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Kinetic Studies of the Reactions of OH($X\ ^2\Pi$) with Hydrogen Chloride and Deuterium Chloride at Elevated Temperatures by Time-resolved Resonance Fluorescence ($A\ ^2\Sigma^+$–$X\ ^2\Pi$)

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We present a kinetic study of the reactions of the OH radical with the molecules HCl and DCl over the temperature range 300–700 K in order to investigate the 'intermediate' region between room-temperature measurements and flame investigations. Ground-state OH radicals were generated by the repetitive pulsed irradiation of H_2O vapour in a flow system, kinetically equivalent to a static system, and monitored in the time-resolved mode by resonance fluorescence at $\lambda = 307$ nm [OH($A\ ^2\Sigma^+ \rightarrow X\ ^2\Pi$), (0, 0)] following optical excitation. Decay profiles of the OH radical in the presence of HCl and DCl were constructed following pre-trigger photomultiplier gating, photon counting, signal averaging and computerised analysis. A specially constructed high-temperature stainless-steel reactor, particularly designed for photon-counting meausrements on a high-temperature system and critical to the extension of previous rate measurements of such reactions of OH by *ca.* 250 K, is described in detail with particular emphasis for procedures for minimising large background photon counts normally encountered in this type of system. The resulting rate data obtained in this investigation for the range 300–700 K may be summarised in the Arrhenius forms:

$$\text{OH}(X\ ^2\Pi) + \text{HCl}: k_R = (2.94 \pm 0.48) \times 10^{-12} \exp[-(446 \pm 32)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$\text{OH}(X\ ^2\Pi) + \text{DCl}: k_R = (4.04 \pm 0.74) \times 10^{-12} \exp[-(718 \pm 33)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

These data are compared with the results of temperature-dependent studies that have been carried out by direct monitoring of the OH radical, employing both resonance absorption and resonance fluorescence of OH(A–X), on pulsed systems and discharge–flow systems up to temperatures of 460 K. The extrapolation of these results to flame temperatures, for which rate data for the reaction between OH + HCl have been reported from mass-spectrometric sampling of stable molecules, is considered in some detail. The temperature dependence of the diffusional loss of OH($X\ ^2\Pi$), which dominates removal of the radical in the absence of HCl or DCl, when fitted to the standard form $k_{\text{diff}} = C + n \ln(T)$ yields $n = 1.77 \pm 0.14$. Estimates of the geometrical parameters for light collection of the resonance fluorescence signal, coupled with the measured temperature dependence for diffusional loss, in turn yields $D_{12}(\text{OH—He}) = 0.28 \pm 0.06\ \text{cm}^2\ \text{s}^{-1}$ at s.t.p. The observed temperature dependence is further considered quantitatively in terms of the appropriate Lennard-Jones parameters for interaction.

The determination of absolute rate data for the reactions of ground-state OH radicals with hydrogen halides is of both fundamental and practical interest. Kinetic isotope effects for the reactions of OH with HCl and DCl, for example, have been studied in some detail by Smith and Zellner[1] using a modified transition-state theory based on semi-empirical potential functions, including LEPS potentials and interaction energies based on the BEBO method,[2] to estimate properties of the transition state. Reactions of the OH radical with the hydrogen halides are also of direct relevance both to atmospheric chemistry[3,4] and to flames.[5,6] Absolute rate data for the reactions of OH + HCl and DCl, in particular, are therefore required for a wide temperature range, preferably resulting from direct monitoring of the OH radical.

The relatively recent compilations of Baulch *et al.*[7,8] summarise the various rate measurements that have been made up to 1981 on the reaction between OH + HCl, much of which has been determined by techniques depending either upon resonance absorption or resonance fluorescence employing OH($A\ ^2\Sigma^+$–$X\ ^2\Pi$). Four main studies of this reaction involving direct monitoring of OH as a function of temperature have been reported yielding different temperature dependences. Zahniser *et al.*[9] have studied the reaction in the temperature range 225–460 K using resonance fluorescence detection of OH on a discharge–flow system and report an activation energy $E/R = 310 \pm 10$ K. The time-resolved resonance absorption measurements of Smith and Zellner[1] in the range 210–460 K on OH following flash photolysis yielded $E/\boldsymbol{R} = 530 \pm 25$ K for this reaction and $E/\boldsymbol{R} = 780 \pm 35$ K for the reaction between OH and DCl. Ravishankara *et al.*[10] give a result of $E/\boldsymbol{R} = 470 \pm 40$ K for the reaction between OH and HCl from time-resolved resonance fluorescence on OH following flash photolysis in the temperature range 250–402 K. Hack *et al.*[11] obtained $E/\boldsymbol{R} = 313$ K for this reaction from e.p.r. measurements on OH in the temperature range 293–567 K. Of the various compilations,[7,8,12,13] the most recent[8] gives $E/\boldsymbol{R} = 514$ K for this reaction, essentially omitting the effect of the lower value reported by Hack *et al.*[11] However, there are significant differences in the compiled values[7,8,12,13] and also marginal variations in the Arrhenius parameters quoted from the same papers. The rate of the reaction between OH and HCl has been reported from measurements made by Wilson *et al.*[6] on CH_4O_2 flames inhibited by HCl. The system did not employ direct monitoring of OH, but involved complex measurements of concentration profiles of stable molecules in the flame obtained by mass-spectrometric sampling through quartz capillaries. The OH concentration was determined by measurements of the concentrations of CO and CO_2 and inferred from the reaction rate of $OH + CO \rightarrow CO_2 + H$. Thus these authors[6] report $k(OH + HCl,\ T = 1920\text{–}1940\ K) = 1.3 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$. There is clearly a large gap between the temperatures at which rate measurements have been carried out by direct monitoring of OH for this reaction (*ca.* 500 K; see earlier) and flame temperatures. This is a standard problem in gas kinetics and is often referred to in this context as the intermediate region. Jensen and Jones in their compilation[5] conclude that all the rate data for $k(OH + HCl)$ can be characterised by an activation energy of $E/\boldsymbol{R} = 1000$ K.

The present paper describes absolute rate data for the reactions between OH and HCl or DCl in the temperature range $T = 300$–700 K using time-resolved resonance fluorescence with photon counting on OH($A\ ^2\Sigma^+$–$X\ ^2\Pi$) following the pulsed irradiation of water vapour. This has involved major reconstruction of the system reported hitherto for our room-temperature measurements on OH with HCl, DCl, HBr and DBr.[14] In particular, we describe a new design for a high-temperature stainless-steel reactor for this work that may also be coupled to a heat-pipe oven for the study of reactions with alkali elements. Particular attention is paid to the crucial procedure for eliminating the large background counts necessarily generated when photon-counting equipment at room temperature is physically coupled to a high-temperature reactor. The present results, extending rate measurements at elevated temperatures on OH and HCl or DCl using direct monitoring by *ca.* 250 K, substantially supports the resonance absorption measurements on OH in the lower-temperature range (210–460 K) employed by Smith and

Zellner[1] and the resonance-fluorescence measurements on OH (250–402 K) by Ravishankara *et al.*[10] The high activation energy for the reaction between OH and HCl reported by Jensen and Jones[5] in their paper on flame chemistry was necessarily strongly influenced by the high-temperature rate reported by Wilson *et al.*,[6] which we consider too high.

EXPERIMENTAL

GENERAL

The general nature of the experimental arrangement for the kinetic investigation of OH by time-resolved resonance fluorescence $OH(A\,^2\Sigma^+ \rightarrow X\,^2\Pi)$ using photon counting following pulsed irradiation in the repetitive mode has been given in our earlier paper for rate processes studied at room temperature.[14] In constructing a high-temperature reaction system for the present investigation, the same principle of employing an orthogonal arrangement of (*a*) a repetitively pulsed irradiation source for the generation of $OH(X\,^2\Pi)$ from water vapour, (*b*) a microwave-powered spectroscopic source for optical excitation of $OH(A\,^2\Sigma^+ \leftarrow X\,^2\Pi)$ and (*c*) photon counting with signal averaging of the resulting resonance fluorescence at $\lambda = 307$ nm ($f = 8 \times 10^{-4}$),[15] follows that given previously in general terms for the room-temperature studies.[14] However, the construction of the high-temperature reactor was subject to a range of constraints arising from the physical coupling of this cell, operating up to $T = 700$ K, with the optical components, especially the photoelectric detection system which is designed to function at room temperature. The efficiency of this aspect of the procedure is, in turn, manifest by the magnitude of the background count rates against which the small photon count representing resonance fluorescence must be discriminated. For example, in the high-temperature resonance fluorescence studies of the reaction between OH and H_2 or D_2 described by Ravishankara *et al.*,[16] these authors indicate background count rates in the region of 100–200 kHz. After extensive efforts (see later) the background count was reduced in the present system to *ca.* 30 kHz. Finally, this reactor has been developed not only as a general-purpose high-temperature reactor but also specifically for the study of the kinetics of refractory species. The reactor has therefore been manufactured from stainless steel, which is inert to hot alkali-metal vapour, rather than quartz, which has been used in other high-temperature studies (*e.g.* those of Ravishankara *et al.*[16]). The design also includes the facility for flushing the various optical windows coupled to the reaction vessel with a small flow of some inert gas to prevent metal deposition, following the design of Fontijn and coworkers.[17]

THE REACTOR

The reaction vessel was constructed of stainless steel and mounted inside a fire-brick, electrically heated furnace capable of achieving temperatures up to *ca.* 1000 K. The reactor is essentially a broad cylinder (i.d. = 6 cm, $l = 10$ cm) capped conically in the direction of the photomultiplier detection system for greater light collection of the resonance-fluorescence signal with suitable optical baffling and mounted on a base plate holding a cassegrain mirror and vacuum coupled by means of a copper O-ring. The orthogonally placed optical ports, comprising (*a*) a plano-concave calcium fluoride lens ($d = 38$ mm, $f = 5$ cm at $\lambda = 180$ nm) for weak focussing of the pulsed irradiation source, (*b*) a quartz window for entry of the $OH[A\,^2\Sigma^+–X\,^2\Pi, (0, 0)]$ resonance radiation from the spectroscopic source and (*c*) the outlet quartz widow for passage of the resonance fluorescence signal to the interference filter and photoelectric detection system, were placed *ca.* 15 cm from the centre of the reaction vessel. They were all demountable by means of O-ring flanges and were water-cooled. The reactor was designed to act as both a mixing vessel for the flows and as a reaction vessel for the flash-photolysis experiment. This is in contrast to the room-temperature apparatus described previously[14] and to other studies using flash photolysis and resonance fluorescence [see *e.g.* ref. (16)] which have a separate mixing vessel to ensure that the flows are thoroughly mixed before they are introduced into the reaction vessel. This innovation has been made in the present design with a view to using the reactor to study alkali-metal kinetics, where reactions between the hot solid/liquid metal in a heat pipe and gaseous reagents such as water vapour have to be avoided. Indeed, one flow enters the reactor *via* stainless-steel tubing coaxial with that of the resonance-fluorescence source. This tube can also thus act as the heat pipe following the design of Vidal and Cooper.[18] With flow rates of the order of 5–50 sccm and total pressures of *ca.* 40 Torr ($1\ \text{Torr} = 133.3\ \text{N m}^{-2}$), measured and regulated by means of electronic flow meters (Advanced Semiconductor Materials model 261, which have been calibrated and checked against known flows of helium), simple gas-kinetic considerations indicate that mixing should readily be achieved in the reactor. The flows were permitted to equilibrate to a given temperature, controlled by means of a Eurotherm controller (model 020) to better than ±10 K and measured at three positions around the reactor by means of T1/T2 thermocouples, for at least 5 min before proceeding with kinetic measurements. Subsequent linearity in the plots of the first-order coefficients for the decay of OH($X\ ^2\Pi$), *i.e.* k' against [HCl, DCl] at given temperatures (see later), indicated that essentially complete mixing had been achieved. The maximum temperature for operation of the reactor of *ca.* 700 K was determined by the copper gasket, which had to be replaced periodically on account of oxidation at the higher temperatures.

THE PHOTOLYSIS SOURCE

By contrast with the Garton–Wheaton light source[19] employed previously[14] for the pulsed irradiation of water vapour to generate OH, the present measurements employed a more conventional nitrogen spark-discharge lamp operating at atmospheric pressure (1 μF, *ca.* 9 kV, $E = ca.$ 40 J, repetition rate 1 Hz). The output of the lamp reaching the reaction vessel was considerably enhanced by placing a concave mirror ($f = 10$ cm) behind the electrodes to focus the discharge onto the CaF_2 lens. This lens was seen to improve significantly the optical coupling from the spark discharge to the centre of the reaction vessel, as judged from the observed yields of OH($^2\Pi$), by the use of a CaF_2 lens compared with a high-purity quartz lens (Spectrosil, $\lambda > 165$ nm), a material employed by Ravishankara *et al.*[16] and which was tested in the present system. This can readily be justified by treating the spark discharge as crudely approximating to a black body of $T \approx 6500$ °C following Christie and Porter.[20] Thus, integrating the light output of this source over the extinction coefficient of water vapour,[21] attenuated by the light transmission of high purity quartz and CaF_2,[22] indicates that the overall yields of OH($X\ ^2\Pi$) should be approximately in the ratio of two to one, and this is empirically observed in the magnitudes of the resonance fluorescence signals obtained here. It should, however, be noted that at high temperatures, > *ca.* 700 K, CaF_2 starts to be degraded because of the formation of colour centres.[17]

We have previously discussed[14] the main photochemical processes for the photolysis of H_2O in the low-wavelength regions, $\lambda < 240$ nm, $\lambda < 177$ nm and $\lambda < 140$ nm, following Okabe,[21] that is the primary production of OH($X\ ^2\Pi$), the chemical reaction of the photochemically generated O($2\ ^1D_2$) to yield OH($X\ ^2\Pi$),[23-25] optical[15] and collisional[26] relaxation of the photochemically produced OH($A\ ^2\Sigma^+$) and physical relaxation of the small quantity of OH($X\ ^2\Pi$, $v'' = 1$) that is also produced.[27] Thus O($2\ ^1D_2$), OH($A\ ^2\Sigma^+$) and OH($X\ ^2\Pi$, $v'' = 1$) are rapidly converted into OH($X\ ^2\Pi$, $v'' = 0$) during the time-scales over which the decays of OH are monitored in these experiments.

SPECTROSCOPIC RESONANCE SOURCE

A minor modification to the microwave-powered flow emission source for optical excitation of OH($X\ ^2\Pi$) to OH($A\ ^2\Sigma^+$) [apart from small variations in operating conditions compared with those employed previously[14] (2% H_2O + He, $p_{\text{total}} \approx 0.8$ Torr, incident power 150 W employed here)] was found to have a dramatic effect on the background count from scattered light, reducing it to a level that allowed the present photon-counting electronics to be used with the reactor described above. The general arrangement, as before,[14] employed a quartz flow lamp and an air-cooled Fehsenfeld cavity.[28] However, in this case a pinched plasma using quartz tubing of internal bore *ca.* 5 mm replaced the straight quartz tubing of o.d. *ca.* 12 mm that fitted the cavity geometry. The resonance source was placed *ca.* 60 cm from the appropriate cooled quartz entrance of the reactor and carefully focussed by means of two quartz lenses of focal lengths 10 and 15 cm along the axis of the entrance side arm, through the centre of the reactor.

RESONANCE FLUORESCENCE DETECTION AND ANALYSIS

Following pulsed irradiation of the water vapour, the resonance fluorescence signal at $\lambda = 307$ nm was monitored in the photon-counting mode and analysed essentially as described previously.[14] Some optical discrimination was achieved by means of a broad-band interference filter (Barr and Stroud, type U1). It was, however, found necessary in these measurements also to reduce the very large long-wavelength background count from the hot reaction-vessel walls that is observed at higher temperatures, using a long-wavelength blocking filter (Oriel Scientific, type UG11, thickness 3 mm; percentage transmission at $\lambda = 307$ nm *ca.* 74, percentage transmission at $\lambda = 614$ nm < 0.1). The resonance-fluorescence signals were monitored by means of the E.M.I. 9816 QB photomultiplier tube (1.8 kV, Fluke 408B power supply) employed for the room-temperature resonance-fluorescence studies[14] using the 'pre-trigger' photomultiplier gating circuitry previously described,[14,29] initiated by means of a thyratron 'double pulser' ($\Delta t = 75$ μs).[14,29] All measurements described here employed a 'gate-on' time[14,29] of 250 μs. It was found that as a result of the physical coupling between the photomultiplier housing and the high-temperature stainless-steel reactor, the photomultiplier tube itself became warm (>30 °C) and the measured dark-current count increased by an order of magnitude and could not be discriminated out using the Panax Nucleonics AAU-11 discriminator. A flow of cooled air was therefore introduced into the photomultiplier housing to reduce the dark current below 500 Hz. It was found that at high temperatures the resonance fluorescence signal became weak compared with the scattered light from the flash. This was possibly due to degradation of the CaF_2 lens by infrared radiation from the hot centre of the reaction vessel,[17] although it was also observed that extraneous material from the surface of the stainless steel, which was always initially baked out, was deposited on the cooled optical windows. Under these conditions of low signal, a procedure was usually adopted of subtracting from the accumulated total of 200–500 shots approximately the same number of flashes with the resonance lamp turned off. This takes account of both scattered light from the flash and fluorescence from $OH(A\,^2\Sigma^+)$ produced in the flash ($\lambda < 140$ nm). The histogram stored in the DL406 multi-scalar following the data-capture procedure described hitherto[14] thus represents the fluorescence decay signals, $I_F(t)$ ($\lambda = 307$ nm), representing the summation of at least 128 individual sets of photon counts, but at higher temperatures it was often necessary to increase this to 512 individual pulses. The output was subsequently fed onto paper tape in ASCII code (Data Dynamics Punch 1133) for direct input into the University of Cambridge IBM 3081 computer.

MATERIALS

All materials were prepared and used as described previously[14] except for DCl, which was prepared from the reaction of D_2O (isotopic purity > 99.8%) with $SiCl_4$, under vacuum conditions (<10 mTorr). It was then thoroughly purified by repeated distillation from ethanol slush temperature (−117 °C) to −196 °C, and was shown from an infrared spectrum to have a purity greater than the cylinder DCl (B.O.C., 99% stated purity) used previously.[14]

RESULTS AND DISCUSSION

Concentrations of water vapour significantly larger than those employed for the room-temperature resonance-fluorescence studies of OH that were described previously[14] (*i.e.* 150–300 mTorr in the present study compared with <100 mTorr

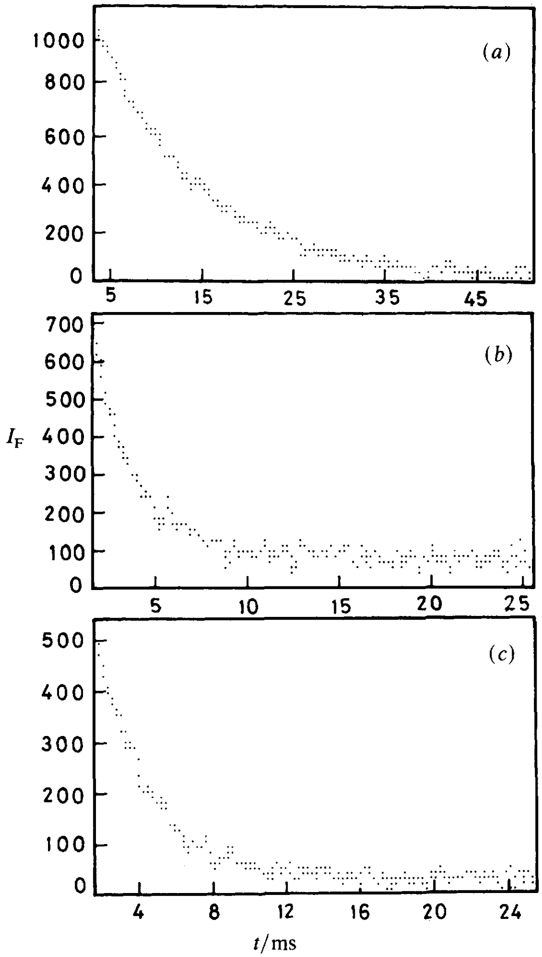

Fig. 1. Digitised time-variation of the light intensity at $\lambda = 307$ nm indicating the decay of resonance fluorescence [I_F, counts per channel, (0, 0), $A\ ^2\Sigma^+ - X\ ^2\Pi$] from ground-state OH radicals following the pulsed irradiation of H_2O in the presence of HCl and DCl at $T = 298$ K. $E = 40$ J; repetition rate = 1 Hz; no. of channels = 256; $p_{\text{total with He}} = 5.5$ kN m^{-2}; smoothed data. (*a*) $p_{H_2O} = 40$ N m^{-2}, no. of individual experiments = 128; (*b*) $p_{H_2O} = 36$ N m^{-2}, $p_{HCl} = 2.2$ N m^{-2}, no. of individual experiments = 256; (*c*) $p_{H_2O} = 36$ N m^{-2}, $p_{DCl} = 2.6$ N m^{-2}, no. of individual experiments = 256.

previously), and approximately of the same magnitude as employed by Ravishankara *et al.*,[16] were required in order to generate radical concentrations suitable for kinetic studies, particularly at the elevated temperatures on account of the physical constraints of the reactor design. Fig. 1(*a*) shows an example of the computerised output of the digitised time-variation of the light intensity at $\lambda = 307$ nm, indicating the decay at 300 K of resonance fluorescence (I_F) from ground-state OH radicals following the pulsed irradiation of water vapour in the presence of excess helium, the buffer gas employed in these measurements. The data smoothing, employed purely for visual presentation, followed the procedure of Savitsky and Golay.[30] The data in fig. 1(*a*) are of comparable quality to decay traces for OH presented previously employing lower pressures of H_2O.[14] Again, we must stress for reasons concerned with estimation of diffusion coefficients (see later) that order-of-magnitude calculations of rates of radical–radical reactions based on rate data given in the compilation of Baulch *et al.*[31] show such processes to make negligible contributions in this system, in accord with the results of rate measurements made on OH reported by Davis *et al.*[32] The removal of OH under the conditions of fig. 1(*a*) is principally by diffusion. Fig. 1(*b*) and (*c*) show examples of the effect of, respectively, the addition of HCl and DCl on the decay of OH at this temperature (300 K). Similar sets of results were obtained with increasing temperature but exhibited a regular reduction in the quality of the computerised output because of the poorer signal-to-noise ratios, and the consequent need to construct decay traces for OH from a larger number of individual experiments.

We have discussed in detail[14] the expression for the resonance fluorescence from the decay of OH, which is given by

$$I_F(t) = \phi[\mathrm{OH}]_{t=0} \exp(-k't)/(1 + k_Q[\mathrm{Q}]/A_{nm}) \qquad \text{(i)}$$

where the symbols have their usual significance and where the term $k_Q[\mathrm{Q}]$ represents an average first-order contribution to the collisional quenching of $\mathrm{OH}(A\,^2\Sigma^+, v' = 0)$ in the various rotational states.[14] Radiation trapping[33] can clearly be neglected at the low concentrations of OH involved in these experiments, as indicated by the low photon counts due to this transient species and the low *f*-value for the (0, 0) transition ($f = 8 \times 10^{-4}$).[15] Thus the value of $A_{nm}[\mathrm{OH}(A\,^2\Sigma^+ - X\,^2\Pi), (0,0)]$ in eqn (i) can be taken as *ca.* $1.4 \times 10^6\ \mathrm{s}^{-1}$.[15] The temperature dependence of the collisional quenching coefficients, k_Q, should be taken into consideration, particularly for $\mathrm{Q} = H_2O$, since this may be a further factor which causes a reduction in the observed fluorescence signal at elevated temperatures. Vonogradov and Vilesov[34] report a linear dependence of $k_Q(\mathrm{Q} = H_2O)$ for the fluorescence quenching of $\mathrm{OH}(A\,^2\Sigma^+)$ in the temperature range $T = 300$–600 K. However, more recently Fairchild *et al.*[35] have clearly shown that this quantity is sensibly independent of temperature up to $T \approx 1430$ K and their value of $k[\mathrm{OH}(A\,^2\Sigma^+) + H_2O] = 4.7 \times 10^{-10}$ $\mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ is employed here. This result, coupled with the observation of negligible quenching by He,[36] yields $k_Q[\mathrm{Q}]/A_{nm} = 3.2$ for the conditions of fig. 1(*a*). This fractional loss of $\mathrm{OH}(A\,^2\Sigma^+)$ by fluorescence quenching is larger than values for this quantity employed for the conditions of the earlier room-temperature experiments.[14] In the absence of radiation trapping, where the effective value of A_{nm} is $f\{[\mathrm{OH}(X\,^2\Pi)]\}$, the collisional-quenching term, $k_Q[\mathrm{Q}]/A_{nm}$, does not affect the time dependence of the resonance fluorescence from which the overall first-order coefficient for the decay of $\mathrm{OH}(k')$ is derived, but only the sensitivity.[14,33]

Fig. 2 shows standard first-order kinetic plots [$\ln(I_F)$ against *t*] for the data given in fig. 1. These are presented solely to demonstrate sensible first-order decays for the OH radical in these experiments. The raw data of the type indicated in fig. 1 are analysed computationally by means of the now standard form:

$$I_F(t) = \theta_1 + \theta_2 \exp(-k't) \qquad \text{(ii)}$$

using the LAMFIT procedure of Powell[37] as before.[14] The greater relative contribution to the signal by the steady scattered-light component, θ_1, with increasing temperature can be seen from the ratio θ_2/θ_1 which yields, for example, $\theta_2/\theta_1 \approx 9.5$ and 4 for $T = 300$ and 573 K, respectively. Thus, simplified first-order plots of the type given in fig. 2 become increasingly curved at higher temperatures. The property

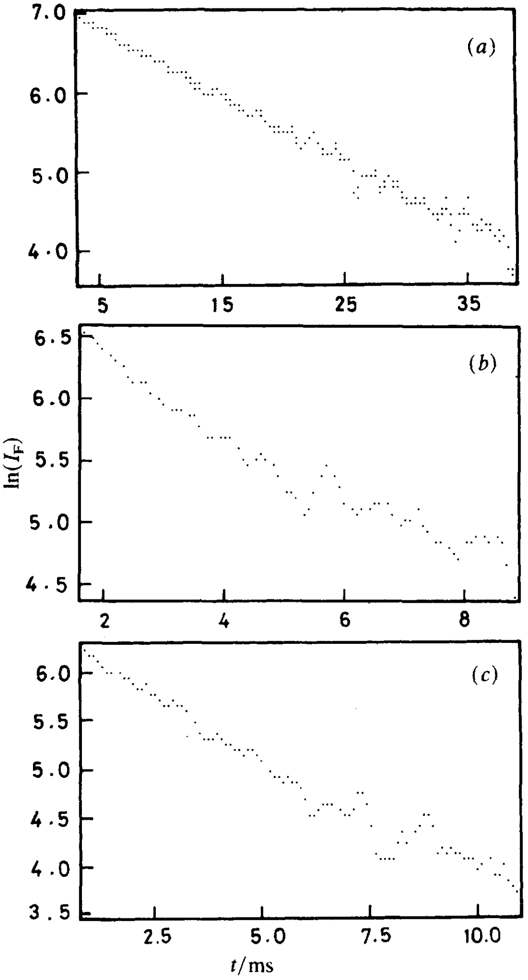

Fig. 2. Pseudo-first-order plots of the fluorescence intensity [ln(I_F)] at $\lambda = 307$ nm indicating the decay of resonance fluorescence from ground-state OH radicals following the pulsed irradiation of H_2O in the presence of HCl and DCl at $T = 298$ K. $E = 40$ J; repetition rate = 1 Hz; no of channels = 256; $p_{\text{total with He}} = 5.5$ kN m^{-2}; smoothed data. (*a*) $p_{H_2O} = 40$ N m^{-2}, no. of individual experiments = 128; (*b*) $p_{H_2O} = 36$ N m^{-2}, $p_{HCl} = 2.2$ N m^{-2}, no. of individual experiments = 256; (*c*) $p_{H_2O} = 36$ N m^{-2}, $p_{DCl} = 2.6$ N m^{-2}, no. of individual experiments = 256.

of kinetic interest, k', is thus always determined by computerised analysis of the raw data through eqn (ii).

For a given temperature, k' is expressed in the form

$$k' = K + k_R[R] \qquad \text{(iii)}$$

where R = HCl or DCl and k_R is the appropriate absolute second-order reaction rate constant for OH at that temperature; K represents the loss of OH, primarily by diffusion out of the reaction volume probed by the resonance lamp in the centre of the vessel, and is identified with k_{diff}.

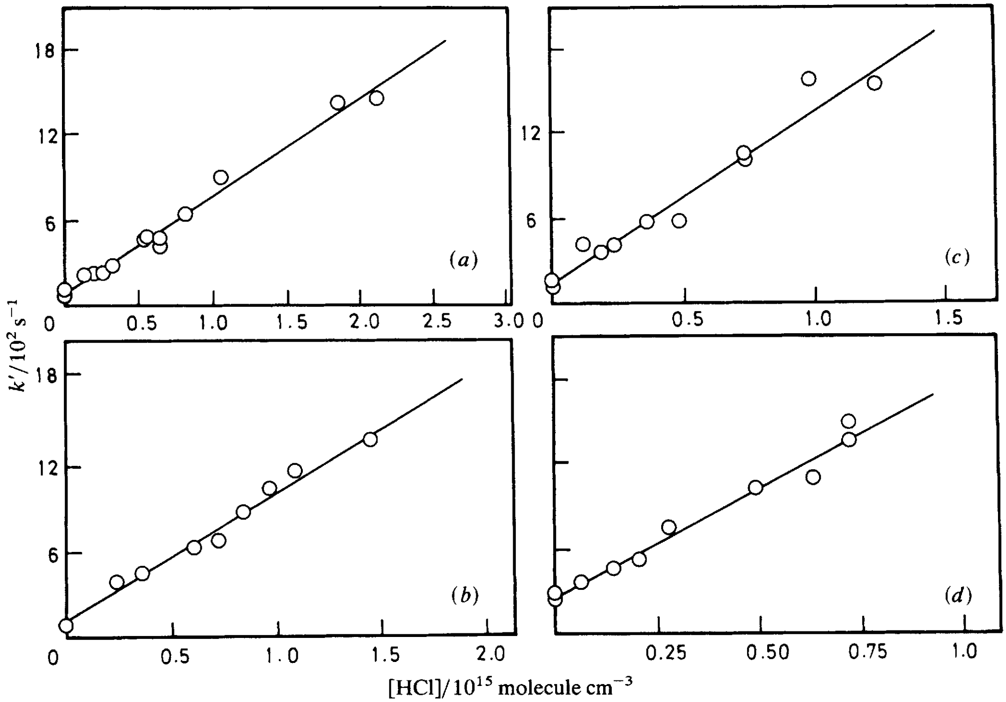

Fig. 3. Variation of the pseudo-first-order rate coefficient (k') at various temperatures for the decay of OH in the presence of HCl obtained by time-resolved resonance fluorescence at $\lambda = 307$ nm following the pulsed irradiation of H_2O. T/K: (*a*) 300, (*b*) 373, (*c*) 473 and (*d*) 573.

Plots based on eqn (iii) are given in fig 3 and 4 for the reaction of OH with HCl and DCl, respectively, at the temperatures $T = 300$, 373, 473 and 573 K. Fig. 5 shows the data for OH and HCl or DCl at $T = 700$ K, which is the region of highest temperature for the reaction of OH($X\ ^2\Pi$) studied by resonance fluorescence with the present system.

In accord with procedures for the presentation of rate constants used in data compilations,[7,8,12,13] the rate constants for the reactions of OH with HCl and DCl at the individual temperatures are listed in table 1. (The errors that are quoted refer to two standard deviations.)

First, we may note the agreement with the room-temperature data for k_R(OH+HCl) obtained with this system (table 1) compared with our previous result [k_R(OH+HCl) = $(6.66 \pm 0.52) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}][14] and with the 'preferred value' from a standard compilation[7] (6.6×10^{-13} cm^3 $molecule^{-1}$ s^{-1}) for what can be regarded as a kinetic standard at room temperature. Secondly, the room-temperature result for k_R(OH+DCl) is in accord both with our earlier result using resonance fluorescence [k_R(OH+DCl) = $(3.48 \pm 0.30) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}][14] and that derived from resonance-absorption measurements on OH reported by Smith and Zellner [k_R(OH+DCl) = 3.43×10^{-13} cm^3 $molecule^{-1}$ s^{-1}].[1]

The Arrhenius plots [ln (k_R) against K/T] for the data from the present study are given in fig. 6(*a*) and (*b*) for HCl and DCl, respectively. Weighted least-squares

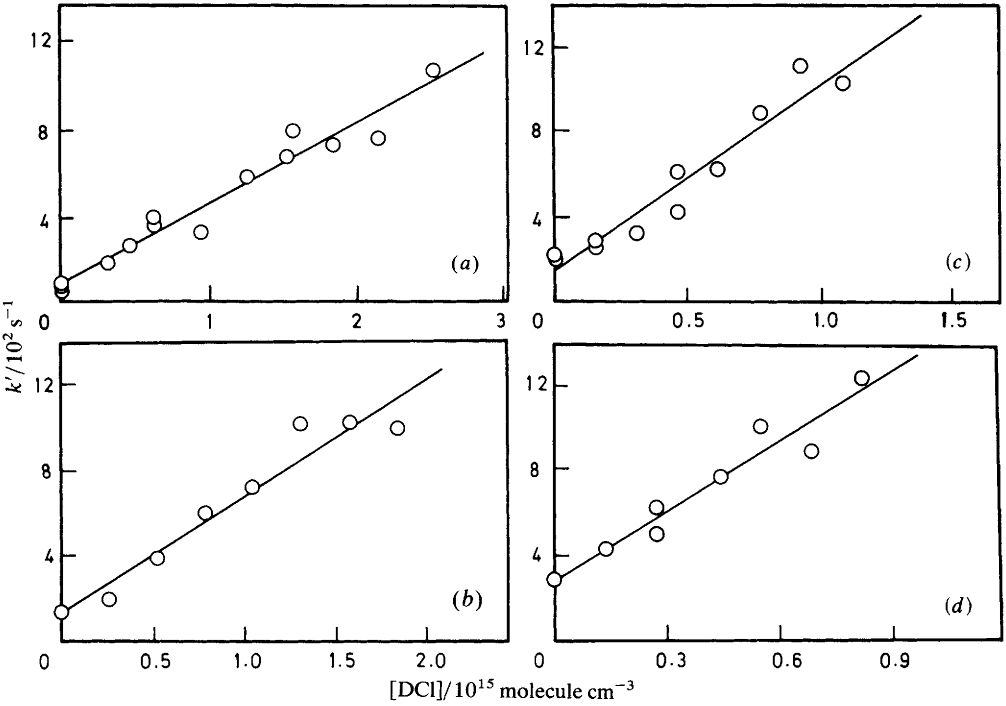

Fig. 4. Variation of the pseudo-first-order rate coefficient (k') at various temperatures for the decay of OH in the presence of DCl obtained by time-resolved resonance fluorescence at $\lambda = 307$ nm following the pulsed irradiation of H_2O. T/K: (*a*) 300, (*b*) 373, (*c*) 473 and (*d*) 573.

Table 1. Absolute second-order rate constants ($k_R/\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$) for the reaction of OH($X\ ^2\Pi$) with HCl and DCl in the temperature range 300–700 K determined by time-resolved resonance fluorescence at $\lambda = 307$ nm [OH($A\ ^2\Sigma^+$–$X\ ^2\Pi$), (0, 0)]

T/K	k_R(OH+HCl)	k_R(OH+DCl)
300	$6.7 \pm 0.46 \times 10^{-13}$	$3.75 \pm 0.22 \times 10^{-13}$
373	$9.1 \pm 0.76 \times 10^{-13}$	$5.59 \pm 0.59 \times 10^{-13}$
473	$1.21 \pm 0.16 \times 10^{-12}$	$8.70 \pm 0.77 \times 10^{-13}$
573	$1.39 \pm 0.14 \times 10^{-12}$	$1.10 \pm 0.12 \times 10^{-12}$
700	$1.46 \pm 0.16 \times 10^{-12}$	$1.52 \pm 0.14 \times 10^{-12}$

analyses of the data in table 1 yield the following results, presented in the form normally employed in the standard compilations [*e.g.* ref. (7)]:

$$k_R(\text{OH+HCl}) = (2.94 \pm 0.48) \times 10^{-12} \exp[-(446 \pm 32)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$k_R(\text{OH+DCl}) = (4.04 \pm 0.74) \times 10^{-12} \exp[-(718 \pm 33)/T]\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

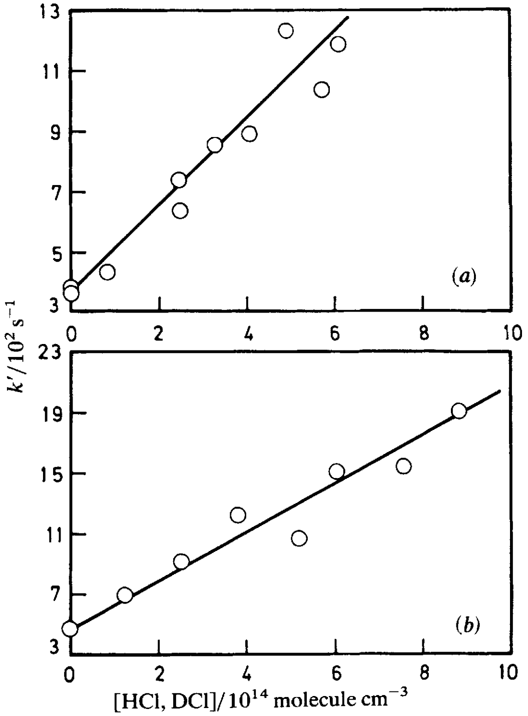

Fig. 5. Variation of the pseudo-first-order rate coefficient (k') for the decay of OH in the presence of (*a*) HCl and (*b*) DCl at $T = 700$ K obtained by time-resolved resonance fluorescence at $\lambda = 307$ nm following the pulsed irradiation of H_2O.

These results are compared in table 2 with data derived from previous determinations of the temperature-dependence of these reaction rate constants. (All errors are given as two standard deviations.)

Our results for $k_R(OH+HCl)$ are in better accord with the data from time-resolved resonance fluorescence measurements of Ravishankara *et al.*[10] than those of Smith and Zellner[1] obtained from time-resolved resonance absorption, although the difference is small and the overall agreement with both sets of data up to 460 K is good. The flash-photolysis studies therefore indicate an average activation energy of *ca.* 480 K, which is *ca.* 60% higher than the value of 310 K obtained by Zahniser *et al.*[9] (table 2) and the small temperature dependence of 313 K reported by Hack *et al.*,[11] both using discharge–flow systems. The reasonable agreement between the three flash-photolysis studies, where OH radicals were generated by the photolysis of either water vapour, an $N_2O + H_2$ mixture[1] or an $O_3 + H_2$ mixture,[10] demonstrates the independence of the flash-photolysis results upon OH radical generation methods. Whilst there is good agreement between the flash-photolysis and discharge–flow studies at room temperature, there is the possibility that the interference of secondary reactions at higher termperatures has resulted in a low estimate of the activation energy from discharge–flow studies.[9,11]

Jensen and Jones[5] did not consider the form of their expression for $k_R(OH+HCl)$ in table 2 to constitute a compilation in the standard sense, but simply presented it in that form to indicate the activation energy required to reconcile the magnitudes

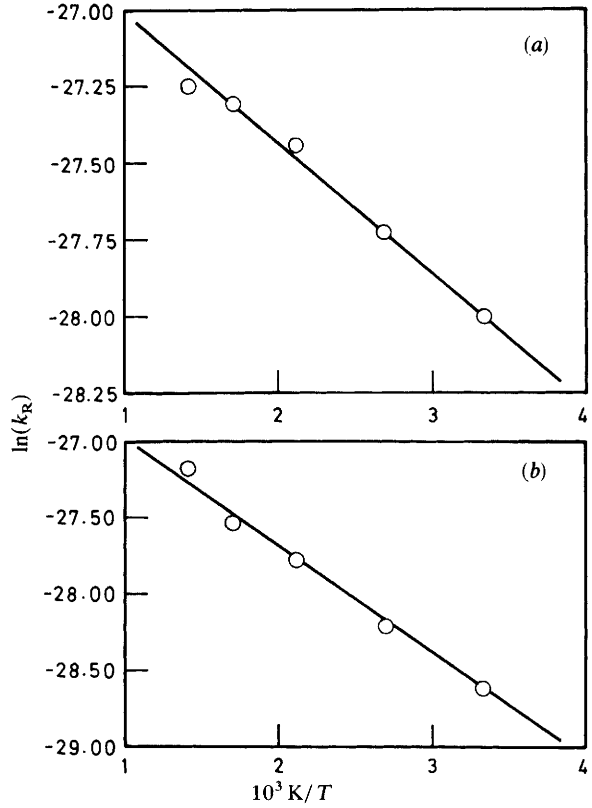

Fig. 6. Arrhenius plots [ln(k_R) against K/T] for the reaction of OH($X\,^2\Pi$) with (*a*) HCl and (*b*) DCl in the temperature range 300–700 K.

of the rate data in the region of room temperature and in flames. Extrapolation of the result from the present study to the mean flame temperature for which k_R(OH+HCl) was reported yields k_R(OH+HCl, $T = 1930$ K) $= 2.2 \times 10^{-12}$, which may be compared with the reported value at this temperature of 1.3×10^{-11} cm^3 molecule^{-1} s^{-1}.[6] Indeed, Wilson *et al.*[6] considered their value possibly to be low on account of HCl formation in the flame. All the measurements of the temperature dependence of this reaction rate,[1,9-11] including the present work, would conclude that the flame datum is too high by about a factor of ten. This discrepency must presumably lie in the necessary simplifications required to extract the rate data from the complex medium of the flame and it indicates the possible participation of processes in the flame which remove HCl and which were not accounted for.

Our result for the temperature dependence of k_R(OH+DCl) (table 2) is in good accord with that reported by Smith and Zellner[1] for the range 210–460 K. These two sets of data for resonance absorption and fluorescence for OH(A–X) clearly overlap. Ideally, further development in technique is required to extend rate measurements involving direct monitoring of OH either by absorption or fluorescence if extrapolation of rates for OH+HCl and DCl to flame temperatures is to be made with fuller confidence. Takacs and Glass[38] have made a similar estimate

Table 2. Absolute second-order rate data in Arrhenius form, $k_R = A\exp(-B/T)$

temperature range/K	$A/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	B/K	method
	OH+HCl		
300–700	$2.94 \pm 0.48 \times 10^{-12}$	446 ± 32	(*)[a]
225–460	$2.0 \pm 0.2 \times 10^{-12}$	310 ± 20	(9)[b]
210–460	$4.1 \pm 2.0 \times 10^{-12}$	530 ± 25	(1)[c]
250–402	$3.3 \pm 0.3 \times 10^{-12}$	470 ± 40	(10)[a]
293–567	$2.0 \pm 1.0 \times 10^{-12}$	310 ± 20	(11)[d]
220–300	2.96×10^{-12}	425	(12)[e]
220–300	3.0×10^{-12}	425	(13)[e]
210–460	3.0×10^{-12}	425	(7)[e]
210–500	3.74×10^{-12}	514	(8)[e]
210–1940	2×10^{-11}	1000	(5)[f]
	OH+DCl		
300–700	$3.42 \pm 0.36 \times 10^{-12}$	718 ± 33	(*)[a]
210–460	$4.7 \pm 2.0 \times 10^{-12}$	780 ± 35	(1)[c]

* This work. [a] Time-resolved resonance fluorescence OH(A–X)+flash photolysis. [b] Steady resonance fluorescence OH(A–X)+discharge flow. [c] Time-resolved resonance absorption OH(A–X)+flash photolysis. [d] E.p.r. spectroscopy. [e] Compilation. [f] Compilation with best fit to include flame data.

of the activation energy for the reaction between OH+HCl ($E = 8.6\ \mathrm{kJ\ mol^{-1}}$, $E/\boldsymbol{R} = 1034$ K) to that indicated by Jensen and Jones[5] ($E/\boldsymbol{R} = 1000$ K) in order to combine rate data for this reaction determined by e.p.r. at room temperature[38] with the flame data.[6] Both Takacs and Glass[38] and Smith and Zellner[1] recognise that the Arrhenius plot may well be curved over such a wide temperature range, although the curvature that would be required to reconcile the flame data with the various measurements indicated in table 2 is not apparent from the present measurements. It may be the case that Jensen's and Jones's Arrhenius extrapolation[5] constitutes the best practical procedure for estimating the rate at flame temperatures, notwithstanding differences in Arrhenius forms for lower-temperature regimes, until the detailed form of the curvature is established. On the other hand, the range of the measurements made at lower temperatures indicates that the value of k_R(OH+HCl) at flame temperatures is too large.

Finally, whilst subsidiary to the primary concern of this paper, some detailed consideration may be given to the term K in eqn (iii), which we have indicated may be ascribed to diffusional loss of OH($X\,^2\Pi$) as opposed to removal by secondary reactions following the photolysis of H_2O. Fig. 3–5 indicate that the measurements we have carried out have been taken at essentially the same total pressure (*i.e. ca.* $5.6\ \mathrm{kN\ m^{-2}}$). Hence the intercepts of these plots (fig. 3–5) which we may term k_{diff} provide a measure of the diffusional loss as a function of temperature. k_{diff}, in turn, can be approximated to the 'long-time' solution of the diffusion equation for a cylinder:[39,40]

$$k_{\mathrm{diff}} = (\pi^2/l^2 + 2.41^2/r^2)D_{12}. \qquad \text{(iv)}$$

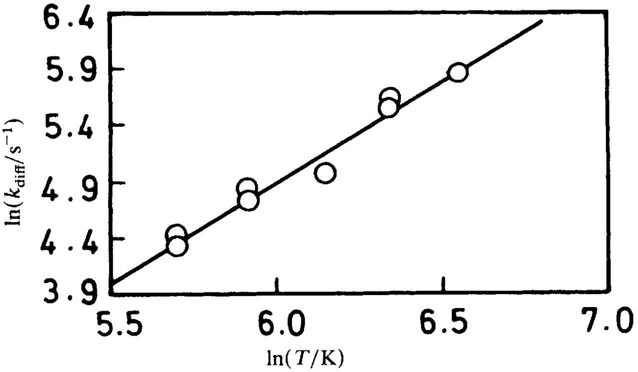

Fig. 7. Variation of the first-order contribution to the loss of OH($X\ ^2\Pi$) by diffusion (k_{diff}) as a function of temperature [ln(k_{diff}) against ln(T/K)] in the rage 300–700 K following the pulsed irradiation of H_2O in the presence of excess helium buffer gas (p_{He} = 5.6 kN m^{-2}).

The geometrical parameters in eqn (iv) can only be approximately defined ($l \approx 2$ cm, $r \approx 0.75$ cm) as these are determined by the constraints of the light-baffle system and the geometry of the light-gathering section of the optical detection system, a standard limitation in time-resolved resonance fluorescence measurements. These parameters do not, however, affect the determination of the temperature dependence of D_{12}[OH($X\ ^2\Pi$)—He]. It is customary to express this in the form

$$\ln(D_{12}) = C + n \ln(T). \qquad \text{(v)}$$

Fig. 7 shows the equivalent plot to eqn (v) of ln(k_{diff}) against ln(T) taken from the data in fig. 3–5, yielding $n = 1.77 \pm 0.14$. This can be compared with the value of $n = 1.5$ from simple gas-kinetic theory and with the examples of the values of n lying between 1.6 and 1.9 for the diffusion of CO_2 in flames[41] and $n = 1.89$ for the diffusion of water in air at high temperatures.[42] Finally, the data of fig. 7, coupled with eqn (iv) and (v) and the above geometrical parameters, yield D_{12}[OH($X\ ^2\Pi$)—He] (s.t.p.) = 0.28 ± 0.06 cm^2 s^{-1} (2σ). This is of the same order of magnitude as the diffusion coefficients that have been reported for a range of atoms. Hence the kinetic data in fig. 3–5 yield both the expected temperature dependence of D_{12}[OH—He] and its absolute magnitude.

Particularly accurate data for the dependence of the diffusion coefficient on temperature are required in order to model the measured macroscopic property, D_{12}, to the standard Lennard-Jones parameters, σ_{12} and ε_{12}, using the 'first-approximation' Chapman–Enskog equation.[43,44] We have used the data in fig. 7 for the standard procedure[43] of fitting D_{12}(OH—He) expressed in terms of the Chapman–Enskog equation using the modified form[45] of Buckingham's method[46] normally employed for deriving potential interaction parameters from measurements of second virial coefficients. Whilst the routine technique of seeking 'localised intersections'[43–46] yields values of σ_{12} in the range 3.42–3.90 Å, wider variation is found in the accompanying values of ε_{12} satisfying the data of fig. 7 (ε_{12}/k = 257–125 K). There are clearly limitations in using a spherical Lennard-Jones model for fitting data on D_{12}(OH—He) as a function of temperature where one species is highly polar [μ(OH) = 1.98 D].[47] However, average values of σ_{12} = 3.66 Å and ε_{12}/k = 190 K, when used in the Chapman–Enskog equation,[43] yield values of D_{12}(OH—He) that are in sensible accord with the data obtained here, as seen in

Table 3. Comparison of diffusion coefficients [D_{12}(OH—He)/cm^2 s^{-1} at atmospheric pressure] calculated on the basis of the first-approximation Chapman–Enskog equation using the Lennard-Jones parameters $\sigma_{12} = 3.66$ Å and $\varepsilon_{12}/\boldsymbol{k} = 190$ K with experimental data

T/K	D_{12} (calc.)	D_{12} (exptl)
300	0.34	0.34
373	0.51	0.51
473	0.79	0.62
573	1.11	1.15
700	1.57	1.58

table 3. Whilst the fit is not ideal, the values of σ_{12} and ε_{12} do provide a basis of extrapolating D_{12}(OH—He) to the conditions of flame temperatures.

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