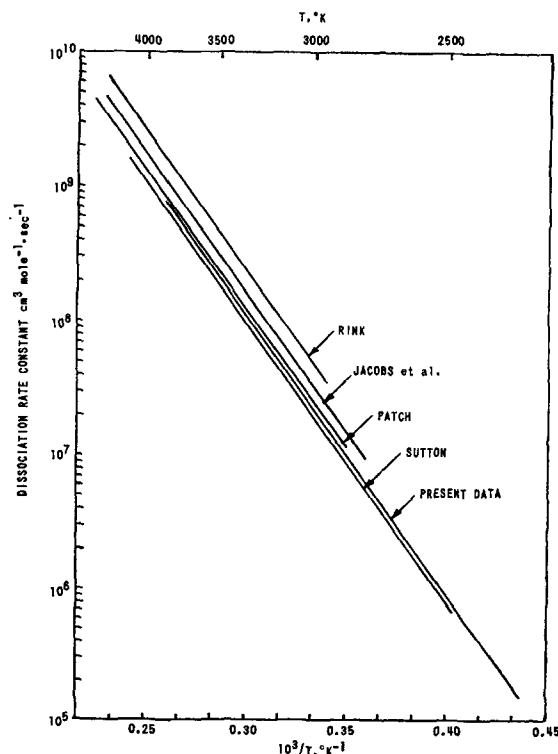

FIG. 4. Comparison of these data with previous literature rate constants for hydrogen dissociation in argon.

[17] M. Camac and A. Vaughan, J. Chem. Phys. **34**, 448, 460 (1961).

were carried out with deuterium as the emitting species in the source and shock-produced hydrogen atoms as the absorber.

Here absorption occurs in the wings of the line rather than at the line center. As a result, the absorption coefficient is much lower, and larger concentrations of hydrogen atoms are required to produce measurable absorption. The hydrogen-atom concentration produced at equilibrium by dissociation of a few torr of 1% hydrogen in argon at 3000°–4000°K is found to provide ideal conditions for calibrating the source. The measured absorption coefficient can then be applied directly to the rate data without any other considerations.

The calibration data for the absorption of ^{2}H radiation by ^{1}H atoms are given in Table II. Here it can be seen that, despite some scatter in the data, the measured absorption coefficient is $50\% \pm 15\%$ of the calculated value. Data are shown for the temperature range 3290°–3785°K, but there is no apparent temperature dependence of the measured absorption coefficient. The calculated absorption coefficient κ_ν, which is a function of both pressure and temperature, is obtained by using the expression[15]

$$\kappa_\nu = \kappa_{\nu 0} \frac{a'}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)}{a' + (\omega - y)^2} \, dy. \qquad (11)$$

Dissociation measurements were made in the temperature range given, for mixtures of 10% hydrogen in argon. The data have been reduced to yield dissociation-rate constants by taking the appropriate atomic absorption coefficients to be 50% of those calculated, as found. As a result of the higher hydrogen content of the test gas, the relative collision efficiency of the hydrogen molecule to the argon atom could be assessed. The rate constants obtained are shown in Fig. 5. It can be seen that these rate constants are slightly greater than those obtained for dissociation where only collisions of the hydrogen molecule with argon are important. In addition, these data are fitted best by a rate 40% greater than the hydrogen–argon dissociation rate. This leads to a relative efficiency of 5/1 for dissociation by hydrogen–hydrogen collisions compared
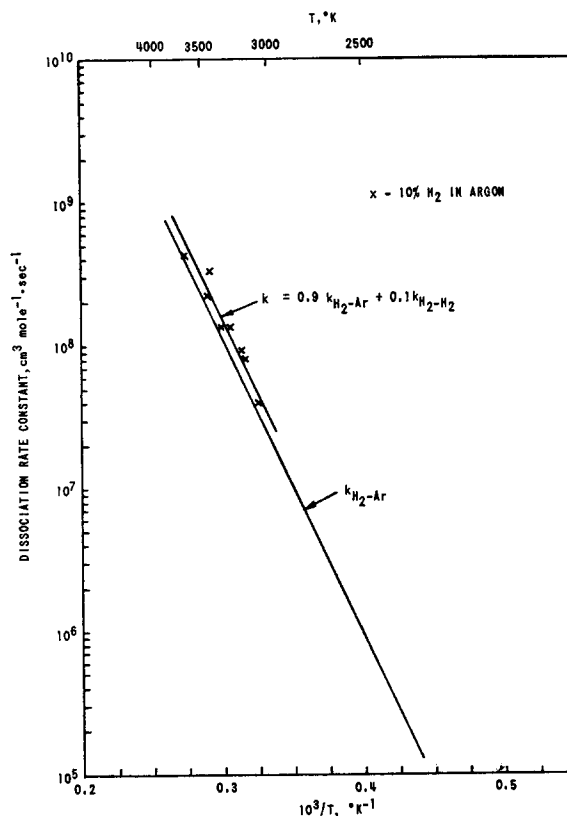

FIG. 5. Arrhenius plot of the experimental data for the dissociation rate constant for 10% H_2 in Ar using an ^{2}H light source.

with hydrogen–argon collisions. Previous data[1–6] have suggested that this ratio is between 3/1 and 7/1.

In these experiments the dissociation no longer takes place at constant temperature. From immediately behind the shock to the point where measurements are made (50% absorption), the temperature drops by 30°–75°K for the data points shown. The temperature assigned to each point is the average of the temperature immediately behind the shock and that at the observation time. The error involved in this way is small, since the rate constant does not change rapidly with temperature in this temperature range.

There have been six previous determinations of the rate of dissociation of hydrogen with hydrogen as the collision partner. Of these, four determinations[2,3,5,6] are in excellent agreement with each other and give dissociation-rate constants in the range $9 \pm 2 \times 10^8$ cm^3 mole^{-1}·sec^{-1} at 3500°K. The present result at this temperature is 11.2×10^8 cm^3 mole^{-1}·sec^{-1}.

The principal source of error in the present technique lies in the value obtained for the source linewidth. An uncertainty of 20% in the hydrogen-source linewidth leads to an uncertainty of 25% in the hydrogen–argon dissociation-rate constant. This leads to a 45% uncertainty in the hydrogen–hydrogen dissociation rate. It

TABLE II. Calculated and measured absorption coefficient κ_ν as a function of temperature.

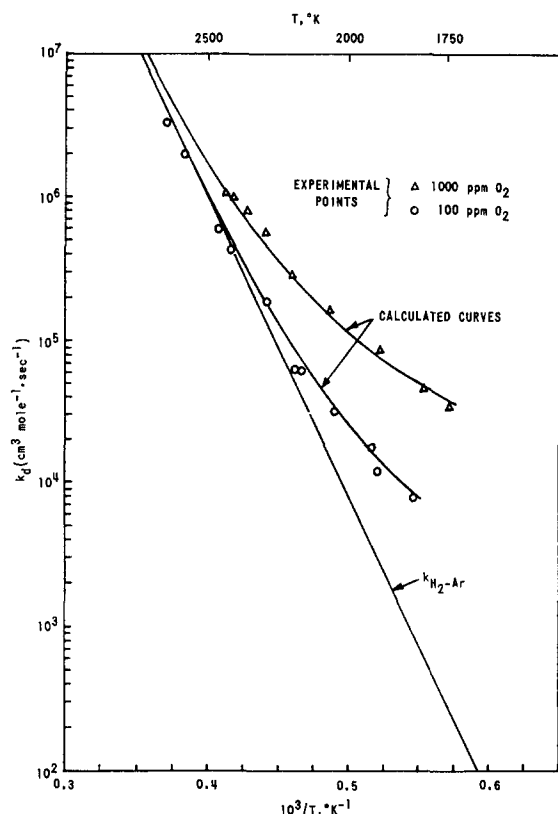| T(°K)	κ_ν calculated (cm^2 mole^{-1})	κ_ν measured (cm^2 mole^{-1})
3290	18.7	9.1
3375	18.3	9.3
3380	18.9	6.5
3520	18.4	7.3
3550	15.4	10.1
3570	19.5	9.5
3690	15.1	6.5
3785	16.1	9.3

FIG. 6. Effect of added oxygen on the dissociation rate constant. The straight line is that for dissociation in the absence of oxygen, i.e., from Fig. 3. The other data are for the indicated amounts of oxygen added to 1% hydrogen in argon.

is believed that the present results fall within these limits.
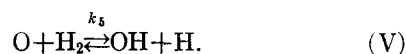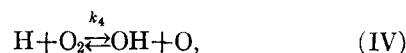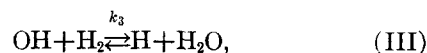
EFFECT OF ADDED OXYGEN

One of the important reasons for developing the high-purity shock tube used in this research was to study the effect of molecular oxygen on hydrogen dissociation as encountered in the preliminary work.[6] A series of observations was made with mixtures of 1% hydrogen in argon containing either 100 or 1000 ppm of oxygen and negligible amounts (<2 ppm) of other impurities. The values for k_d obtained for these mixtures and pure hydrogen–argon mixtures, assuming only the mechanism of Eq. (I) to be operative, are shown in Fig. 6. The effects of even 100 ppm oxygen are quite significant at temperatures below 2250°K and increase with decreasing temperature. It will also be noted that the effect of 1000 ppm oxygen begins at higher temperature than does that of 100 ppm oxygen. These effects, while peculiar to the unique nature of the experiment (particularly with respect to the small fraction of dissociation), nonetheless serve to illustrate the importance of controlling the intrusion of foreign gases.

By means of these data we have been able to show

that the catalytic effect of oxygen in the experiments of Fig. 6 can be explained in terms of the competition for hydrogen-atom production between the reaction

$$H_2+Ar \overset{k_d}{\rightleftharpoons} H+H+Ar \tag{I}$$
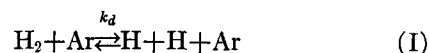
and the reactions important at these low atom concentrations,

$$H_2+O_2 \overset{k_2}{\rightleftharpoons} 2OH, \tag{II}$$

$$OH+H_2 \overset{k_3}{\rightleftharpoons} H+H_2O, \tag{III}$$

$$H+O_2 \overset{k_4}{\rightleftharpoons} OH+O, \tag{IV}$$

$$O+H_2 \overset{k_5}{\rightleftharpoons} OH+H. \tag{V}$$

Calculations of the rate of hydrogen-atom production under normal shock conditions were made by means of a computer program developed at this Laboratory.[18] Not only were the rates of Reactions (I)–(V) and their reverse entered into the computation, but rates of production as yielded by the individual reactions were monitored for hydrogen atoms and the other species. In this manner, it was possible to conclude that when oxygen is present, the departure of k_d from the curve for pure hydrogen in argon provides a single value for the rate of Reaction (IV) which fits both the case of 100 and 1000 ppm O_2.

Reaction (II) was readily eliminated as a serious contributor to the mechanism for hydrogen-atom production because of both too slow a rate and an incompatible temperature dependence. Also, Reaction (III) is not rate determining for the conditions prevailing here, so that the values of k_2 and k_3 were not varied in the computer calculations. It was established through

TABLE III. Rate constant for the reaction $H+O_2 \rightarrow OH+O$.

Reference	$k_4 \times 10^{-12}$ (cm^3 mole^{-1}·sec^{-1}) at 2000°K
Present work	3.19
Gutman, Hardwidge, Dougherty, and Lutz[a]	2.42
Baldwin[b]	3.36
Dixon-Lewis, Sutton, and Williams[d]	2.22[c]

[a] Reference 20.

[b] Reference 21.

[c] Extrapolated from 915°K by means of its relationship to the value given in Ref. 21 at that temperature.

[d] G. Dixon-Lewis, M. M. Sutton, and A. Williams, Symp. Combust. 10th Cambridge, England, 1964, 495 (1965).

[18] L. J. Garr and P. V. Marrone, "Inviscid, Nonequilibrium Flow Behind Bow and Normal Shock Waves, II. The IBM 704 Computer Programs," Cornell Aeronautical Lab. Rept. No. QM-1026-A-12 (II), 1963.

a series of computations that Reaction (IV) is the rate-determining step for this system and that there exists only a limited range of values of k_5 for which the over-all rate of production of atomic hydrogen does not lose its normally considerable sensitivity to k_4. On the other hand, $d[H]/dt$, in the range of values of interest, is insensitive to k_5. A single set of values for k_4 and k_5 was finally selected which yielded the theoretical curves shown in Fig. 6. It will be seen that the calculated curves follow the experimental points closely.

The values for k_2 and k_3 taken from the literature[19] were as follows:

$$k_2 = 5.6 \times 10^{12} T^{1/2} \exp(-67\,000/RT) \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1},$$

$$k_3 = 3.3 \times 10^{12} T^{1/2} \exp(-6450/RT) \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1},$$

with, of course, the value k_d taken from Eq. (7).

The final values for k_4 and k_5 which provide the best fit as shown on Fig. 6 are

$$k_4 = 6.0 \times 10^{12} T^{1/2} \exp(-17\,750/RT) \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1},$$

$$k_5 = 3.3 \times 10^{12} T^{1/2} \exp(-6450/RT) \text{ cm}^3 \text{ mole}^{-1} \cdot \text{sec}^{-1}.$$

Adjustments were made principally through the preexponential factors, since the curve fits are relatively insensitive to the activation energies. The latter were readily chosen on the basis of the preponderance of investigators reporting energies close or equal to these values. In Table III the value obtained here for k_4 at 2000°K is compared with a number of literature values including that from the most recent shock-tube investigation, that of Gutman, Hardwidge, Dougherty, and Lutz.[20] Also included are values for k_4 from earlier work, that given by Baldwin[21] representing an average of five values resulting from a variety of methods, most of them involving temperatures lower than those obtained in shock tubes. It is seen that the presently obtained value for k_4 is closest to the value resulting

from Baldwin's[21] survey and is approximately 30% higher than the shock-tube result quoted.[20]

Induction Periods for Hydrogen-Atom Formation

In the experiments with 1000 ppm oxygen, at temperatures below 2000°K, induction periods up to several hundred microseconds (particle time) were observed before hydrogen-atom production was detected. An example of this is illustrated in Fig. 2(c). This delay is a measure of the hydrogen-atom concentration required for the chain-branching process to overtake the dissociation process as the predominant mechanism for producing hydrogen atoms. It would also indicate that, for the temperature range and reactant concentrations of these experiments, the dissociation of hydrogen is the initiating step in the H_2–O_2 reaction mechanism. The lengths of these observed induction times are predicted by the computed results within experimental error.

CONCLUSIONS

The technique of atomic resonance absorption spectrophotometry has been applied to the measurement of the rate of hydrogen-atom formation behind shock waves in hydrogen–argon mixtures. The sensitivity afforded by the method has required the development of an ultrahigh-purity shock tube which in turn has made it possible to observe quantitatively the considerable effect of added oxygen on the atom-formation rate. Rate constants have been obtained for the reactions $H_2 + Ar \rightarrow 2H + Ar$, $H_2 + H_2 \rightarrow 2H + H_2$, and $H + O_2 \rightarrow OH + O$.

This method of atomic resonance absorption spectrophotometry is currently being used to study dissociation and vibration–dissociation coupling in oxygen and carbon dioxide.

ACKNOWLEDGMENTS

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