$$\Delta H^{\Theta}_{f,298}(t-C_4H_9) = 47.3 \pm 3.5 \text{ kJ mol}^{-1}$$

Conclusions

Reaction R-1 has been studied at room temperature by monitoring the rate of formation of Br following initial photolytic generation of $t-C_4H_9$ in HBr/He. A rate coefficient of $(3.2 \pm$ 1.0) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ was obtained, confirming the high value determined by Russell et al.6

The approach to equilibrium was monitored following photolytic generation of Br in the presence of HBr and i-C₄H₁₀, enabling k_1, k_{-1} , and hence K_1 to be determined at elevated temperatures (~600 K). Values of k_1 are in good agreement with independent measurements made, using the same technique, under irreversible conditions. The k_{-1} values are in satisfactory agreement with the measurements of Russell et al.6 and confirm the negative temperature dependence in k_{-1} .

The k_{-1} value at 298 K can be combined with the measurements of k_1 by Russell et al.⁶ to give $\Delta H^{\Theta}_{1,298}(t-C_4H_9)$; estimates of this quantity can also be made from the k_1 and k_{-1} determinations in the equilibration experiments. Combining these several estimates gives $\Delta H_{1,298}^{\Theta}(t-C_4H_9) = 47.3 \pm 3.5 \text{ kJ mol}^{-1}$.

Acknowledgment. We thank SERC for an equipment grant and SERC and ICI for a research studentship to P.W.S. We are grateful to D. Gutman and D. M. Golden for helpful discussions and to P. H. Wine for making his results on $t-C_4H_9$ + HBr available before publication.

Registry No. Br, 10097-32-2; i-C4H10, 75-28-5; HBr, 10035-10-6; CF₂Br₂, 75-61-6; t-C₄H₉, 1605-73-8; azoisobutane, 3896-19-3.

Time-Resolved Study of H + HBr \rightarrow Br + H₂ and Reanalysis of Rate Data for the H₂ + Br, Reaction over the Temperature Range 214–1700 K

Paul W. Seakins[†] and Michael J. Pilling^{*}

School of Chemistry, University of Leeds, Leeds LS29JT, U.K., and Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, U.K. (Received: May 29, 1991; In Final Form: July 22, 1991)

The rate coefficient, k_1 , for the reaction H + HBr \rightarrow H₂ + Br has been measured by laser flash photolysis of HBr at 193 nm, observing both the rate of disappearance of H and the rate of appearance of Br by resonance fluorescence, over the temperature range 298-546 K, giving $k_1 = 1.87 \times 10^{-11} \exp(-310 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Combining the data with other measurements of k_1 and of estimates of k_{-1} from higher temperature photolysis and pyrolysis studies of the H₂ + Br₂ chain reaction, coupled with the equilibrium constant, K_1 , gives $k_1 = 2.1 \times 10^{-14} (T/K)^{1.05} \exp(-82 K/T) \text{ cm}^3$ molecule⁻¹ s⁻¹ over the temperature range 214–1700 K and $k_{-1} = 6.9 \times 10^{-12} (T/K)^{0.43} \exp(-8970 K/T) \text{ cm}^3$ molecule⁻¹ s⁻¹. Finally, combination of the expression for k_1 with the inhibition term for the H₂ + Br₂ chain reaction results in $k_2 = (1.6 \pm 0.6) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ for the reaction H + Br₂ \rightarrow HBr + H over the temperature range 300-500 K, rising to (5⁺⁵-3) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 1700 K.

Introduction

High-precision measurements of rate coefficients for metathesis reactions over a wide range of temperatures have revealed distinct curvature in Arrhenius plots.¹⁻³ This curvature is most evident for reactions with low activation energies as evidenced by the extreme behavior for the CO + OH reaction.⁴ Non-Arrhenius behavior can lead to difficulties in the comparison of rate coefficient quotients with equilibrium constants if the forward and reverse reactions have been studied in different temperature ranges. This problem may be illustrated by reference to the reactions

$$H + HBr \rightleftharpoons Br + H_2 \qquad (1, -1)$$

At high temperatures, the available rate data are based on classical thermal and photochemical studies of the H_2/Br_2 chain reaction.⁵ In the thermal reaction the rate of production of HBr depends on the rate coefficient for the slow propagation step

$$Br + H_2 \rightarrow HBr + H$$
 (-1)

on the ratio of the rate coefficients for the inhibition reaction

$$H + HBr \rightarrow Br + H_2 \tag{1}$$

and for the fast propagation step

$$H + Br_2 \rightarrow HBr + Br$$
 (2)

and on the equilibrium constant K_c , for Br_2 dissociation. The evaluation of the rate coefficients for these elementary reactions by Baulch et al.⁵ is derived from the steady-state expression for the rate of HBr production

$$d[HBr]/dt = k[H_2][Br_2]^{1/2}/(1 + k_1[HBr]/k_2[Br_2])$$

where $k = 2k_{-1}K_c^{1/2}$. k_{-1} was obtained by combining k and the equilibrium constant for bromine dissociation. k_1 was then calculated from $k_{-1}K_1$ and k_2 from the inhibition ratio. The recommended rate coefficient expression for k_1 , shown in Table I, was limited to the experimental temperature range, 500-1700 K, and quite large uncertainties (up to a factor of 2) were proposed.

There is poor agreement between the extrapolation of k_1 to 300 K and recent direct studies of k_1 by Husain and Slater⁶ (flash photolysis, Lyman α resonance fluorescence), Jourdain et al.⁷ (discharge flow/EPR), and Umemoto et al.⁸ (pulse radiolysis, resonance absorption), the values differing by a factor of ≈ 3.5 (Table I). Better agreement is found with the earlier discharge flow/EPR study of Endo and Glass,9 who obtained an activation energy of 10.7 kJ mol⁻¹, close to that proposed Baulch et al. (10.1

(1) Sutherland, J. W.; Michael, J. V.; Klemm, R. B. J. Phys. Chem. 1986, 90, 5941. (2) Marshall, P.; Fontijn, A. J. Chem. Phys. 1987, 87, 6988.

(3) Hughes, K. J.; Pilling, M. J. Annu. Rep. Prog. Chem. Sect. C 1988, 86, 91.

- (4) Ravishankara, A. R.; Thompson, R. L. Chem. Phys. Lett. 1983, 99, 377
- (5) Baulch, D. L.; Duxbury, J.; Grant, S. J.; Montague, D. C. J. Phys.
- Chem. Ref. Data 1981, 10, Suppl. 1. (6) Husain, D.; Slater, J. J. Chem. Soc., Faraday Trans. 2 1980, 76, 276. (7) Jourdain, J. L.; LeBras, G.; Combourieu, J. Chem. Phys. Lett. 1981, 78. 483.
- (8) Umemoto, H.; Wada, Y.; Tsunashima, S.; Takayanagi, T.; Sato, S. Chem. Phys. 1990, 143, 333.
- (9) Endo, H.; Glass, G. P. J. Phys. Chem. 1976, 80, 1519.

[†]Present address: Joint Institute for Laboratory Astrophysics, Boulder, CO 80309.

TABLE I: Comparison of Experimental Determination of k₁

T/K	$k_1(T)/\text{cm}^3$ molecule ⁻¹ s ⁻¹	
230-318	$2.77 \times 10^{-10} \exp(-1290 \text{ K}/T)$	
500-1700	$1.04 \times 10^{-10} \exp(-1210 \text{ K/T})$	
298	- ,	
298		
214-300	$2.5 \times 10^{-11} \exp(-397 \text{ K}/T)$	
296-523	$1.87 \times 10^{-11} (-310 \text{ K/T})$	

kJ mol⁻¹).¹ This value is inconsistent with the molecular beam study of Hepburn et al.,¹⁰ who observed a translational energy threshold of $\leq 4 \text{ kJ mol}^{-1}$. Modeling studies, based on these molecular beam results, predict a threshold energy of $\sim 1 \text{ kJ}$ mol^{-1,11}

Reaction 1 is sufficiently exothermic ($\Delta H^{\circ}_{298} = -69.7 \text{ kJ mol}^{-1}$) to generate electronically excited bromine (Br*, Br(${}^{2}P_{1/2}$)), which has an excitation energy of 44.1 kJ mol⁻¹ or H_2 (v = 1) (excitation energy = 53 kJ mol⁻¹). Disagreement between rate coefficient ratios and equilibrium constants can occur when excited products are formed. There is, however, some disagreement over the production of Br^{*12-14} and of H₂ (v = 1) in reaction 1.^{15,16}

In an effort to resolve these conflicts, we have measured the temperature dependence of k_1 by laser flash photolysis/resonance fluorescence over the temperature range 298-546 K, which provides some overlap with the evaluation of Baulch et al.⁵ The experimental rate coefficients are based on measurements of the time dependence of both [H] and [Br]. The relationship of these new results to k_{-1} and k_2 is discussed.

Experimental Section

Hydrogen and bromine atoms were produced by the photolysis of HBr at 193 nm (σ (HBr) = 8.8 × 10⁻¹⁸ cm²)¹⁷ by a pulsed excimer laser (Lumonics TE861S) operating at 3 Hz. HBr and the bath gas (either He or N_2) were flowed through the Pyrex reactor at total pressures of 100-200 Torr. Resonance fluorescence of either H or Br was observed perpendicularly to both photolysis and resonance lamp beams by a solar blind photomultiplier (Thorn EMI 9413 CsI). Separate resonance lamps were employed for the H and Br experiments to prevent interference from Br fluorescence, derived from Br_2 adsorbed on the lamp surface, affecting the H atom experiments. CaF2 windows were used for the Br experiments to filter out any Lyman α signal. The fluorescence signals were digitized and stored on a Biomation 8100 waveform recorder. Once a suitable signal to noise ratio had been achieved (typically 300-1000 repetitions), the data were transferred to a microcomputer for analysis.

The cell was heated electrically, giving temperatures in the range 298-546 K. Temperatures were monitored and controlled by two thermocouples placed above and below the reaction zone. The temperature was controlled to ± 1 K, and the stated accuracy of the thermocouples over this temperature range is ± 2 K. HBr (BDH) was degassed using several freeze-pump-thaw cycles and was then fractionally distilled from 193 to 77 K to remove any residual Br₂. It was stored diluted in He.

Results

Photolysis of HBr at 193 nm generates translationally hot H and some electronically excited Br:18

HBr
$$\xrightarrow{193 \text{ nm}}$$
 H + Br $(^{2}P_{3/2})$ 85%
 \longrightarrow H + Br $(^{2}P_{1/2})$ 15%

- (10) Hepburn, J. W.; Klimek, D.; Liu, K.; Macdonald, R. G.; Northrup, F. J.; Polanyi, J. C. J. Chem. Phys. 1981, 74, 6226.
 - (11) Sudhakaran, M. P.; Raff, L. M. Chem. Phys. 1985, 95, 165.
 - (12) Husain, D.; Donovan, R. J. Faraday Trans. 1966, 62, 2643.
- (13) Davies, P. B.; Thrush, B. A.; Stone, A. J.; Wayne, F. D. Chem. Phys. Lett. 1972, 17, 19.
- (14) Bly, S. H. P.; Brand, D.; Polanyi, J. C. Chem. Phys. Lett. 1979, 65, 399
- (15) Quick, C. R.; Moore, D. S. J. Chem. Phys. 1985, 79, 1983.
 (16) Aker, P. M.; Germann, G. J.; Valentini, J. J. J. Chem. Phys. 1989. 90, 4795.
- (17) Huebert, B. J.; Martin, R. M. J. Phys. Chem. 1968, 72, 3046.
 (18) Xu, Z.; Koplitz, B.; Wittig, C. J. Chem. Phys. 1987, 87, 1062.



Figure 1. Pseudo-first-order plot of k_1' vs [HBr] from the rise of Br (\bullet , -) and the decay of H (\Box , ---). T = 298 K.

TABLE II: Experimental Rate Coefficients

T/K	$10^{12}k_1/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	no. of experiments
296	6.48 ± 0.65	40
337	7.47 ± 0.30	21
373	8.26 ± 0.53	18
437	9.40 ± 0.50	18
546	10.6 ± 0.76	18

Helium is a poor deactivator of $Br({}^{2}P_{1/2})$,¹⁹ but experiments in a nitrogen bath gas showed that any excited Br generated had little effect on the hydrogen atom or ground-state bromine atom time profiles.

Under the experimental conditions used, the fluorescence intensity is proportional to the atom concentrations. [H] decays exponentially

$$[H]_t = [H]_0 \exp(-kt)$$

where [H], is the hydrogen atom concentration at time t, [H]₀ is that at zero time, and $k = k_1' + k_h$, where $k_1' = k_1$ [HBr] and $k_{\rm h}$ is the rate coefficient for diffusive loss of H from the monitoring zone. [Br] shows biexponential behavior

$$[\mathbf{Br}]_t = A \exp(-k_b t) - C \exp(-kt)$$

where $k_{\rm b}$ is the rate coefficient for diffusive loss of Br

$$A = (k_1'[H]_0 + (k - k_b)[Br]_0)/(k - k_b)$$

$$C = k_1' [H]_0 / (k - k_b)$$

The hydrogen and bromine atom profiles were fitted by nonlinear regression using the Marquardt algorithm,²⁰ floating $[H]_0$ and k (for H) and A, B, and k (for Br). Only relative atom concentrations were required for the analysis. $k_{\rm b}$ and $k_{\rm b}$ were determined in separate experiments under the same total pressure conditions, photolyzing CF_2Br_2 at 248 and 193 nm (for k_b) and N_2O/H_2 mixtures at 193 nm (for k_h). Figure 1 shows a plot of k_1' vs [HBr] from observation of both the H atom decay and the Br atom growth; there is good agreement between the two techniques. Table II lists average values for k_1 obtained from plots such as that shown in Figure 1. H atom fluorescence could not

⁽¹⁹⁾ Donovan, R. J.; Husain, D. J. Chem. Soc., Faraday Trans. 1966, 62, 1062

⁽²⁰⁾ Bevington, P. R. S. Data Reduction and Error Analysis for the Physical Sciences; McGraw-Hill: New York, 1969.



Figure 2. Arrhenius plot for k_1 over the temperature range 200-550 K: this work $(\blacksquare, ---)$; Umemoto et al.⁸ $(\triangle, ...)$; Endo and Glass⁹ $(\Box, --)$; Husain and Slater⁶ (∇) ; Jourdain et al.⁷ (\blacklozenge) . The upper full line is the linear fit to all the data except that of Endo and Glass.

be used at temperatures above 373 K, because of absorption of the Lyman α signal,²¹ and only the Br atom profiles were employed at the higher temperatures. An Arrhenius fit to the data gives

$$k_1 = (1.87 \pm 0.30) \times 10^{-11} \exp((-310 \pm 50) \text{ K}/T)$$

where the uncertainties refer to 95% confidence limits.

Discussion

Table I compares the present experimental results with the evaluation of Baulch et al.5 and other recent data. Baulch et al.5 based their recommendation on an evaluation of k_{-1} from data on the H₂ + Br₂ reaction,²²⁻²⁸ coupled with the equilibrium constant, K_1 .²⁹ At 500 K, the lower temperature limit of their recommendation, their expression gives $k_1 = 9.2 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹, in excellent agreement with the present measurements, which give $k_1 = 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Extrapolation of their expression to 300 K, however, results in very poor agreement with the present results (Table I).

Endo and Glass⁹ used discharge flow/EPR to study reaction 1 over the temperature range 230-318 K. Husain and Slater⁶ generated H from the photolysis of H₂S and monitored H via Lyman α fluorescence. They criticized the experiments of Endo and Glass⁹ because the reaction conditions were either not first-order in H or were so fast that significant convolution effects were introduced by the time of flow through the EPR cavity. Jourdain et al.,⁷ who also employed discharge flow/EPR, worked with higher flow rates and lower [H]₀/[HBr], so that these problems were not significant in their experiments. Table I shows that the present results are in good agreement with the results of Husain and Slater,⁶ Jourdain et al.,⁷ and Umemoto et al.⁸ Figure 2 shows an Arrhenius plot for the experimental rate coefficients. An unweighted linear Arrhenius fit to all the data except that of Endo and Glass gives

 $k_1 = 2.19 \times 10^{-11} \exp(-369 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

The present measurements are compatible with the results of Hepburn et al.,¹⁰ who used a crossed molecular beam system with a supersonic H atom source and a tuneable VUV laser to excite Br fluorescence. The collision energy was varied over the range

- (25) Bodenstein, M.; Lind, S. C. Z. Phys. Chem. 1906, 57, 168.
- (26) Bach, F.; Bonhoeffer, K. F.; Moelwyn-Hughes, E. A. Z. Phys. Chem.
- 1935, B27, 71 (27) Kistiakowsky, G. B.; Van Artsdalen, E. R. J. Chem. Phys. 1944, 12, 469

4-29.4 kJ mol⁻¹. They fitted their data to three reaction crosssection $(S_r(E))$ models, one with $S_r(E)$ constant so that $k_1(T)$ varies as $T^{1/2}$, one with a step in $S_r(E)$ at an energy of 3.2 kJ mol⁻¹, and one based on a line of centers model $(S_r(E)) = S_0(1 - E_0/E)$, with $E_0 = 0.67$ kJ mol⁻¹. The first model predicts an increase in $k_1(T)$ of 18% between 230 and 318 K, the second an increase of 50%, and the third an increase of 20%. Endo and Glass reported an increase of a factor of 4, while the present results, if extrapolated, give an increase of only 42%; this increase is further reduced if $k_1(T)$ shows modified Arrhenius behavior (see below). Sudhakaran and Raff¹¹ modeled the reaction using LEPS surfaces, comparing their results with those of Hepburn et al.¹⁰ They varied the barrier over the range 0.8-4.22 kJ mol⁻¹, obtaining the best agreement with the molecular beam experiment with the lowest value used. It should be noted, however, that the thermal rate coefficient calculated at 300 K with this optimal surface exceeds the present experimental results by a factor of 2.

The weight of experimental evidence, therefore, favors a low activation energy for reaction 1, but the poor agreement with the value calculated from the reverse rate coefficient of Baulch et al.⁵ requires examination.

One possible alternative explanation is an incompatibility between k_1/k_{-1} and the equilibrium constant K_1 . Nonequilibrium effects, associated with enhanced rates into and, by detailed balance, out of excited electronic or vibrational states, coupled with slow relaxation, can, in principle, generate such incompatibilities.

Studies on the production of Br* from reaction 1 have generated conflicting results. Donovan and Husain¹² photolyzed HBr at λ > 160 nm and saw a rise in [Br*] after the end of the photoflash, which they attributed to the reaction

$$H + HBr \rightarrow H_2 + Br^*$$

They were, however, unable to establish the channel efficiency. Davies et al.13 reported an 8.3% yield of Br* in an EPR experiment conducted at 0.3 Torr. In an infrared chemiluminescence study of the reaction, under single-collision condition, Bly et al.¹⁴ detected Br*, setting an upper limit of 1.3% on its yield. They proposed that the observation of Davies et al.¹³ resulted from the formation of Br* in a secondary vibrational-electronic energy-transfer process. The molecular beam study of Hepburn et al.¹⁰ confirms the result obtained by Bly et al.,¹⁴ setting an upper limit of 2% on the yield of Br. The two methods were in agreement in reporting a yield of 7% of Br* in F + HBr, and the sensitivity of the molecular beam technique is illustrated by the determination of a 1% yield of Br* in F + DBr. These several observations confirm the low yield of Br* in reaction 1. It is also difficult to rationalize the production of Br* on grounds of electronic correlation. It is necessary to examine the overall angular momentum of the reactant and product states, because of the large spin-orbit coupling in Br. In the reactants, this results in a surface of $E_{1/2}$ symmetry for the C_s point group while $Br(^{2}P_{3/2}) + H_{2}$ gives two surfaces of $E_{1/2}$ symmetry and $Br({}^{2}P_{1/2}) + H_{2}$ one such surface. Thus, symmetry arguments do not suggest preferential formation of Br*; indeed, the operation of the noncrossing rule points instead to the favored production of $Br^2P_{3/2} + H_2$.

Quick and Moore¹⁵ used CARS to detect both Br and H₂ from the H + HBr reaction, following photolysis of HBr at 193 nm. They observed H_2 (v = 1), with a rotational temperature of 3000 K. They employed a total pressure of ~ 1 Torr, so that secondary reactions cannot be precluded, an explanation supported by more recent measurements of Aker et al.¹⁶ They again used CARS to detect H_2 under single-collision conditions from H + HBr at a collision energy of 1.6 eV. Even at this high energy, the degree of vibrational excitation was small ($\sim 9\%$), although 18% of the available energy was channeled into rotation. Thus, the available experimental evidence argues strongly against the predominant production of electronically or vibrationally excited species in reaction 1 so that agreement should be expected between k_1/k_{-1} and the equilibrium constant.

Figure 3 shows an Arrhenius plot for reaction 1 over an extended temperature range and includes the data for the reverse

⁽²¹⁾ Nel, J. B.; Suto, M.; Lee, L. C. J. Chem. Phys. 1986, 85, 4919.
(22) Britton, D.; Cole, R. M. J. Phys. Chem. 1961, 65, 1302.
(23) Fans, R. A. J. Phys. Chem. 1970, 74, 984.
(24) Vidal, C. J. Chem. Phys. 1971, 68, 1360.
(25) Patrovici M. M. M. S. G. T. 1971, 68, 1360.

⁽²⁸⁾ Levy, A. J. Phys. Chem. **1958**, 62, 570. (29) Stull, D. R.; Prophet, H. JANAF Thermochemical Tables, 2nd ed.; NSRDS-NBS37; National Bureau Standards: Washington, DC, 1971.



Figure 3. Nonlinear Arrhenius plot for k_1 over the temperature range 200-1700 K: this work (**D**); Umemoto et al.⁸ (**A**); Husain and Slater⁶ (**V**); Jourdain et al.⁷ (**•**). Values for k_1 calculated from $k_{-1}K$: Britton and Cole²² (**•**); Vidal²⁴ (**O**); Bodenstein and Lind²⁵ (**D**); Bach et al.²⁶ (**A**); Kistiakowsky and Van Artsdalen²⁷ (**A**).

reaction (-1), employed in the evaluation of Baulch et al.⁵ and transformed into k_1 using the equilibrium constant. The expression

$$K_1 = 3.04 \times 10^{-3} (T/K)^{0.62} \exp(8884 K/T)$$

was employed on the basis of a nonlinear least-squares fit to the JANAF values for $\Delta G^{\circ}_{1}(T)$.²⁹ Figure 3 shows the best unweighted nonlinear least-squares fit to the rate coefficients which gives $k_{1} = 2.1 \times 10^{-14} (T/K)^{1.05} \exp(-82 K/T) \text{ cm}^{3}$ molecule⁻¹ s⁻¹

Although the plot is strongly curved, the temperature exponent is physically reasonable and the low-temperature data for the forward reaction are clearly compatible with the high-temperature data for the reverse reaction, when linked via K_1 . If the exponential term is used to obtain a barrier height, then a value of 0.68 kJ mol⁻¹ is obtained, which agrees well with the optimal value proposed by Sudkaharam and Raff¹¹ of <0.8 kJ mol⁻¹. It should be appreciated, however, that there is very strong correlation between the parameters in the non-Arrhenius expression.

Figure 4 shows an Arrhenius plot for reaction -1 and includes values for k_1/K_1 in addition to the high-temperature measurements of k_{-1} . A nonlinear least-squares fit to these data (Figure 4) gives $k_{-1} =$

$$3.3 \times 10^{-14} (T/K)^{1.14} \exp(-8610 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

although this is indistinguishable from the expression determined from k_1/K_1

$$k_{-1} =$$

$$6.9 \times 10^{-12} (T/K)^{0.43} \exp(-8970 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

which is also shown in Figure 4. This latter expression is preferred because of the direct compatibility of k_1/k_{-1} and K_1 .

Finally, these results can be employed to refine the recommendation of Baulch et al.⁵ for k_2 , obtained from an analysis of the inhibition term in the H_2/Br_2 reaction. They obtained

$$k_1/k_2 = 2.75 \times 10^2 (T/K)^{-1} \exp(-990 K/T)$$

over the temperature range 300-1700 K. Taking the higher precision linear Arrhenius parameters determined in the present study over the temperature range 300-500 K (Table I) gives $k_2 = 6.8 \times 10^{-14} (T/K) \exp(680 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

$$(300 \le T/K \le 500)$$

The nonlinear Arrhenius parameters for k_1 (Figure 3) give $k_2 = 7.6 \times 10^{-17} (T/K)^{2.05} \exp(-810 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$



Figure 4. Nonlinear Arrhenius plot for k_{-1} . The data points are as for Figure 3. (--) Nonlinear least-squares fit; (---) k_1/K_1 .

over the temperature range 300-1700 K.

Once again, these parameters should not be interpreted too literally. The temperature dependence is weak, and Baulch et al. quote an uncertainty in their expression of $\pm 40\%$. A more realistic recommendation is

$$k_2 =$$

$$(1.6 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (300 < T/K < 500)$$

with some evidence that k_2 increases to $(5^{+5}_{-3}) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 1700 K.

Conclusions

1. Direct measurements reported here give

 $k_1 = 1.9 \times 10^{-11} \exp(-310 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

over the temperature range 300-500 K.

Combination with previous data gives

 $k_1 = 2.2 \times 10^{-11} \exp(-370 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

over the temperature range 200–500 K, with an uncertainty of $\pm 15\%$.

2. Contrary to previous analyses, the present data for k_1 are fully compatible with higher temperature data for k_{-1} provided quite modest curvature is permitted in the Arrhenius plot, giving

$$k_1 = 2.1 \times 10^{-14} (T/K)^{1.05} \exp(-82 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 200–1700 K. The uncertainty at low temperatures is $\pm 15\%$. In the absence of confirmation of the high-temperature results of Britton and Cole,²² a factor of 2 uncertainty is probably resonable at 1700 K. The compatible expression for k_{-1} is

$$k_{-1} = 6.9 \times 10^{-12} (T/K)^{0.43} \exp(-8970 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

3. The analysis of the inhibition term for the H₂ + Br₂ chain reaction by Baulch et al.⁵ to yield k_2 has been revised to give k_2 = (1.6 ± 0.6) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (300-500 K), rising to (5⁺⁵-3) × 10¹⁰ cm³ molecule⁻¹ s⁻¹ at 1700 K.

Acknowledgment. We are grateful to SERC for an equipment grant and to SERC and Jesus College, Oxford, for a studentship (P.W.S.).

Registry No. H, 12385-13-6; HBr, 10035-10-6; Br₂, 7726-95-6.