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Rate constant of H atom reaction with Br_2 determined between 220 and 950 K

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ABSTRACT

Rate constant of the reaction H + Br_2 $\rightarrow$ HBr + Br (1) has been measured in a discharge flow reactor with mass spectrometric monitoring of the species involved: $k_1 = 7.06 \times 10^{-11} (T/298)^{0.88} \exp(182/T)$ cm^3 $molecule^{-1}$ s^{-1} at T = 220 – 950 K (with estimated total uncertainty on the rate constant of 15% at all temperatures). The kinetic data in the present work challenge previous experimental measurements and support the most recent theoretical calculations.

Keywords: Hydrogen atom, Bromine, Kinetics, Rate constant, Temperature dependence.

1. Introduction

The reaction of hydrogen atoms with molecular bromine

$$H + Br_2 \rightarrow HBr + Br \qquad (1)$$

has been the subject of several kinetic [1-4], dynamic [5, 6] and theoretical [7-10] investigations. Reaction (1) leads to the formation of the vibrationally excited HBr, hence it is of potential practical interest associated with the chemical lasers' issues [11]. It is also of theoretical interest as a prototypical example of atom-diatom reactions [9, 10]. Theoretical models and calculations require a reliable experimental basis to be tested and validated. In particular, an accurate experimental determination of Arrhenius parameters for the rate constants is of great importance, since they provide information on the energetics of the chemical process. With regard to the kinetic studies of reaction (1), the experimental data available on its rate constant (k_1) are very limited. Some early high temperature kinetic data based on the studies of the H_2+Br_2 chemical system are summarized in reference [12]. Three absolute measurements of the reaction rate constant are available [2-4] and only in one of them the temperature dependence of k_1 was explored [3]. Wada et al. [3] observed relatively strong (for such a fast reaction as H + Br_2) temperature dependence with activation energy of 6 kJ mol^{-1} at T = 215 – 295 K. A much weaker temperature dependence was reported in a recent theoretical study of reaction (1) [10]: the calculated rate constant increased by 20% in the temperature range between 215 and 295 K compared to the factor of 2.5 measured experimentally by Wada et al. [3]. Obviously, to resolve this discrepancy between theory and experiment, additional measurements of the rate constant of the title reaction and/or improvement of the theoretical model are required.

In this regard, the objective of the present experimental study was the determination of the rate constant of the H + Br_2 reaction in an extended temperature range, T = 220-950 K, in order to verify the temperature dependence of k_1 and to provide a new experimental basis for a better theoretical description of the reaction.

2. Experimental

The rate constant of the title reaction was measured at total pressure of 2 Torr of helium and T = 220 – 950 K in a discharge-flow reactor combined with modulated molecular beam mass spectrometer with electron impact ionization (25–30 eV energy). The flow reactor used at low temperatures (220 – 325 K) consisted of a halocarbon wax coated Pyrex

tube (45 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation (Fig. S1, Supplementary Material). The second reactor used at high temperatures (295 – 950 K) was an electrically heated Quartz tube (45 cm length and 2.5 cm i.d., Fig. S2) [13].

Absolute measurements of the rate constant of reaction (1) were carried out under pseudo-first order conditions, monitoring either the kinetics of hydrogen atom or Br_2 consumption in excess of Br_2 or of the H atoms, respectively. Hydrogen atoms were produced using two methods: by discharging trace amounts of H_2 in He and through rapid reaction of fluorine atoms with H_2,

$$F + H_2 \rightarrow H + HF \quad (2)$$

$k_2 = 1.24 \times 10^{-10} \exp(-507/T)$ cm^3 molecule^{-1} s^{-1} (T = 220 – 960 K) [14],

F atoms being formed in the microwave discharge of F_2/He mixtures. Several methods were employed for detection of hydrogen atoms using different schemes for their chemical conversion. In experiments with high concentrations of H atoms (Br_2 kinetics in an excess of H), they were monitored at m/z = 80/82 (HBr^+) or m/z = 128 (HI^+) upon conversion to HBr or HI in reactions with excess Br_2 (reaction 1) or I_2 added in the end of the reactor 5 cm upstream of the sampling cone:

$$H + I_2 \rightarrow I + HI \quad (3)$$

$k_3 = (6.0 \pm 2.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (T = 250 – 420 K) [15],

This method was not suitable for the detection of low concentrations of H atoms, due to the presence of HBr (HI) impurities in Br_2 (I_2) and the contribution of Br_2 (I_2) at m/z = 80 /82 (m/z = 128). Therefore, in experiments with low concentrations of H atoms (H kinetics in an excess of Br_2), another scheme for the chemical conversion of H atoms was used: the NO_2/Br_2 mixture was added at the end of the reactor and the H atoms were transformed to HOBr (m/z = 96/98) in two successive rapid reactions:

$$H + NO_2 \rightarrow OH + NO \quad (4)$$

$k_4 = (1.47 \pm 0.26) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (T = 195 – 2000 K) [16],

$$OH + Br_2 \rightarrow Br + HOBr \quad (5)$$

$k_5 = 2.16 \times 10^{-11} \exp(207/T)$ cm^3 molecule^{-1} s^{-1} (T = 220 – 950 K) [17],

In a few experiments Br_2 was replaced with I_2 and OH radicals formed in reaction (4) reacted with I_2 leading to formation of HOI:

$$OH + I_2 \rightarrow I + HOI \quad (6)$$

$k_6 = (2.1 \pm 0.6) \times 10^{-10}$cm^3 molecule^{-1} s^{-1} (T = 240 – 348 K) [18],

Thus, the hydrogen atoms could be converted to HOI and detected at m/z = 144 (HOI^+). The concentrations of NO_2 and Br_2 (I_2) were chosen so as to provide $k_4[NO_2] >> k_1[Br_2]$ ($k_3[I_2]$).

The absolute calibration of the mass spectrometer for HBr was realized using two methods. The first one employed chemical conversion of H-atom to HBr in reaction (1) relating the concentration of HBr formed to the fraction of Br_2 consumed. In the second method, the absolute concentration of HBr was calculated from the flow rate obtained from the measurements of the pressure drop of the manometrically prepared HBr/He mixture stored in calibrated volume flask. The absolute concentrations of HBr determined with two methods employed were consistent within a few percent. The absolute concentrations of the other stable species (Br_2, NO_2, F_2, H_2) in the reactor were derived from their flow rates. I_2 was introduced into the reactor by flowing helium through a column containing iodine crystals. The absolute calibration of I_2 was realized using a method linking concentrations of I_2 and Br_2. It consisted of a titration of the same concentration of H atoms with excess Br_2 ($[H]_0 = \Delta[Br_2]$) and I_2 ($[H]_0 = \Delta[I_2]$). This procedure allowed the absolute calibration of I_2 signals using that of Br_2.

The purities of the gases used were as follows: Br_2 > 99.99% (Aldrich); I_2, 99.999 % (Aldrich), F_2, 5% in helium (Alphagaz); HBr ≥ 99.99 % (48 wt. % in H_2O, Aldrich); NO_2 > 99% (Alphagaz); H_2 > 99.998 % (Alphagaz). He (the carrier gas) was taken directly from high-pressure tank and had stated purity better than 99.999 % (Alphagaz).

3. Results and Discussion

3.1. Rate constant of reaction (1).

Br_2 kinetics in excess of H atoms. The rate constant measurements for reaction (1) were performed under pseudo-first order conditions in an excess of H atoms over Br_2. The initial concentrations of Br_2 were in the range (0.5 – 2.8) x 10^{11} molecules cm^{-3}. Fig. S3 shows examples of first order decays of Br_2, $[Br_2] = [Br_2]_0 \times \exp(-k_1't)$, where $k_1' = k_1 \times [H]$ is the pseudo-first order decay constant and t is the reaction time, defined as the distance from the tip of the movable injector to the sampling cone of the mass spectrometer, divided by the linear flow velocity in the reactor (2200 - 3090 cm s^{-1}). Experimental pseudo-first-order rate constants determined from observed Br_2 decays have been corrected (usually a few percent correction and up to 16% in a few kinetic runs) for Br_2 diffusion [19]. Fig. 1 shows examples of plots of k_1' versus mean concentration of hydrogen atoms which was calculated

as [H] = $[H]_0$-$\Delta[Br_2]/2$ to take into account the depletion of H during the reaction. H-atom consumption along the reaction zone was generally < 10%, but in some experiments, it reached 20%. The wall loss of hydrogen atoms ($k_w \leq 5\ s^{-1}$) had negligible impact on the concentration of H atoms under experimental conditions of the measurements. The values of k_1 derived from the slopes of the plots like those in Fig. 1 at different temperatures are summarized in Table 1.

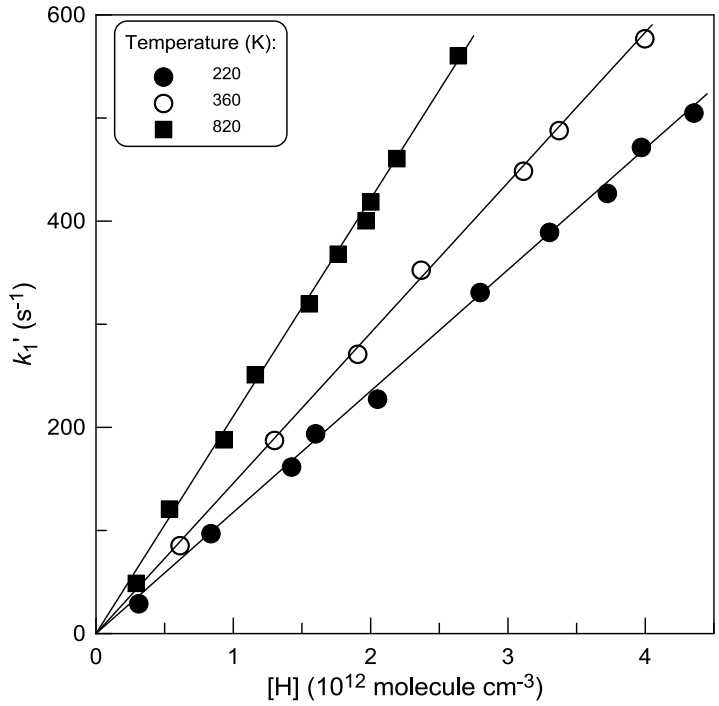

Fig. 1. Examples of typical dependencies of the pseudo-first order rate constant, $k_1' = k_1[H]$, on the concentration of H atoms.

Table 1
Summary of the Absolute Measurements of the Rate Constant of Reaction (1).

T (K)[(a)]	Excess reactant	[Excess reactant][(b)]	k_1 (± 2σ)[(c)]	Reactor surface[(d)]
220	H	0.31-4.35	1.18±0.02	HW
235	H	0.71-4.32	1.25±0.02	HW
240	Br_2	0.22-3.20	1.28±0.03	HW
250	H	0.22-4.07	1.23±0.02	HW
270	H	0.28-4.17	1.35±0.02	HW
280	Br_2	0.25-3.30	1.29±0.03	HW
290	H	0.38-4.10	1.30±0.02	HW
297	H	0.43-5.15	1.31±0.02	Q
298	Br_2	0.38-4.96	1.30±0.03	Q

315	H	0.38-4.96	1.25±0.02	HW
320	H	0.72-5.04	1.3±0.03	Q
350	H	0.39-3.80	1.36±0.02	Q
360	H	0.61-4.00	1.45±0.02	Q
360	Br_2	0.32-3.17	1.36±0.05	Q
410	H	0.41-4.83	1.42±0.03	Q
410	Br_2	0.26-2.87	1.55±0.05	Q
475	Br_2	0.29-2.46	1.65±0.05	Q
480	H	0.74-4.23	1.48±0.02	Q
580	H	0.48-3.82	1.63±0.02	Q
725	H	0.39-2.49	2.09±0.03	Q
820	H	0.29-2.63	2.11±0.03	Q
950	H	0.33-1.85	2.39±0.05	Q

[a] 8-12 decay traces at each temperature.
[b] units of 10^{12} molecule cm^{-3}.
[c] units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}.
[d] HW: halocarbon wax; Q: quartz.

H-atom kinetics in excess of Br_2. In this series of experiments the rate constant of reaction (1) was determined from the kinetics of H atoms monitored (at m/z = 96/98 or 144 ($HOBr^+$or HOI^+, respectively), see Experimental section) in an excess of Br_2 in the reactor. Examples of H-atom decays observed at different concentrations of Br_2 are shown in Fig. S4. Examples of the dependence of the pseudo-first order rate constant $k_1' = k_1 \times [Br_2] + k_w$ on concentration of Br_2 are shown in Fig. 2. One can note good agreement between the results obtained with two different methods of H-atom detection at T = 280 K. Diffusion corrections (≤ 11 %) were applied to all the measured values of k_1' to take into account the axial and radial gradient of H-atom concentration in the flow tube [19]. The slopes of the straight lines in Fig. 2 provide the values of k_1 at respective temperatures. All the results obtained for k_1 are shown in Table 1 and Fig. 3. The combined uncertainty on the absolute measurements of k_1 in both series of experiments was estimated to be ~ 15 %, including (in quadrature) statistical error and those on the measurements of the flows (5%), pressure (3%), temperature (1%) and absolute concentration of excess reactant (≈10%).

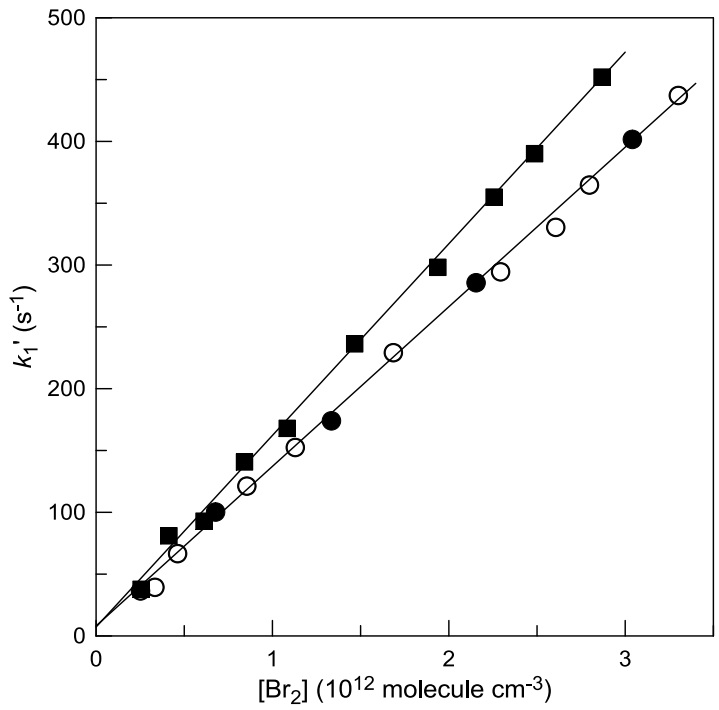

Fig. 2. Examples of typical dependencies of the pseudo-first order rate constant, $k_1' = k_1[Br_2] + k_w$, on the concentration of Br_2: circles, T = 280 K; squares, T = 410 K. Open and filled symbols correspond to H atom detection as HOI and HOBr, respectively (see text).

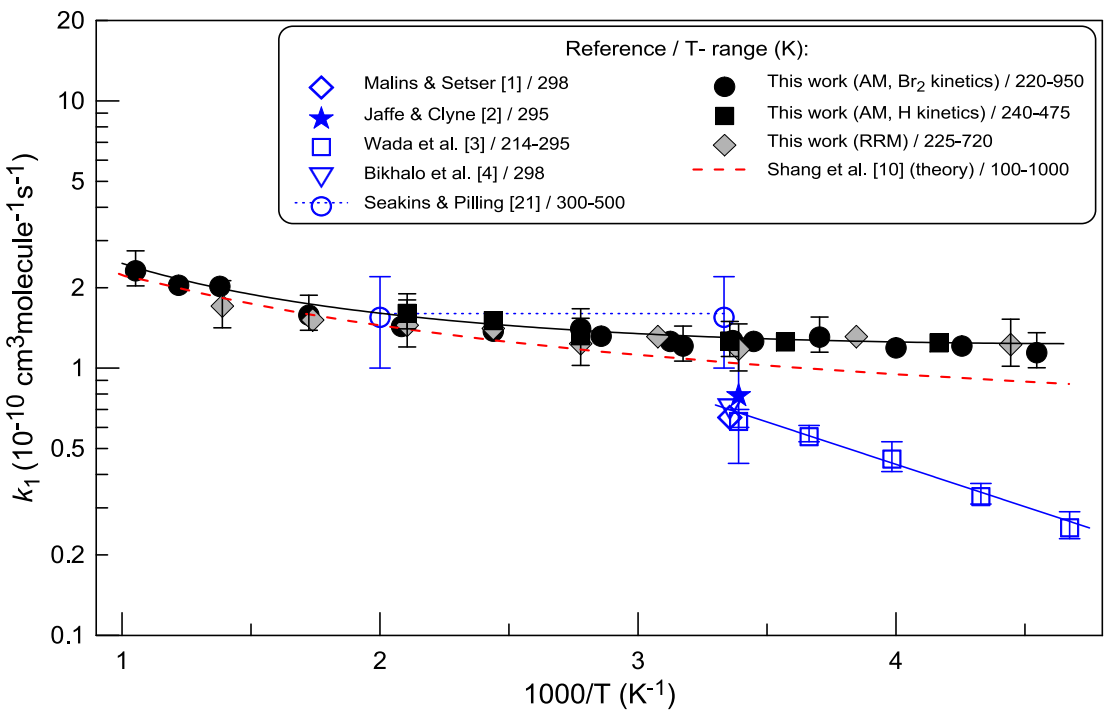

Fig. 3. Temperature dependence of the rate constant of reaction (1): AM, absolute measurements; RRM, relative rate method. Partly shown uncertainties on the values of k_1 from the present study correspond to estimated 15 and 20% for the absolute and relative measurements, respectively.

Relative measurements of k_1. The present absolute measurements provide the values of k_1 significantly higher than the most of previous studies (Fig. 3). For more confidence, we performed additional experiments where k_1 was measured with a relative rate method. The measurements consisted in monitoring the consumption of Br_2 in reactions (1) and (7) carried out with the same initial concentrations of H and F atoms:

$$F + Br_2 \rightarrow Br + FBr \qquad (7)$$

$k_7 = (1.28 \pm 0.20)\times 10^{-10} cm^3\ molecule^{-1}\ s^{-1}$ (T = 299 – 940 K) [20],

Indeed, the F atoms generated in the microwave discharge and introduced in the reactor through the movable injector could be transformed stoichiometrically into H atoms upon addition of excess concentration of H_2 in the movable injector. The relative consumptions of Br_2 in reactions (1) and (7) are related by the ratio of the rate constants of these reactions:

$$\ln([Br_2]_0/[Br_2])_{reaction\ 1} = k_1/k_7 \times \ln([Br_2]_0/[Br_2])_{reaction\ 7}$$

It should be noted that the applied method differs from the conventional relative rate technique where the consumptions of the reactant under study and of the reference one are observed simultaneously. The present approach consists in measuring the decrease of $[Br_2]$ resulting from the reaction with either H or F atoms. Note that an important condition for the applicability of the method is the similarity not only of the initial concentrations of H and F, but also of those along the reaction zone. This condition appears to be satisfied, given the relatively low wall loss of both atoms and the similar rate constants (within the range of experimental uncertainties) of reactions (1) and (7), at least at T = 220 – 400 K (that is similar potential consumption of F and H in reactions with Br_2). Examples of the experimental data are shown in Fig. 4.

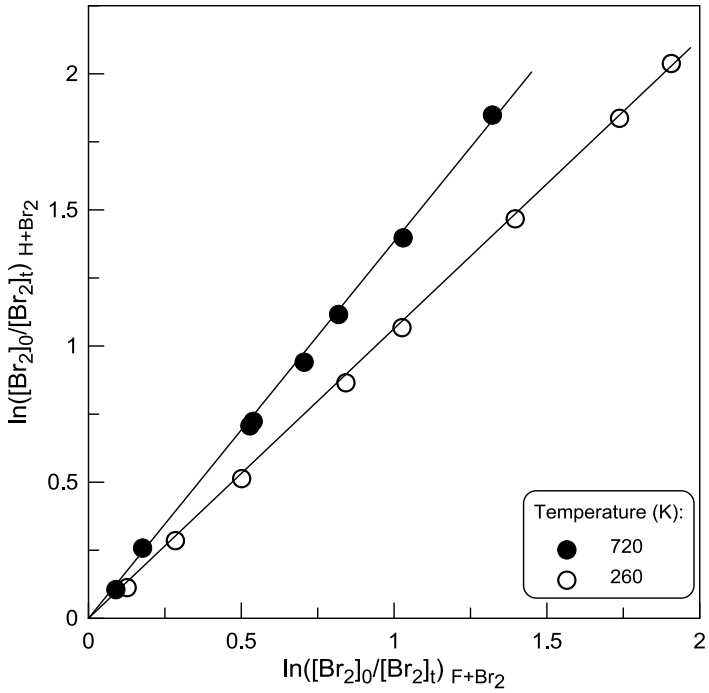

Fig. 4. Relative consumption of Br_2 in reaction H+Br_2 as a function of that in reaction F+Br_2 for the same concentrations of H and F atoms.

The slopes of the straight lines in Fig. 4 provide the values of k_1/k_7 at respective temperatures. The values of k_1/k_7 obtained in this series of experiments as well as the values of k_1 calculated with independent of temperature $k_7 = 1.28 \times 10^{-10}$cm^3 molecule^{-1} s^{-1} [20], are shown in Table 2 and Fig. 3. The results of the relative measurements are in good agreement with the absolute measurements. Small discrepancy at high temperatures (although within the limits of the combined systematic uncertainties) is probably due to the breakdown in the criteria of similarity of [F] and [H] associated with the fact that $k_1 > k_7$ at these temperatures.

Table 2
Summary of the relative measurements of k_1.

T (K)	k_1/k_2 (± 2σ)	k_1 [(a)]	Reactor surface[(b)]
225	0.99±0.02	1.27	HW
260	1.06±0.01	1.36	HW
295	0.95±0.02	1.22	Q
325	1.06±0.02	1.36	HW
360	1.00±0.02	1.28	Q
410	1.14±0.02	1.46	Q
475	1.17±0.02	1.50	Q
575	1.23±0.02	1.57	Q

720	1.38±0.02	1.77	Q

[a] Units of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}, estimated total uncertainty on k_1 is nearly 20% and includes that on the reference reaction.
[b] HW: halocarbon wax; Q: quartz.

3.2. Comparison with previous studies.

All data available for k_1 are shown in Fig. 3. With regard to the results of this work, one can note an excellent agreement between the data obtained by three different methods. As noted above, the approach used in the relative rate measurements was not entirely straightforward. For this reason, the results of the relative measurements were not used in determining the expression for the temperature dependence of k_1. The fit to the present absolute measurements of k_1 (solid line in Fig. 3) yields the following modified Arrhenius expression:

$$k_1 = 7.06 \times 10^{-11} (T/298)^{0.88} \exp(182/T)\ cm^3\ molecule^{-1}\ s^{-1}$$

at T = 220-950 K, with conservative 15% uncertainty in the whole temperature range.

The results of the present study can be compared with previous measurements of k_1. As can be seen from Fig. 3, the present room temperature value of k_1 = (1.3 ± 0.2)×10^{-10} cm^3 $molecule^{-1}$ sec^{-1} (T = 298 K) is by a factor of (1.6 – 1.9) higher compared to the results of the three previous measurements [1, 2, 4]. However, it should be noted that at least two of these studies appear to underestimate the rate constant.

Jaffe and Clyne [2] carried out a direct measurement of k_1 in a discharge-flow reactor with resonance absorption to measure the H-atom concentrations: k_1 = (8.2±3.8)×10^{-11} cm^3 $molecule^{-1}$ sec^{-1}. This value is in agreement with the present room temperature data in the range of the reported experimental uncertainties. In addition, the value of k_1 reported by Jaffe and Clyne [2] may be somewhat underestimated. The point is that most of the measurements were carried out under experimental conditions ($[Br_2]/[H]_0$ = 1.4 – 5), where it was necessary to take into account the consumption of Br_2. The authors hypothesized that virtually all of the Br atoms formed in reaction (1) were recombined on the walls of the uncoated glass reactor reproducing Br_2 and the overall H:Br_2 consumption was 2:1,

$$Br + Br \rightarrow \tfrac{1}{2} Br_2 \qquad (8)$$

Consequently, the concentrations of Br_2 used to calculate the rate constant $k_1 = k_1'/[Br_2]$ could be overestimated.

The rate constant k_1 = (7.3±0.9)× 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}, measured by Bikhalo et al. [4] in a discharge-flow reactor using the electron spin resonance method to detect hydrogen atoms, also seems to be underestimated. The reported value of k_1 was extracted from only one experimental curve which, moreover, was measured under experimental conditions poorly suited for kinetic measurements in a flow reactor: reaction time ≈ 10^{-3} s, $k_1' = k_1 \times [Br_2]$ ≈ 2500 s^{-1}. Indeed, the measured value of k_1' must be increased by at least a factor of 1.4 taking into account the axial diffusion of the H atoms [19], not to mention the problem of reagents mixing and correction on Br_2 consumption (≈ 20%).

A rather complex approach was employed in the study of Malins and Setser [1] to determine the rate constant of the reaction (1). The authors, using infrared chemiluminescence technique, measured the rate constant for HBr(υ ≥ 1) formation in reaction (1), relative to that of HCl(υ) in the reaction H + Cl_2:

$$H + Cl_2 \rightarrow HCl + Cl \qquad (9)$$

The relative rate k_1/k_9 = 3.3 converted to absolute value using k_9 = 2.06×10^{-11} cm^3 $molecule^{-1}$ sec^{-1} yielded k_1 = (6.8±0.5)× 10^{-11} cm^3 $molecule^{-1}$ sec^{-1}.

In a single absolute measurement of k_1 as a function of temperature, Wada et al. [3] employed pulse radiolysis of H_2/Br_2 mixtures combined with resonance absorption technique to monitor the pseudo-first-order decays of hydrogen atoms. The authors reported the following Arrhenius expression: k_1 = (6.7 ± 0.1)×10^{-11}exp(-(680 ± 60)/T) cm^3 $molecule^{-1}$ sec^{-1} in the temperature range (214 – 295) K. The observed well-pronounced temperature dependence of k_1 (an increase of the rate constant by a factor of 2.5) is in contradiction with the present observation of the actual independence of the rate constant of temperature in this temperature range (Fig.3). The absolute values of k_1 from the two studies are also very different: up to a factor of 4 at T = 220 K, the lowest temperature of the present work. It is difficult to establish the reason for the disagreement, in particular because the article of Wada et al. [3] does not detail the experimental conditions of the measurements and does not present the original experimental data.

Seakins and Pilling [21] measured the rate coefficient for the reaction

$$H + HBr \rightarrow H_2 + Br \qquad (10)$$

using laser flash photolysis of HBr and monitoring both the H-atom consumption and the Br-atom production by resonance fluorescence: k_{10} = 1.87×10^{-11} exp(-310/T) cm^3 $molecule^{-1}$ s^{-1}

over the temperature range 296-546 K. Combining the data for k_{10} with largely uncertain k_1/k_{10} ratio from Baulch et al. [12], they reported a rough estimate of k_1 = (1.6 ± 0.6) ×10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the temperatures between 300 and 500 K. One can note a good agreement of this estimate with the present absolute measurements of k_1 (Fig. 3).

In a recent theoretical study, Shang et al. [10] constructed a new ab initio potential energy surface (PES) for the H + Br_2 reaction. It was reported, in particular, that the total reaction probabilities show no threshold due to the submerged barrier (−0.351 kcal/mol) of the PES. The authors also calculated the thermal rate constants for the reaction (1) in the temperature range between 100 and 1000 K. These data are shown in Fig. 3 as dashed red line. One can note that the theoretical values of k_1 overestimated the experimental data available at that time, however are in very good agreement with those of the present work.

In conclusion, the temperature dependence of the rate constant of the H + Br_2 reaction was measured in a wide temperature range, T = 220 - 950 K (for the first time above room temperature). The present results challenge previous experimental measurements, support recent theoretical calculations of k_1, and provide a new reliable experimental basis for further theoretical developments.

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Appendix A. Supplementary material

Supplementary data related to this article can be found at ...

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