

Study of the reactions of OH with HCl, HBr, and HI between 298 K and 460 K

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Abstract

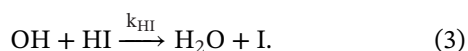
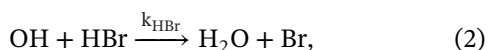
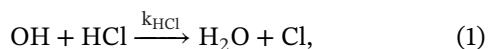
The reactions between OH radicals and hydrogen halides (HCl, HBr, HI) have been studied between 298 and 460 K by using a discharge flow-electron paramagnetic resonance technique. The rate constants were found to be $k_{\text{HCl}}(298 \text{ K}) = (7.9 \pm 1.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with a weak positive temperature dependence, $k_{\text{HBr}}(298\text{--}460 \text{ K}) = (1.04 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $k_{\text{HI}}(298 \text{ K}) = (3.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The homogeneous nature of these reactions has been experimentally tested.

KEYWORDS

HBr, HCl, HI, hydroxyl radical, OH, rate constant

1 | INTRODUCTION

Halogen atoms (Cl, Br, and I) are key players in the stratospheric ozone destruction due to the chain chemical process initiated by the release of halogen-containing compounds into the atmosphere.^{1–3} Iodine chemistry also plays a role in tropospheric ozone loss.⁴ Hydrogen halides (HCl, HBr, and HI) are considered as reservoirs of chemically active halogen atoms in the atmosphere, whereas their reactions with hydroxyl radicals (OH) regenerate halogen atoms in the atmosphere:



Reactions (2) and (3) also play an important role in combustion chemistry when Br-containing compounds (halons) and I-containing compounds (eg, CF_3I , $\text{C}_2\text{F}_5\text{I}$) are used as fire retardants.⁵ Reaction (3) is believed to play a role in tropospheric ozone loss.⁶

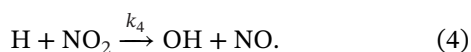
Reaction (1) has been intensively studied, and the experimental data obtained over the wide range of temperatures from 138 to 1055 K are available. Although the rate constant of this reaction is assumed to be well established^{7,8} due to numerous studies, the noticeable scattering of the data exists even at room temperature. There are fewer data available for reaction (2), which has been studied between 23 and 416 K. Although reported room temperature data vary by a factor of two, the current recommendations^{7,8} are based on studies resulted in larger values of $k_{\text{HBr}}(298 \text{ K})$. Room temperature results reported for reaction (3) vary by a factor of 7. The single study of temperature dependence of the rate constant was done between 246 and 353 K.

One of the main problem in studying these reactions is the chemical nature and properties of reactants. Hydrogen halides are water-soluble compounds, and they are prone to adsorption especially at the metal surfaces. Thus, hydrogen halides can be lost from the prepared mixtures during storage and when flowing through the gas handling lines and in a reactor. The least stable compound, HI, can decompose on surfaces and via absorption of the near UV radiation. Also, HI can form aerosol when mixed with other chemicals in the reactor.⁹ Thus, the availability of data obtained at different conditions by using

different techniques is of primary importance for clarifying the rate constants of these reactions, especially the reaction between OH and HI.

2 | EXPERIMENTAL

Detailed descriptions¹ of the apparatus and 10 experimental methods employed in the present work are given elsewhere.^{10–12} Thus, only a brief overview is provided here. The principal component of the discharge flow–electron paramagnetic resonance (DF-EPR) apparatus is a quartz tubular reactor of 1.5 cm i.d. with its internal surface coated with perfluorinated Teflon-like coating (F-46) to reduce wall loss of OH and to prevent heterogeneous reactions. The temperature of the reactor was maintained (± 0.3 K) with water (298 and 370 K) or mineral oil (460 K) circulated through its outer jacket. We could not obtain the reliable data at lower temperatures, which is probably due to heterogeneous processes. All reactants were added to the main carrier gas, He, and flow through the reactor at the total pressure of 0.2–0.4 kPa (1.5–3.0 Torr) with the average linear gas flow velocity (v_0) ranging from 10 to 27 m/s. Some test experiments described later were performed at increased pressure of 1.1 kPa (8 Torr). The total pressure was measured at both ends of the reactor. OH radicals were generated in the main flow tube near the tip of a movable quartz injector in the fast reaction:



Hydrogen atoms were generated by the microwave discharge (2.45 GHz, 10–20 W) in the H₂/He mixture flowing through the movable quartz injector. Both NO₂ and the reactant under study (HX, where X is Cl, Br, or I) were injected into the flow reactor upstream of the movable injector tip. They were always in large excess over H-atoms. The concentration of NO₂ of $(3 - 6) \times 10^{13}$ molecule/cm³ was used thus converting H-atoms into OH radicals in 0.1–0.2 ms. The OH concentration was monitored using EPR spectroscopy at the end of the flow reactor. The initial OH concentration in this study was estimated as $(1 - 2) \times 10^{11}$ molecules/cm³ when the rate constant were measured and up to $\approx 10^{12}$ molecules/cm³ in some test experiments at higher reactant concentrations. Pure undiluted reactants were stored in glass bulbs and flew to the reactor through the glass delivery lines equipped with vacuum grease-free

Teflon valves. Flow rates of all gases were determined by direct measurements of the pressure change rate in calibrated volumes, which were the parts of gas delivery lines. The overall instrumental uncertainty of measurements was estimated to be $\sim 10\%$. The decay rate of hydroxyl radical concentration, [OH], was measured by varying the distance, z , from the movable injector tip to the center of the EPR spectrometer cavity between 4 and 30 cm. The OH loss rate coefficients (k') at any reactant concentration, [HX], were obtained from the equation

$$k' = -v_0 \times \frac{\partial \ln [\text{OH}](z)}{\partial z}, \quad (5)$$

where [OH](z) is the concentration of OH (EPR signals) at distance z from the EPR resonator center. The k' values obtained from experiments with movable injector (expression 5) were slightly corrected for the axial diffusion to obtain the pseudo-first-order rate coefficients, k , using the expression

$$k = k' \times \left(1 + k' \times \frac{D}{v_0^2} \right), \quad (6)$$

where D is the OH diffusion coefficient. Finally, the bimolecular rate constant, k_{HX} , at a particular temperature was derived from the slope of a plot of k versus the reactant concentration using the following expression:

$$k = k_w + k_{\text{HX}} \times [\text{HX}], \quad (7)$$

where k_w is the first-order OH decay rate due to its heterogeneous OH removal in the absence of the reactant and [HX] is the concentration of the reactant (HCl, HBr, or HI, respectively). Note that the length of the OH detection zone (EPR cavity) does not affect results of these measurements.¹⁰

Another series of experiments was carried out with a fixed distance, z_0 (10–21 cm) between the injector and the detection zone (the center of an EPR cavity). The dependence of the OH concentration (EPR signal) versus the concentration of HX was measured to obtain the k_{HX} value. Under conditions of plug flow, the rate constant can be obtained as

$$k_{\text{HX}} = -\frac{v_0}{z_0} \times \frac{\partial \ln [\text{OH}](z)}{\partial [\text{HX}]}. \quad (8)$$

Small corrections to account for the axial diffusion were also applied to these data. Note, that although the physical dimension of an EPR cavity (≈ 3 cm) is not much smaller than the distance between the injector and the center of the cavity, z_0 , it does not introduce an additional uncertainty

¹ Certain commercial equipment, instruments, or materials are identified in this article in order to adequately specify the experimental procedure. Such identification does not imply recognition or endorsement by the National Institute of Standards and Technology.

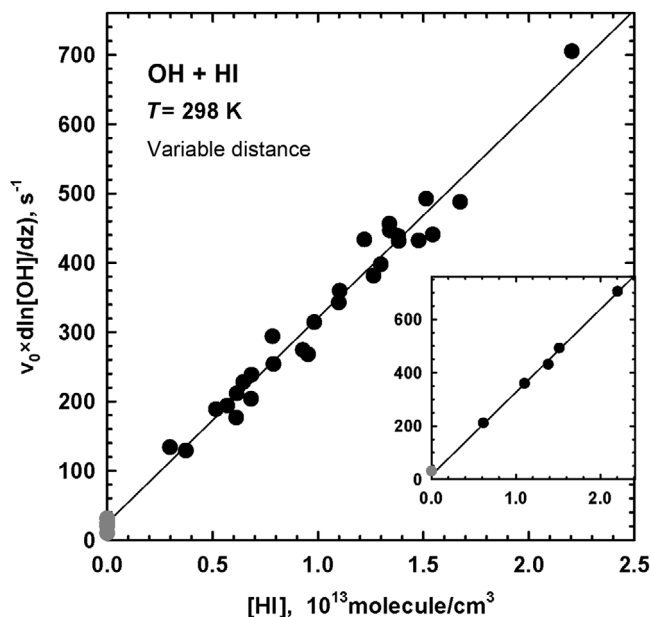


FIGURE 1 Cumulative plot of OH concentration decay rates versus reactant concentration obtained with a movable injector for the reaction between OH and HI at $T = 298$ K. Insert: data obtained in the single series of experiments during the same day. Grey circles are decay rates measured in the absence of the reactant; they were not used to draw regression lines

to the measured rate constant. The EPR signal for any [HX] is an integral of the exponentially decreasing [OH] multiplied by the sensitivity distribution along the EPR cavity. Using thus calculated values instead of [OH] in expression 8 results in $\approx 0.5\%$ underestimation of the derived rate constant even for the shortest $z_0 = 10$ cm under conditions of our experiments (v_0 , [HX]).

These complementary experimental approaches are illustrated in Figures 1 and 2, which show results obtained for reaction (3) with a movable injector and fixed reaction distance, respectively. Note that the total data scattering is mainly due to difference between results obtained in different series of measurements performed in different days. Data obtained in the single series of measurements (during the same day) are usually less scattered as illustrated in small inserts. Rate constants reported in this paper for each experimental approach were derived from combined fits to the entire data set obtained at the particular temperature.

3 | MATERIALS

All reactants except carrier flow gas, He (99.999% pure) and H_2 (99.98% pure), were prepared in the laboratory following Ref. 13 to be aware of their purity. Nitrogen dioxide, NO_2 , was prepared from nitrous oxide in the excess

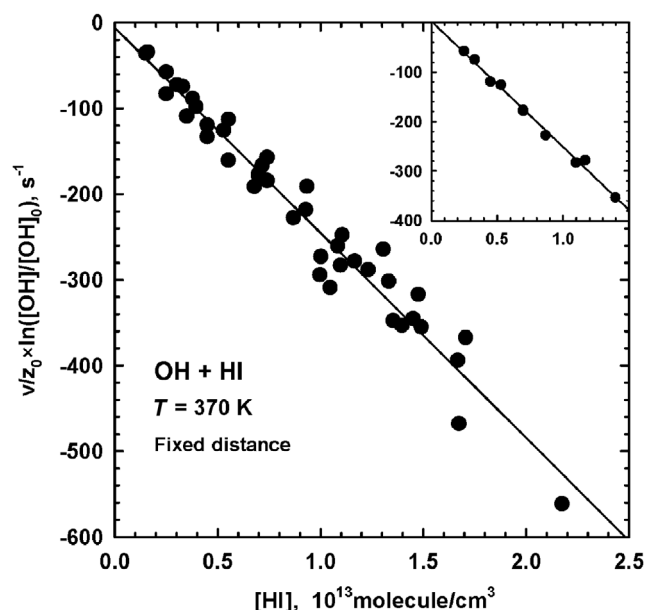


FIGURE 2 Cumulative plot of OH concentration decay rates versus reactant concentration obtained with a fixed distance (10 and 12 cm) between the OH injector and the center of EPR cavity for the reaction between OH and HI at $T = 370$ K. Insert: data obtained in the single series of experiments during the same day. $[NO_2] \approx 6 \times 10^{13}$ molecule/cm³

of molecular oxygen followed by low-temperature distillation. Nitrous oxide in turn was synthesized in the reaction of metal copper with dilute nitric acid followed by low-temperature distillation. Nitrogen dioxide was appeared as white (colorless) snow when frozen in the liquid nitrogen cooled trap thus indicating the absence of other nitrogen oxides as impurities. The concentration of NO_2 in the flow reactor was estimated by taking into account its dimerization in the storage bulb and in the flow rate measurement section of the gas handling manifold. HCl, HBr, and HI were also prepared in the laboratory. HCl was synthesized in the reaction of dilute sulfuric acid with sodium chloride. More readily oxidizing HI was synthesized by dripping a suspension of phosphorus and water onto molecular iodine. Similarly, HBr was synthesized by dripping liquid molecular bromine onto wet phosphorus. Thus obtained hydrogen halides were dehydrated by using concentrated sulfuric acid (HCl only) and phosphorus anhydride (P_2O_5). All samples were carefully degassed, and the residual water was removed through multiple freeze-pump-thaw-boil cycles. The same freeze-pump-thaw-boil procedure was used every day before a series of rate constant measurements. All hydrogen halides appeared as white (colorless) snow when frozen in a liquid nitrogen trap for outgassing thus indicating the absence of the corresponding molecular halogen impurities. Then, the reactants were delivered to the flow

reactor without prior dilution with the inert gas in the storage bulb.

4 | RESULTS AND DISCUSSION

4.1 | Effect of wall reactions

In the previous paper,¹¹ we reported a possibility of heterogeneous reaction between OH and HCl in the low-pressure flow tube experiments. The experimental technique and data analysis have been suggested to separate the possible heterogeneous reaction channel from the gas phase reaction under study. It was shown that the per-fluorinated polymer coating allows to avoid this potential complication in a discharge flow study of the reaction between OH and HCl. The same type of experiments were performed in the current study to check a potential effect of heterogeneous channels on the measured rate constants of OH reactions with HBr and HI. The approach is based on the very different effect of the diffusion rate on the measured OH decay rate in case of the homogeneous reaction and heterogeneous removal of OH, respectively. In the case of wall reactions, the observed rate constant, $k_{\text{HX}}^{\text{obs}}$, measured at relatively slow diffusion in the flow reactor should become noticeably smaller than the rate constant k_{HX} measured in the absence of limiting effect of diffusion. The test experiments using a movable injector were performed at the increased total pressure in the flow reactor of ≈ 1.1 kPa (8 Torr) followed by the data analysis suggested in Ref. 11. The results in the appropriate dimensionless units are presented in Figure 3 along with the net of calculated curves corresponding to various contributions of wall reaction. These results indicate that the measured rate constants k_{HBr} and k_{HI} characterize the gas phase reactions and the possible effect of wall reactions is negligible.

4.2 | $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$

Results of our study are presented in Table 1 and shown in Figure 4. Although results obtained with the movable injector and the fixed distance between the injector tip and the center of the detection zone are slightly different, they overlap within their combined uncertainties with no obvious reason to reject any of them. Both numbers are shown in Table 1 at $T = 298$ and 370 K. Therefore, we present the rate constant as a simple average of those obtained with two different techniques and a conservative estimate of uncertainty to encompass results of both measurements with their individual uncertainties (bold highlighted data). The fit to thus obtained data (bold highlighted) at three

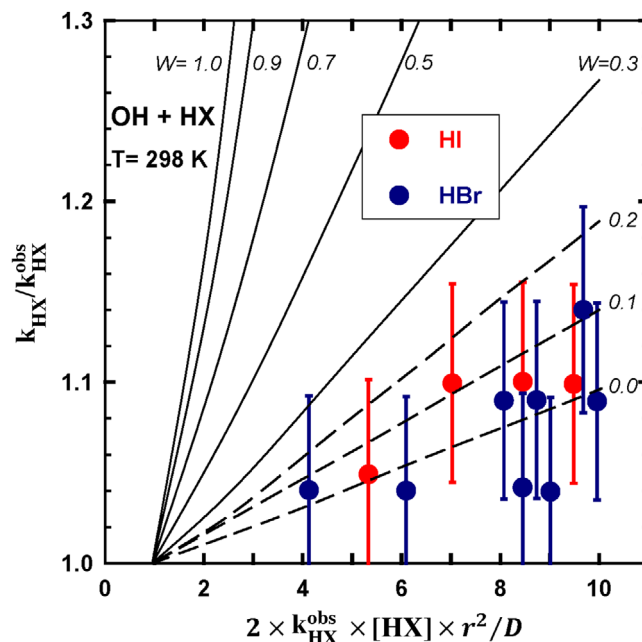


FIGURE 3 Dependence of the ratio of the rate constant measured in the absence of diffusional effects (k_{HX}) to the rate constant measured at increased pressure of 8 Torr ($k_{\text{HX}}^{\text{obs}}$) for OH reactions with HBr and HI. Lines are calculated values of $k_{\text{HX}}/k_{\text{HX}}^{\text{obs}}$ for various fractions of the total reaction rate due to the potential heterogeneous reaction, W (see Ref. 11). D is a diffusion coefficient, and r is the flow tube radius [Color figure can be viewed at wileyonlinelibrary.com]

temperatures yields the following Arrhenius expression:

$$k_{\text{HCl}}(T) = (4.0 \pm 0.57) \times 10^{-12} \times \exp[-(480 \pm 50)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (9)$$

where the uncertainties are only two standard errors from the fit. The room temperature rate constant determined in this work can be presented as

$$k_{\text{HCl}}(298 \text{ K}) = (7.9 \pm 1.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (10)$$

where the uncertainty is the value chosen to overlap those obtained in all measurements with two different experimental approaches.

Figure 4 shows all the available data for this reaction normalized to the three-parameter modified Arrhenius expression derived from the combined fit to the data obtained between 200 and 1055 K in two sets of measurements,^{14,15}:

$$k(T) = 3.2 \times 10^{-13} \times (T/298)^{1.96} \times \exp(+267/T). \quad (11)$$

Such presentation was chosen to better show data scattering over the wide temperature range. The choice of the

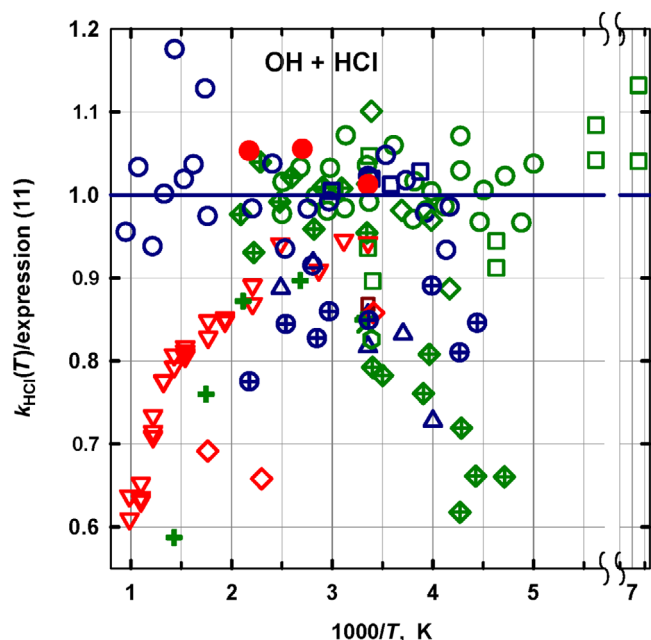


FIGURE 4 Rate constants measured for the reaction between OH and HCl after normalization to expression (11). ∇ , Bryukov et al.²⁴ (PLP-LIF); $\circ$, Battin-Leclerc et al.¹⁵ (PLP-LIF); $\square$, Sharkey and Smith²³ (PLP-LIF); $\circ$, Ravishankara et al.¹⁴ (FP-RF/PLP-RF); $\diamond$, Molina et al.²¹ (PLP/FP-RF); $\square$, Keyser²⁰ (DF-RF); $\times$, Husain et al.²⁶ (FP-RF); $\triangle$, Ravishankara et al.¹⁹ (FP-RF); $\square$, Canon et al.²⁷ and Smith and Williams²⁸ (FP-LIF); $\diamond$, Hack et al.¹⁸ (DF-EPR); $+$, Husain et al.²² (FP-RF); $\oplus$, Zahnider et al.¹⁷ (DF-RF); $\diamond$, Smith and Zellner¹⁶ (FP-RA); $\circ$, Takacs and Glass²⁵ (DF-EPR); $\bullet$, this work (DF-EPR) [Color figure can be viewed at wileyonlinelibrary.com]

“reference” expression is arbitrary to some extent. Both sets of measurements were obtained in the same laboratory with spectrometric control of reactant (HCl) concentration, when combined they span over the entire temperature range of all measurements of this rate constant and reasonably coincide over the overlapping temperatures both above and below room temperature and resulting in the same derived $k(298\text{ K})$.

Eleven studies of the temperature dependence of this reaction have been published,^{14–24} and four measurements have been done at room temperature only.^{25–28} All results exhibit substantial scattering including the most abundant results at room temperature. The reason for such data scattering can be of both instrumental and chemical nature reasons. Thus, the authors of Ref. 14 suggested disappearance of the reactant (HCl) from the storage, gas handling, or reactor due to adsorption to explain the underestimated rate constant measured in their earlier pulse experiments¹⁹ and, probably, in other earlier studies. They employed a UV absorption at 185 nm to optically control the amount of HCl in the system and thus obtained consistent sets of measurements covering the temperature interval between 200 and 1055 K. Our results obtained

between 298 and 460 K by using undiluted HCl in the reactant supply lines are in good agreement with these data thus supporting the recommended^{7,8} room temperature value of $k_{\text{HCl}}(298\text{ K}) = 7.8 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ and proving our experimental approach. The rate constant $k_{\text{HCl}}(298\text{ K}) = (8.2 \pm 0.4) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ derived in our earlier study¹¹ should be slightly corrected by $\approx 3.5\%$ to account for axial diffusion processes and thus coincides with the present result. There is substantial disagreement between data from two studies extended to higher temperature of 1000 K.^{14,24} The difference increases from $\sim 7\%$ at 298 K to $\sim 60\%$ at 1000 K with rate constants reported in Ref. 24 being smaller. The reason for this increasing disagreement is not clear. Although authors of Ref. 24 did not optically monitor the HCl concentration they used various diluted mixtures of HCl to find no variation of the measured reaction rate constant. The data available below room temperature are also noticeably scattered and the results of the latest study by Battin-Leclerc et al.¹⁵ are the highest. Very low temperature data obtained using a Laval nozzle cooling²³ are in reasonable agreement with expression (11) extrapolated to lower temperatures.

4.3 | OH + HBr $\rightarrow$ H₂O + Br

Results of our measurements are presented in Table 1. Again, we report the rate constant at 298 and 370 K as a simple average of those obtained with two different approaches and a conservative estimate of uncertainty to encompass results of both measurements with their individual uncertainties (bold highlighted numbers). Thus, the rate constant $k_{\text{HBr}}(T)$ measured in our experiments is essentially temperature independent between 298 and 460 K and can be conservatively estimated as

$$k_{\text{HBr}}(298\text{ K} - 460\text{ K}) = (1.04 \pm 0.2) \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}. \quad (12)$$

The preliminary result that we reported for $k_{\text{HBr}}(298\text{ K})$ ²⁹ is essentially unchanged.

Figure 5 shows the data available for this reaction between 23 and 460 K. Six studies^{27,30–34} at room temperature resulted in $k_{\text{HBr}}(298\text{ K})$ laying between 0.9×10^{-11} and $1.2 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, whereas results of three earlier studies^{16,26,35} are about a factor of 2 smaller.

There are two studies of the temperature dependence of this reaction using conventional control of the reactor temperature^{30,34} and a few lower temperature studies using a Laval nozzle to create a supersonic flow of super cold gas.^{33,36–39} A pulse photolysis study by Ravishankara et al.³⁰ revealed no significant variation of the measured

TABLE 1 Rate constants measured in the present work for reactions OH with HCl, HBr, HI^a

<i>T</i> (K)	$k_{\text{HX}}(T)$ ($\times 10^{13}$, cm ³ molecule ⁻¹ s ⁻¹)	Method	[HX] ($\times 10^{-13}$ molecule/cm ³)	Number of decays
OH + HCl				
298	0.79^{+0.14}_{-0.07}	Mean value		
	0.815 ± 0.117	Movable injector	1.32–37.4	43
	0.770 ± 0.052	Fixed distance	0.83–64.9	39
370	1.06^{+0.15}_{-0.31}	Mean value		
	0.97 ± 0.22	Movable injector	2.16–18.6	9
	1.16 ± 0.052	Fixed distance	1.01–22.1	34
460	1.41 ± 0.28	Movable injector	1.82–17.8	21
OH + HBr				
298	1.00 ± 0.15	Mean value		
	0.91 ± 0.05	Movable injector	0.57–4.27	62
	1.08 ± 0.05	Fixed distance	0.57–4.03	85
370	1.14 ± 0.07	Mean value		
	1.12 ± 0.05	Movable injector	0.65–4.45	65
	1.16 ± 0.04	Fixed distance	0.20–4.06	80
460	0.99 ± 0.19	Movable injector	0.60–1.72	9
OH + HI				
298	2.9 ± 0.2	Movable injector	0.37–2.2	28
370	2.5 ± 0.2	Mean value		
	2.57 ± 0.10	Movable injector	0.24–2.07	61
	2.40 ± 0.16	Fixed distance	0.16–2.17	42

^aThe uncertainties are two standard errors from the weighted least-squares fit of a straight line to the measured OH decay rates versus the reactant concentrations. They do not include any instrumental/systematic uncertainty.

^bThe bold-highlighted data are averages of values determined by using two experimental approaches when available. These data are shown in Figures 4–6.

rate constant with the temperature between 249 and 416 K. The same conclusion can be made based on our discharge flow data, which extended the temperature range up to 460 K. However, we failed in obtaining the reliable data below room temperature. The latest discharge flow study by Bedjanian et al.³⁴ revealed a weak increase ($\approx 40\%$) of the rate constant when the temperature decreases from 360 to 230 K.

All results obtained with a Laval nozzle cooling are from two research groups, who were making joint efforts to present the consistent data at very low temperatures.^{38,39} Although the major efforts were targeted at the very low temperatures, the studies by Atkinson et al.³⁶ and Jaramillo and Smith³⁷ provide some data over the temperature range up to 242 and 224 K, respectively. (The results of the latter study have been later corrected,³⁹ and these corrected ones are shown in Figure 5.) These studies revealed the significant increase of the rate constant, $k_{\text{HBr}}(T)$, at very low temperatures. The sharp increase of the observed OH decay at lower temperatures can be due to the HOHBr complex formation as was suggested by Atkinson et al.³⁶ to explain the data obtained below 150 K. However, the available results of these studies at $T > 170$ K do not

necessarily support the increasing rate constant over the temperature range of atmospheric interest. This is illustrated in Figure 5. Note that expression $k_{\text{HBr}}(222\text{--}460\text{ K}) = (1.1 \pm 0.2) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ encompasses almost all data (except the lowest temperature point of Ref. 34) obtained between 222 and 460 K in nine studies including the present work and Laval nozzle experiments.^{36,37}

4.4 | OH + HI → H₂O + I

This reaction was studied at $T = 298$ and 370 K only. The results are presented in Table 1. Numerous experiments performed at 370 K with both movable OH injector and fixed reaction time yielded similar rate constants presented in Table 1. The rate constant increases with decreasing temperature from 370 to 298 K by $\sim 20\%$ thus suggesting the following weak negative temperature dependence, which is based on measurements at two different temperatures only

$$k_{\text{HI}}(T) = 1.24 \times 10^{-11} \times \exp(+260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (13)$$

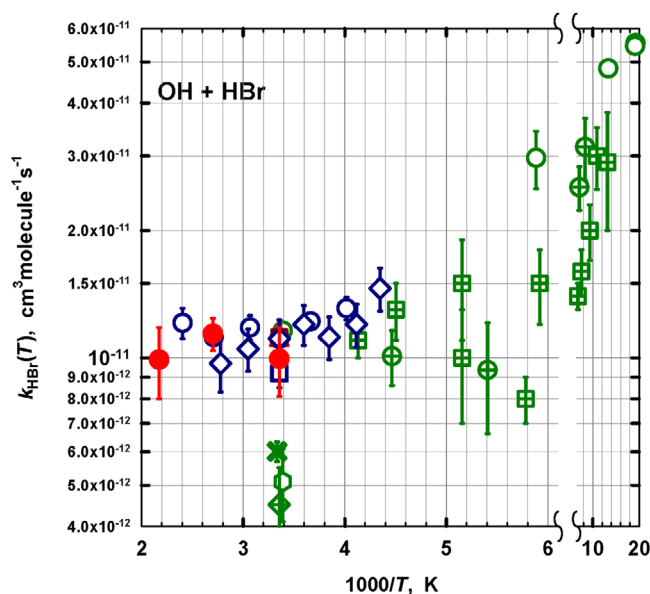


FIGURE 5 Rate constants measured for the reaction between OH and HBr. $\oplus$, Jaramillo and Smith³⁷ (FP-LIF); $\diamond$, Bedjanian et al.³⁴ (DF-MS); $\boxplus$, Atkinson et al.³⁶ (FP-LIF); $\circ$, Sims et al.³³ (PLP-LIF); $\triangle$, Ravishankara et al.³² (PLP-LIF); $\circ$, Ravishankara et al.³⁰ (PLP-RF); $\square$, Canon et al.²⁷ (FP-LIF); $\boxminus$, Jourdain et al.³¹ (DF-EPR); $\times$, Husain et al.²⁶ (FP-RF); $\diamond$, Smith and Zellner¹⁶ (FP-RA); $\circ$, Takacs and Glass³⁵ (DF-EPR); $\bullet$, this work (DF-EPR) [Color figure can be viewed at wileyonlinelibrary.com]

This reaction was neither studied as intensively as the previous two nor its rate constant established well. Figure 6 shows results of five published studies^{9,25,16,40,41} along with our data. Our room-temperature rate constant is in good agreement with results reported in Refs. 40,41. Although both measurements were performed in the same laboratory, the different techniques were employed, pulse laser photolysis with resonance fluorescence detection of OH⁴⁰ and discharge flow with EPR detection of OH.⁴¹ Two earlier studies^{16,25} reported the rate constants, which are smaller than our result by a factor of 2.3 and 3, respectively, similarly to their appearance in the data set for OH + HBr in Figure 5. The most recent study⁹ reported the rate constant, which exceeds our results and data reported in Refs. 40,41 by more than a factor of 2. The temperature dependence derived in this latest study⁹ is shown in Figure 6.

Based on good agreement of our results obtained for k_{HCl} and k_{HBr} with the available data and recommendations,^{7,8} we can be more confident that the data obtained for the OH + HI reaction are correct. The major chemical complication we were facing during this study was a possible decomposition of HI on metal parts of the gas handling system. The flow rate of HI was determined from the pressure rise in the small calibrated volume with the capacitance

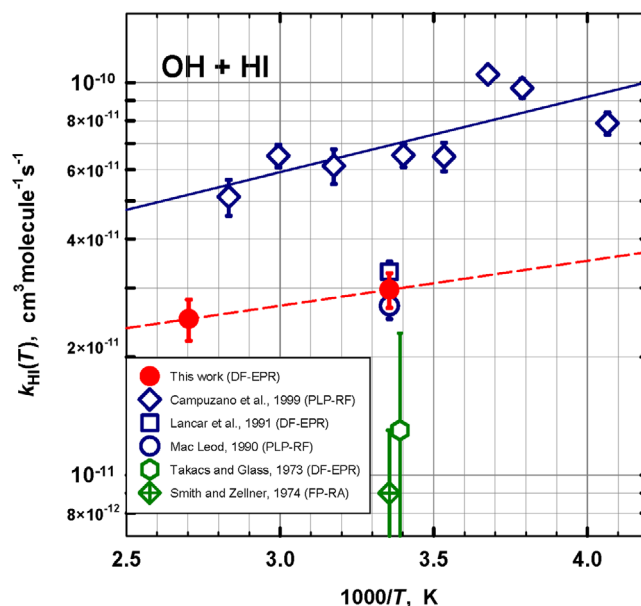


FIGURE 6 Rate constants measured for the reaction between OH and HI. $\diamond$, Campuzano et al.⁹ (PLP-RF); $\square$, Lancar et al.⁴¹ (DF-EPR); $\circ$, MacLeod et al.⁴⁰ (PLP-RF); $\diamond$, Smith and Zellner¹⁶ (FP-RA); $\circ$, Takacs and Glass³⁵ (DF-EPR); $\bullet$, this work (DF-EPR) [Color figure can be viewed at wileyonlinelibrary.com]

manometer, which could be isolated with a Teflon plug glass valve. Both the valve and manometer were located in the side arm of the glass gas handling system so that the HI flow moving to the reactor did not contact the manometer. HI can decompose to produce H_2 and I_2 , and molecular iodine causes a concern in all studies of the target reaction because of the very high rate constant of its reaction with OH,⁷ $1.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. So, the decomposition of HI can lead to the overestimated measured rate constant of the target reaction, $k_{\text{HI}}(T)$. We used undiluted hydrogen iodide and thus avoided this problem in the storage bulb and the part of HI supply line, which was under the same relatively high pressure. Indeed, the saturated vapor pressure of molecular iodine is ≈ 0.3 Torr at room temperature. Therefore, even substantial decomposition of pure HI in the storage bulb and gas handling lines where its pressure is hundreds and even tens of Torr will not result in comparable amounts of I_2 and HI in the gas phase and, thus, cannot affect the results. We also could not lose HI due to its adsorption on the walls here. The only “suspicious” part is the end of the glass delivery line after the needle valve regulating the HI flow rate to the reactor where its pressure is low and uncontrolled. Thus, (i) HI can be lost due to adsorption and (ii) I_2 can reside in the gas phase if HI gets decomposed in this part of the gas delivery line. The residence time of HI in this part is short because of higher flow rate and variates to create different

concentrations of HI in the flow experiment (by a factor of six). This could manifest itself in the observed dependences of the OH decay rate versus HI flow rate (calculated HI concentration in the reactor). For example, the time-dependent formation of reactive I_2 would result in a higher intercept of the regression plot when compared with the OH decay rate measured in the absence of HI. In the case of the time-dependent HI loss due to adsorption, the intercept would be smaller than the measured nonreactive OH decay rate. However, both Figures 1 and 2 show that the intercept of the regression line is consistent with the [OH] decay rate measured in the absence of HI in the reactor. Thus, we did not notice any changes of the observed kinetic data that could be indicative of the noticeable appearance of reactive I_2 or partial loss of HI due to variations of the HI flow rate.

In the latest study, Campuzano-Jost and Crowley⁹ were using very diluted mixtures of HI in the storage bulb (0.013–0.025%). In case of such diluted mixtures, the entire amount of molecular iodine which can appear due to HI decomposition would remain in the gas phase to increase the measured rate constant. However, as much as two thirds of HI should be decomposed yielding more reactive I_2 to explain the larger rate constant measured in this study, which is probably the most detailed study of the reaction describing numerous approaches and complications mainly related to the nature of the reactant, HI. In particular, the authors used a cold trap (−110 °C) in the HI flow line to remove possible I_2 impurities before entering a reactor. On the other hand, three independent studies (using three different gas handling systems for the HI delivery) resulted in essentially the same measured room temperature rate constant thus suggesting the absence of noticeable instrumental errors. There is no obvious explanation of such a large discrepancy between the results obtained by MacLeod et al.,⁴⁰ Lancar et al.,⁴¹ and in our study and the rate constant reported by Campuzano-Jost and Crowley.⁹

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