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Kinetics of the Reactions of the Hydroxyl Radical with Molecular Chlorine and Bromine

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The rates of the reactions of OH with Cl_2 and Br_2:

$$OH + Cl_2 \rightarrow HOCl + Cl, \qquad \Delta H^{\ominus}_{298} = 4.3\ \text{kJ mol}^{-1} \qquad (1)$$

$$OH + Br_2 \rightarrow HOBr + Br, \qquad \Delta H^{\ominus}_{298} = -38.05\ \text{kJ mol}^{-1} \qquad (2)$$

have been investigated over a range of temperatures between 253 and 333 K by using a discharge-flow resonance-fluorescence technique. At 293 K the rate constants for reactions (1) and (2) are

$$k_1 = (6.8 \pm 1.0) \times 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_2 = (3.4 \pm 1.2) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

The rate constant for the reaction of OH with Cl_2 increases with temperature, and can be fitted between 253 and 333 K by the following Arrhenius expression:

$$k_1 = (1.7^{+4.4}_{-1.2}) \times 10^{-12} \exp -(911 \pm 373)/T\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

For the reaction of OH with Br_2, the data are consistent with a zero activation energy, although a small activation energy (not exceeding 5 kJ mol^{-1}) could also be supported.

It is a common assumption that the reactivity of radicals towards molecules is linked to the physical properties of both reacting species [see, for example, ref. (1)]. Many of the OH-halogen radical-molecule reactions have been investigated before, but information on the temperature dependences, which would allow consideration of the activation energies as well as the rate constants, is lacking in several cases. A clearer picture of the mechanisms of radical-molecule reactions can only emerge as knowledge of the rate data becomes more detailed. We have therefore undertaken a study of the temperature dependences of the reactions:

$$OH + Cl_2 \rightarrow HOCl + Cl \qquad (1)$$

$$OH + Br_2 \rightarrow HOBr + Br. \qquad (2)$$

Experimental

Apparatus

The discharge-flow resonance-fluorescence technique was used in the present experiments. Our apparatus has been described in detail in previous publications,[2,3] and only an outline of it is presented here. Hydroxyl radicals were generated in the helium carrier gas by the reaction of H with NO_2 in the upstream section of the flow tube. The molecular halogen reactant was admitted *via* a sliding stainless-steel injector to provide variable contact times. The flow tube was constructed of Pyrex of 25 mm i.d., and it was double-walled to permit circulation of liquids for temperature control. Flow velocities of up to 23 m s^{-1} could be maintained for carrier gas pressures in the range 1-5 mmHg [*ca.* (1.3-6.6) × 10^3 Pa].

Conventional gas-handling techniques were used for the supply and metering of the carrier and reactant gases. All storage bulbs were equipped with electronic Bourdon gauges,[4] and flow rates measured with capillary flow meters. Except in the case of helium-bromine mixtures, pressure differentials were determined with dibutylphthalate manometers. Bromine was found to dissolve substantially in the manometer fluid, and a differential version of the electronic Bourdon gauge was developed for this application. To avoid contact of the differential transformer with corrosive gas, an encapsulated iron core, attached to the Pyrex spoon, moves between externally mounted coils that form two of the arms of an a.c. bridge.

Resonance fluorescence, in the $X\,^2\Pi \leftarrow A\,^2\Sigma^+$ transition, was used to monitor the concentration of OH radicals. The detection system, consisting of collimators, interference filter, chopper, cooled photomultiplier (EMI 9757B) and a microprocessor-controlled two-channel counter was similar to that described previously,[2,3] except that the fluorescence cell was made from stainless steel to allow more rigid attachment of both resonance lamp and detector train to the observation region. The sensitivity towards OH of this detection system, for an integration time of 10 s and a signal-to-noise ratio of unity, was 1×10^{10} molecule cm^{-3}. To minimize the effects of secondary reactions, [OH] was kept below 2×10^{11} molecule cm^{-3} in the experimental runs.

Materials

Helium, hydrogen and NO_2 were obtained from the same sources and purified by the same methods as those described in our previous publication.[3] Chlorine (BDH, purity $>99.5\%$) and bromine (AnalaR, purity 99.9%) were purified by repeated freeze-pump-thaw cycles.

Results

The Reaction of OH with Cl_2

The rate of reaction of OH with Cl_2 is determined by measuring the decay of the OH fluorescence signal as a function of injector position for known excess concentrations of chlorine. Contact times are calculated from the distance between the tip of the sliding injector and the OH detection point. Typical examples of the decay in OH fluorescence are shown logarithmically as a function of contact time in fig. 1. The gradient gives the pseudo-first-order rate coefficient, k_1'.

The pseudo-first-order rate coefficients determined as described should be the product of the second-order rate constant for the reaction multiplied by the reactant concentration so long as two conditions are satisfied. First, loss of OH on the injector must be negligible. We have already established[2,3] that this condition is met with our apparatus. Secondly, the rate of loss of OH on the main flow tube walls must not vary with the amount of halogen added over the concentration range employed. In the absence of added halogen, the wall loss rate can be assessed by producing OH at different points down the tube, as described previously,[3] the values found being typically 5-10 s^{-1} for the Pyrex tube coated with halocarbon wax. Fig. 2 shows k_1' plotted as a function of $[Cl_2]$ for $T=293$ K. In this plot, and its analogues for different temperatures, there is no evidence of significant curvature, and the 95% confidence limits of the apparent small intercept include the origin. There is, therefore, no reason to suppose that varying wall loss rates distort the data in these experiments, and the slopes of figures such as 2 are taken to give the true second-order rate coefficient for the reaction.

Our room-temperature value of k_1 is given in table 1, together with results of previous determinations. The error limits quoted throughout are 95% confidence limits obtained from a linear least-squares analysis.

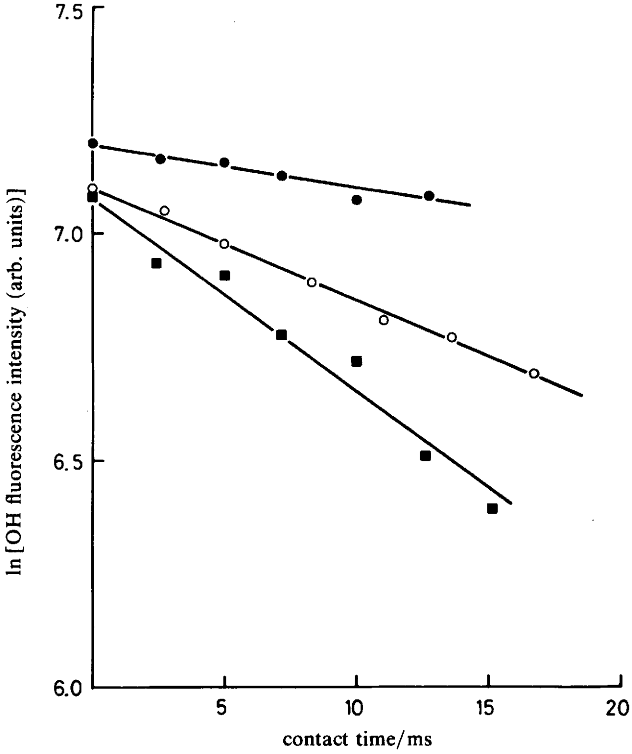

Fig. 1. OH fluorescence intensity as a function of contact time for three chlorine concentrations. $[Cl_2]/10^{14}$ molecule cm^{-3} = 1.82 (●); 3.23 (○); and 5.79 (■).

Reaction (1), the reaction between OH and Cl_2, was studied over the temperature range 253 to 333 K; the rate constant was found to vary from $(4.4 \pm 0.4) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 253 K to $(11.1 \pm 2.6) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 333 K (see table 2). Fig. 3 displays these data in Arrhenius form and yields the following values for the activation energy and the pre-exponential factor:

$$E_A = 7.6 \pm 3.1 \text{ kJ mol}^{-1}$$

$$A = (1.7^{+4.4}_{-1.2}) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The Reaction of OH with Br_2

Experiments entirely analogous to those performed in the study of reaction (1) were conducted to determine the rate of reaction between OH and Br_2. Some typical plots showing the decrease in OH fluorescence intensity with increasing reaction time are presented in fig. 4, while fig. 5 is the plot from which the second-order rate constant is derived. Similar arguments to those used in the case of the Cl_2 reaction argue against a wall loss rate that depends on $[Br_2]$. Previous determinations of k_2 are shown along with our result in table 3.

Since reaction (2) is 'fast' in the sense that substantial fractional conversion of OH occurs on the timescale of our experiments, the possibility of secondary processes involving the product molecules, *e.g.*

$$OH + HOBr \rightarrow \text{products} \qquad (3)$$

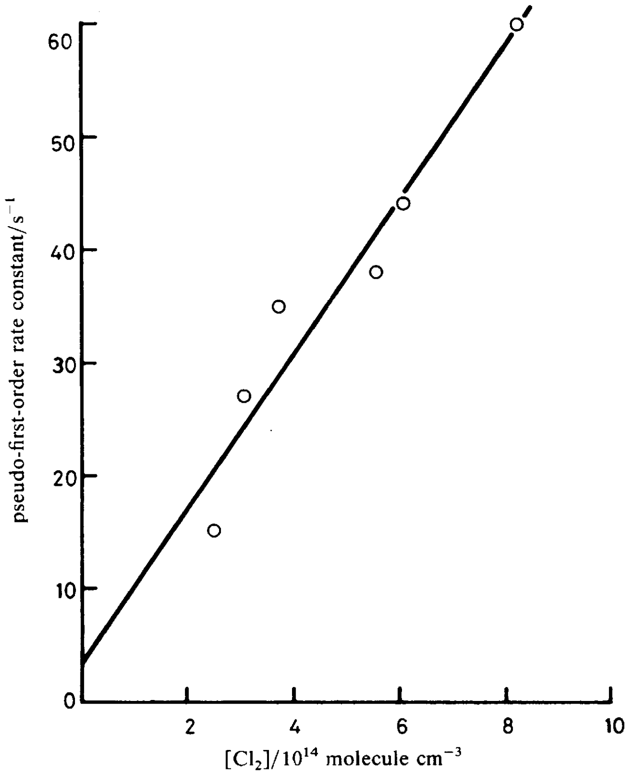

Fig. 2. Pseudo-first-order rate constant as a function of chlorine concentration.

Table 1. Room-temperature values of k_1

$k_1/10^{-14}$ cm^3 molecule^{-1} s^{-1}	ref.
6.8 ± 1.0	this work
ca. 8	3
6.7 ± 0.72	1
5.5 ± 0.3	7

Table 2. Variation of k_1 with temperature

T/K	$k_1/10^{-14}$ cm^3 molecule^{-1} s^{-1}
253	4.4 ± 0.4
273	6.6 ± 1.4
293	6.8 ± 1.0
313	9.5 ± 1.0
333	11.1 ± 2.6

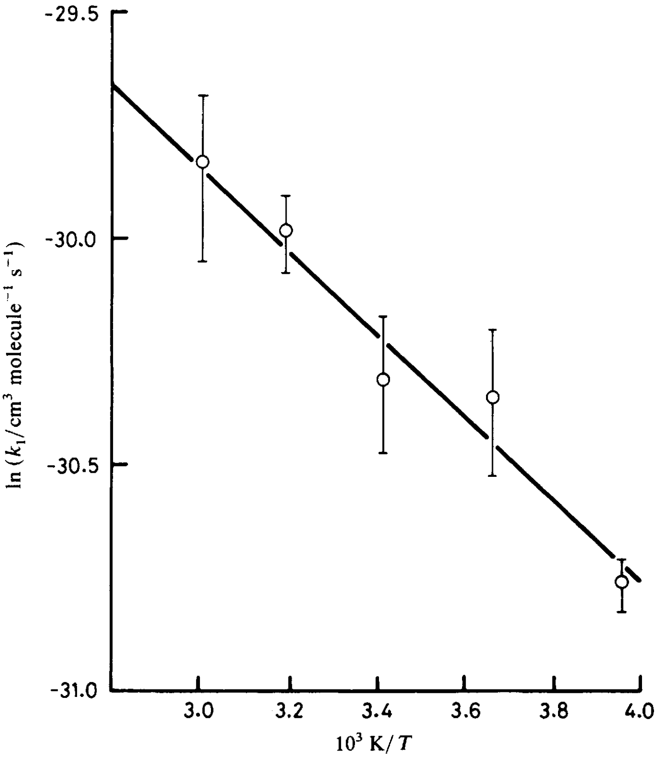

Fig. 3. Arrhenius plot for the reaction $OH + Cl_2$.

must be considered. Because [OH] is kept small ($<2 \times 10^{11}$ molecule cm^{-3}), such secondary reactions can only play a very minor role. For example, a 50% loss of OH implies a maximum concentration of HOBr of 10^{11} molecule cm^{-3}, so that, even with a rate for reaction (3) approaching the gas-kinetic limit, the secondary reaction could contribute only a few percent to the total measured rate of loss of OH. A full numerical integration, using the FACSIMILE package,[5] indicates quantitatively that the contribution of secondary reactions is unlikely ever to exceed 5%. This simulation takes into account further reactions of the products of reaction (3), as indicated in table 4, as well as the measured extent of reaction for any particular [Br_2] added.

Reaction (2) was studied at temperatures between 262 and 303 K; the results are summarized in table 5 and shown as an Arrhenius plot in fig. 6. The rate constants appear to be much less dependent on temperature than are those for k_1, and the errors produced by least-squares fitting to the Arrhenius expression are correspondingly large. Mechanical application of the statistical analysis yields the following Arrhenius parameters:

$$E_A = 7.2 \pm 9.2 \text{ kJ mol}^{-1}$$

$$A = (5.8^{+286}_{-5.7}) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

A reasonable way of interpreting these error ranges is presented in our Discussion.

Discussion

Our room-temperature (293 ± 2 K) value for k_1 is $(6.8 \pm 1.0) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, in good agreement with previous determinations (298 K, see table 1). In all of the

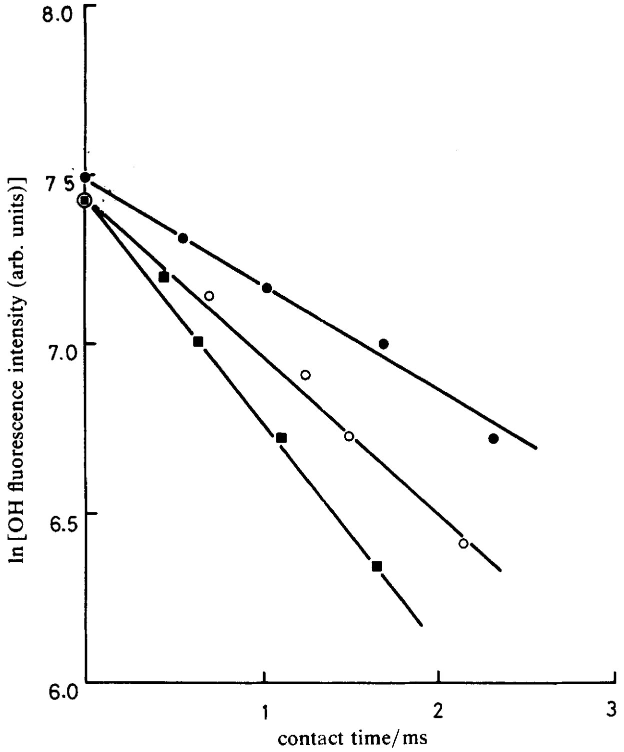

Fig. 4. OH fluorescence intensity as a function of contact time for three bromine concentrations. $[Br_2]/10^{13}$ molecule $cm^{-3} = 1.09$ (●); 2.32 (○); and 3.16 (■).

previous experiments on reaction (1),[1,3,7] the discharge-flow technique with resonance-fluorescence detection of OH was used. At 293 K we found the rate constant for reaction (2), k_2, to be $(3.4 \pm 1.2) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}; this value agrees within experimental error with the results of other workers, shown in table 3. Poulet *et al.*[8] used a discharge-flow method with electron paramagnetic resonance or laser-induced fluorescence to measure [OH]: Loewenstein and Anderson[1] used the discharge-flow resonance-fluorescence technique.

As far as we know, ours are the first investigations of the temperature dependences of the reactions of OH with molecular chlorine and bromine; we can only compare our experimental results with estimates and theoretical predictions. Table 6 shows estimates of the Arrhenius parameters made by Jenkin *et al.*[9] by interpolation between data for the $OH+F_2$[10] and $OH+I_2$ reactions.

We have also calculated theoretical pre-exponential factors for the reactions of OH with the halogen molecules (see table 7) from simple collision theory. The values of the molecular diameters, $D(X_2)$, are derived from measurements of the second virial coefficient.[11] D(OH) was taken, from an electron density mapping study,[12] to be 354.5 pm.

If the pre-exponential factor, A, is equated with the collision frequency factor, Z', our room-temperature measurement of k_1 combined with the value of Z' implies an activation energy of 20.56 kJ mol^{-1} for the reaction $OH+Cl_2$, a value very close to the estimate of Jenkin *et al.*[9] Our measured pre-exponential factor for reaction (1) is much smaller than either the interpolated value or the collision frequency factor, and our activation energy is correspondingly lower. However, the experimental value of E_A is

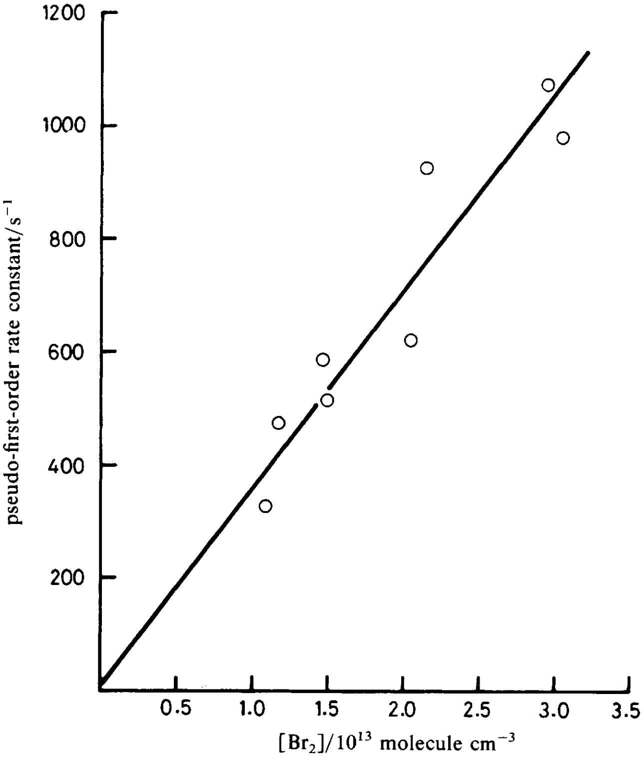

Fig. 5. Pseudo-first-order rate constant as a function of bromine concentration.

Table 3. Room-temperature values of k_2

$k_2/10^{-11}$ cm^3 molecule^{-1} s^{-1}	ref.
3.4 ± 1.2	this work
4.2 ± 0.7	8
5.28 ± 0.63	1

Table 4. Data used in numerical simulations

reaction	rate constant /cm^3 molecule^{-1} s^{-1}
$OH + Br_2 \rightarrow HOBr + Br$	4.8×10^{-11} [a]
$OH + HOBr \rightarrow HO_2 + BrO$	1×10^{-10} [b]
$OH + BrO \rightarrow HO_2 + Br$	1.0×10^{-11} [a]
$OH + Br + M \rightarrow HOBr + M$	1×10^{-14} [b,c]
$HO_2 + Br \rightarrow OH + BrO$	8×10^{-13} [a]

[a] Ref. (6). [b] Estimated value. [c] $[M] = 1.7 \times 10^{17}$ molecule cm^{-3}.

Table 5. Values of k_2 measured at various temperatures

T/K	$k_2/10^{-11}$ cm^3 molecule^{-1} s^{-1}
262	2.1 ± 1.2
273	2.5 ± 1.0
293	3.4 ± 1.2
303	3.0 ± 1.4

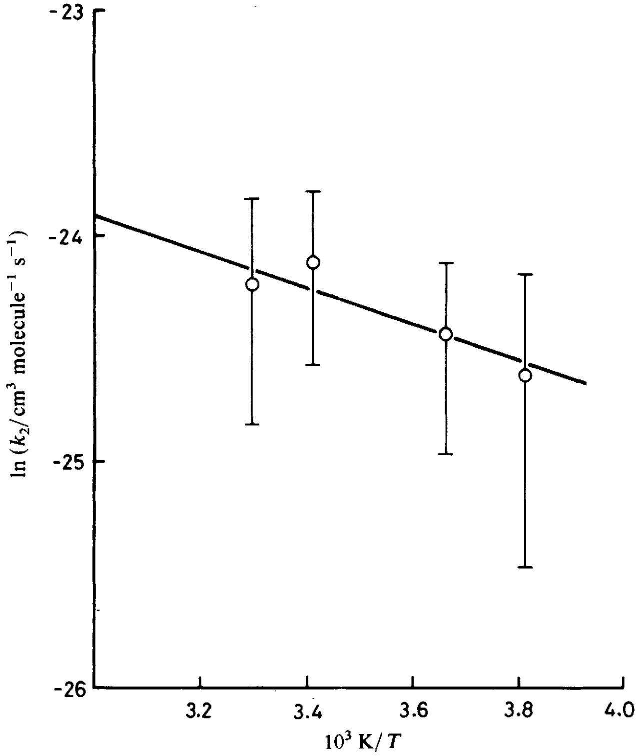

Fig. 6. Arrhenius plot for the reaction OH + Br_2.

supported by evidence from work on the reverse reaction:

$$Cl + HOCl \rightarrow OH + Cl_2 \qquad (4)$$

by Cook *et al.*,[13] who obtained a value of 1.08 kJ mol^{-1} for the reverse activation energy. The endothermicity of reaction (1) (4.3 kJ mol^{-1}) thus suggests a forward activation energy of 5.4 kJ mol^{-1}, a value comparable to ours. For process (2), the reaction between OH and Br_2, the meaning of the Arrhenius parameters must be considered further. Since the 95% confidence limits on E_A reach zero, it might be thought sensible to regard reaction (2) as being temperature-independent over the range studied. In that case, the weighted mean of the second-order rate constants is

$$k_2 = (2.8 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Table 6. Rate parameters for the reactions $OH+X_2$ at 298 K

X_2	$k/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$	$A/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$	$E_A/\text{kJ mol}^{-1}$
F_2	$7.4\times10^{-24\,a}$	$1.2\times10^{-10\,a}$	75.3^a
Cl_2	$5.5\times10^{-14\,a}$	$1.7\times10^{-10\,b}$	20.0^b
Cl_2	$6.8\times10^{-14\,c}$	$1.7\times10^{-12\,c}$	7.6^c
Br_2	$4.2\times10^{-11\,a}$	$1.7\times10^{-10\,b}$	3.5^b
Br_2	$2.8\times10^{-11\,c}$	$\not<2.8\times10^{-11\,c}$	0^c
Br_2	$3.4\times10^{-11\,a}$	$3.1\times10^{-10\,d}$	5.5^d
I_2	$2.1\times10^{-10\,e}$	$2.1\times10^{-10\,b}$	0.0^b

[a] Experimental value.[7,8,10] [b] Inferred value.[9] [c] This work. Pre-exponential factor for the Br_2 reaction will be correspondingly larger if there is any activation energy. [d] This work. *A* factor assumed equal to collision frequency factor, *Z'* (table 7). [e] Experimental value.[9]

Table 7. Collision frequency factors at 293 K[a]

X_2	$D(X_2)/\text{pm}$	$\sigma/10^{-19}\ \text{m}^2$	μ (amu)	$Z'/10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$
F_2	335.7	3.741	11.75	2.72
Cl_2	421.7	4.732	13.72	3.18
Br_2	429.6	4.829	15.37	3.07
I_2	516.0	5.952	15.93	3.72

[a] $D(OH)=354.5$ pm.[12]

and this value will also be the *A* factor. If there really is an activation barrier, then *A* must be correspondingly larger. Since *A* is most unlikely to exceed *Z'* (3.1×10^{-10} cm^3 molecule^{-1} s^{-1}; table 7), the maximum value of E_A that can be accommodated is *ca.* 5.5 kJ mol^{-1}, a value also permitted by the error range quoted for the experimental determination. Our realistic range for E_A is thus 0-5.5 kJ mol^{-1}, and that for *A* is 2.8×10^{-11} to 3.1×10^{-10} cm^3 molecule^{-1} s^{-1}.

Comparison of the predicted[9] values (table 6) of E_A with our experimental estimates shows both values to be small, and easily reconciled within experimental error. For the Cl_2 reaction, however, the predicted E_A is appreciably higher than the centre of our experimental range, and the predicted *A* factor thus two orders of magnitude larger than we find. Even the upper limit of our 95% confidence bounds for *A* is a factor of nearly 30 smaller than the prediction. We have discussed earlier additional arguments that support the measured activation energy, and hence the pre-exponential factor. Indeed, the value obtained seems eminently reasonable for a reaction involving OH. For example, for hydrogen-atom abstraction in the reaction $OH+HCl$, the pre-exponential factor is 2.6×10^{-12} cm^3 molecule^{-1} s^{-1}.[6] In the $OH+Br_2$ reaction the pre-exponential factor must be at least one order of magnitude larger, since the room-temperature rate constant (3×10^{-11} cm^3 molecule^{-1} s^{-1}) places a lower limit on the factor, even assuming that the activation energy is zero. The trend of increasing pre-exponential factor is continued with the $OH+I_2$ reaction, where the lower limit is 2.1×10^{-10} cm^3 molecule^{-1} s^{-1}.[9] It is not possible to make any firm statements about the $OH+F_2$ reaction because the measurements represent long extrapolations from imprecise determinations at flame temperatures, where the reaction probably does not even yield the products $HOF+F$, but rather $HF+F+O$. It is likely that the $OH+F_2$ data distort the interpolated predictions for Cl_2 in table 6. A question arises as to why the pre-exponential factors for the Br_2 and, especially, I_2 reactions are so large. One possible explanation is that the relatively large polarizabilities of the heavier halogens favour the encounters leading to a long-lived HOX_2 complex.

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