Atmospheric Chemistry of PCBs, PCDDs and PCDFs

ROGER ATKINSON

1 Introduction

Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (see Figure 1) are emitted into the atmosphere from the combustion of chlorine-containing materials.\(^1\)\(^-\)\(^{13}\) Additionally, PCBs, which were used as lubricants and dielectric fluids,\(^1\)\(^-\)\(^{13}\) are volatilized into the atmosphere from soils and bodies of water (for example, from the Great Lakes) after their disposal or inadvertent release into, and cycling through, the environment.\(^1\)\(^,\)\(^{14}\)\(^-\)\(^{18}\) Atmospheric concentrations of PCBs, PCDDs and PCDFs have been measured at numerous locations,\(^2\)\(^,\)\(^{15}\)\(^,\)\(^{16}\)\(^,\)\(^{19}\)\(^-\)\(^{62}\) and these organochlorine

compounds have been observed in the atmosphere in remote areas of the world,\textsuperscript{19,32,36,40,48,50,56} including over the Pacific Ocean\textsuperscript{19,56} and in the Arctic.\textsuperscript{32,36,40,48,49} To date, mainly for health risk assessment, the published ambient air measurements of the PCDDs and PCDFs have dealt almost exclusively with the tetrachloro- to the octachlorodibenzo-\(p\)-dioxins, and dibenzofurans. The observations of these organochlorine compounds in lakes and ocean waters remote from direct sources (for example, those in Arctic regions such as northern Canada and Alaska) confirm the occurrence of long-range

\begin{footnotesize}
\begin{itemize}
\item \textsuperscript{26} T. F. Bidleman, U. Wideqvist, B. Jansson and R. Söderlund, \textit{Atmos. Environ.}, 1987, 21, 641.
\item \textsuperscript{27} R. Wittlinger and K. Ballschmiter, \textit{Chemosphere}, 1987, 16, 2497.
\item \textsuperscript{29} W. Christmann, K. D. Klöppel, H. Partscht and W. Rotard, \textit{Chemosphere}, 1989, 19, 521.
\item \textsuperscript{34} C. Rappe, S. Marklund, L.-O. Kjeller and A. Lindskog, \textit{Chemosphere}, 1989, 18, 1283.
\item \textsuperscript{37} P. Larsson and L. Okla, \textit{Atmos. Environ.}, 1989, 23, 1699.
\item \textsuperscript{40} T. F. Bidleman, G. W. Patton, M. D. Walla, B. T. Hargrave, W. P. Vass, P. Erickson, B. Fowler, V. Scott and D. J. Gregor, \textit{Arctic}, 1989, 42, 307.
\item \textsuperscript{41} T. Nakano, M. Tsuji and T. Okuno, \textit{Atmos. Environ., Part A}, 1990, 24, 1361.
\item \textsuperscript{42} R. Wittlinger and K. Ballschmiter, \textit{Fresenius' J. Anal. Chem.}, 1990, 336, 193.
\item \textsuperscript{44} W. T. Foreman and T. F. Bidleman, \textit{Atmos. Environ., Part A}, 1990, 24, 2405.
\item \textsuperscript{46} K. Ballschmiter and R. Wittlinger, \textit{Environ. Sci. Technol.}, 1991, 25, 1103.
\item \textsuperscript{48} M. Oehme, \textit{Sci. Total Environ.}, 1991, 106, 43.
\item \textsuperscript{49} M. Oehme, \textit{Ambio}, 1991, 20, 293.
\item \textsuperscript{50} A. H. Knap and K. S. Binkley, \textit{Atmos. Environ., Part A}, 1991, 25, 1507.
\item \textsuperscript{51} G. T. Hunt and B. E. Maisel, \textit{J. Air Waste Manage. Assoc.}, 1992, 42, 672.
\item \textsuperscript{52} R. M. Hof, D. C. G. Muir and N. P. Grift, \textit{Environ. Sci. Technol.}, 1992, 26, 266.
\item \textsuperscript{54} B. Ngabe and T. F. Bidleman, \textit{Environ. Pollut.}, 1992, 76, 147.
\item \textsuperscript{58} H. Kaupp, J. Towara and M. S. McLachlan, \textit{Atmos. Environ.}, 1994, 28, 585.
\end{itemize}
\end{footnotesize}
transport through the atmosphere.\textsuperscript{32,40,63,64} Because these organochlorine compounds are lipophilic,\textsuperscript{65} bioaccumulation of PCBs, PCDDs and PCDFs occurs in mammals which feed on fish in such northern lakes and ocean waters, with potentially adverse biological effects.\textsuperscript{48,63,64,66–69}

To understand quantitatively the lifetimes and fates of PCBs, PCDDs and PCDFs in the atmosphere, the various potential tropospheric removal processes for these organochlorine compounds need to be assessed and the dominant removal and/or transformation processes identified. In this chapter, the available information concerning the atmospheric removal processes of the PCBs, PCDDs and PCDFs is presented and reviewed.

2 Gas/Particle Partitioning of PCBs, PCDDs and PCDFs in the Atmosphere

As for other chemical compounds,\textsuperscript{70–72} in the atmosphere the PCDDs, PCDFs and PCBs are partitioned\textsuperscript{14,22,23,30,38,39,41,44,45,47,51,62,73} between the gas and particle phases, with the gas/particle partitioning depending on the liquid-phase (or sub-cooled liquid-phase) vapour pressure at the ambient atmospheric temperature, $P_L$, the surface area of the particles per unit volume of air (for example, cm$^2$ of particle per cm$^3$ of air), $\theta$, and the nature of the particles and of the chemical being adsorbed.\textsuperscript{62,70,71} The fraction of the chemical present in the particle phase, $\phi$, depends on these parameters through an equation of the form\textsuperscript{62,70–72}

$$
\phi = c\theta/(c\theta + P_L)
$$

where $c$ is a parameter which depends on the chemical being adsorbed and on the

\begin{itemize}
\end{itemize}
nature of the particle.\textsuperscript{62,70,71} To a first approximation, chemical compounds with liquid-phase vapour pressures of $P_L < 10^{-6}$ Pa ($< 10^{-8}$ Torr) at the ambient atmospheric temperature are present in the particle phase, and those with values of $P_L > 10^{-2}$ Pa ($> 10^{-4}$ Torr) at the ambient atmospheric temperature are essentially totally in the gas phase.\textsuperscript{71,72} Chemicals with intermediate values of $P_L$ are present in both the gas and particle phases and are often termed semi-volatile organic compounds (SOCs).\textsuperscript{71}

The liquid-phase vapor pressures, $P_L$, at 298 K of the PCBs, PCDDs and PCDFs decrease from 7 Pa ($5 \times 10^{-2}$ Torr) for biphenyl\textsuperscript{65,73} to (1–3) $\times 10^{-5}$ Pa [(0.7–2.3) $\times 10^{-7}$ Torr] for decachlorobiphenyl,\textsuperscript{65,73} from 0.5 Pa (4 $\times 10^{-3}$ Torr) for dibenzo-p-dioxin\textsuperscript{74} to (3–5) $\times 10^{-7}$ Pa [(2–4) $\times 10^{-9}$ Torr] for octachloro-dibenzo-p-dioxin,\textsuperscript{74,75} and from 1.4 Pa (1 $\times 10^{-2}$ Torr) for dibenzofuran\textsuperscript{74} to $1 \times 10^{-7}$ Pa (8 $\times 10^{-10}$ Torr) for octachlorodibenzofuran.\textsuperscript{74}

Based on theoretical considerations of gas–particle partitioning\textsuperscript{70,71} and the results of several ambient air studies, the PCBs, PCDDs and PCDFs containing five or less chlorine atoms are present in the atmosphere at least partially in the gas phase at around room temperature.\textsuperscript{14,22,30,38,39,47,51,62} The major PCB congeners observed in ambient air are those containing three and four chlorine atoms,\textsuperscript{14–17,30,60,62} and several studies have reported that the gas-phase PCBs dominate over the particle-phase PCBs\textsuperscript{14–17,30,41,45,60,61} (with, for example, the gas-phase PCBs being reported to comprise >98\%,\textsuperscript{30} 83–97\%\textsuperscript{14} and 96\%\textsuperscript{41} of the total PCBs measured). Because of the variation of $P_L$ with temperature, for a given particle surface area a decrease in ambient atmospheric temperature will increase the fraction of the SOC present in the particle phase (equation 1).

The phase (gas or particle) in which the PCBs, PCDDs and PCDFs occur in the atmosphere greatly affects their tropospheric removal processes and lifetimes. Analogous to other organic compounds, the PCDDs, PCDFs and PCBs in the atmosphere can be removed and/or transformed by a number of physical and chemical processes.\textsuperscript{71,72,76,77} While the present chapter focuses on the chemical transformations of the PCBs, PCDDs and PCDFs, the physical removal processes are also discussed for completeness and to assess the relative importance of the various tropospheric removal processes.

### 3 Physical Removal Processes

Gas- and particle-phase PCBs, PCDDs and PCDFs can be removed from the troposphere by wet and dry deposition.\textsuperscript{71,72,76,77} Wet deposition refers to the removal of the chemical (or particle-associated chemical) from the atmosphere by precipitation events (through the precipitation of rain, fog or snow to the Earth’s surface), while dry deposition refers to the removal of the chemical or particle-
associated chemical from the atmosphere to the Earth’s surface by diffusion and/or sedimentation.\textsuperscript{76}

**Wet Deposition of PCBs, PCDDs and PCDFs**

Wet deposition of a semi-volatile organic compound is characterized in terms of the overall washout ratio, $W$, which is given by

$$W = \frac{\text{concentration of chemical in aqueous phase}}{\text{concentration of chemical in air}} \tag{2}$$

$$W = W_g (1 - \phi) + W_p \phi \tag{3}$$

where $W_g$ is the washout ratio for the gas-phase chemical, $W_p$ is the washout ratio for the particle-associated chemical, and $\phi$ is the fraction of the chemical which is particle associated (see equation 1). For a gas-phase chemical, wet deposition involves the incorporation of the chemical into rain-, fog or cloud-water, followed by precipitation to the Earth’s surface, and is determined by the partitioning of the chemical between the air and aqueous phases. The gas-phase washout ratio, $W_g$ is given by

$$W_g = \frac{C_w}{C_a} = \frac{RT}{H} \tag{4}$$

where $C_w$ is the concentration of the chemical in the aqueous phase, $C_a$ is the concentration of the chemical in air, $R$ is the gas constant, $T$ is the ambient atmospheric temperature (in K) and $H$ is the Henry’s law constant.\textsuperscript{65,71,72} The flux of chemicals to the Earth’s surface due to wet deposition, $F_{\text{wet}}$, is given by

$$F_{\text{wet}} = JW C_a \tag{5}$$

where $J$ is the precipitation rate (for example, cm rain yr$^{-1}$).

Values of $W_p$ for particle-associated chemicals depend on the type of precipitation event (warm or cold and in-cloud versus below-cloud precipitation) and the particle size,\textsuperscript{71} and the magnitude of $W_p$ appears to be in the range $10^2$–$10^6$,\textsuperscript{71,72,78} and generally in the range $10^4$–$10^6$.\textsuperscript{71,72} A value of $W_p = 10^5$ is calculated to result in a residence time for particles and particle-associated chemicals due to wet deposition in the well-mixed troposphere (with a scale height of 7 km) of ~20 days for a constant precipitation rate of 1 m yr$^{-1}$.

The Henry’s law constants for the gas-phase PCBs are generally in the range 20–100 Pa m$^3$ mol$^{-1}$ at 298 K and show little variation with the number of chlorine atoms, and the average value is $H = 48$ Pa m$^3$ mol$^{-1}$ at 298 K.\textsuperscript{65} This value of $H$ corresponds to a washout ratio for PCBs of $W_g = 50$ at 298 K and an atmospheric residence time due to wet deposition of several tens of years (for removal from the well-mixed troposphere at an average temperature of 298 K.

and a rainfall of 1 m yr\(^{-1}\)). Because \(H = \text{(vapor pressure/aqueous solubility)}\), then \(H\) will decrease (and \(W_g\) will increase) with decreasing temperature, by a factor of \(\sim 10\) for a temperature decrease of 25 K within the range 273–313 K.\(^{79}\)

Even though the majority of the PCBs are present in the lower troposphere in the gas phase (see above), the low washout ratios \(W_g\) for gas-phase PCBs results in precipitation scavenging of the particle-associated PCBs dominating over rain-out of gas-phase PCBs.\(^{30,71,72}\)

For the PCDDs and PCDFs, Ligocki \textit{et al.}\(^{80}\) have reported a washout ratio for dibenzofuran of \(W_g = 930 \pm 180\) at 281 K from ambient atmospheric measurements, while Eitzer and Hites\(^{39}\) and Koester and Hites\(^{81}\) derived gas-phase washout ratios for tetrachlorodibenzofuran, pentachlorodibenzo-\(p\)-dioxin and pentachlorodibenzofuran of \((0.6–3) \times 10^4\). These washout ratios \(W_g\) derived from ambient measurements are reasonably consistent with the washout ratios calculated from the Henry’s law constants estimated by Shui \textit{et al.}\(^{82}\) (which range between 0.1 and 15 Pa m\(^3\) mol\(^{-1}\), and decrease by a factor of \(\sim 1.6\) per Cl atom added). The washout ratios \(W_g\) at 298 K estimated by Shui \textit{et al.}\(^{82}\) range from 200 for dibenzo-\(p\)-dioxin to \(2 \times 10^4\) for heptachlorodibenzo-\(p\)-dioxin.

Ambient air studies\(^{39,78,80,81}\) show that the particle-phase (and hence more chlorinated) PCDDs and PCDFs are more efficiently removed from the atmosphere by wet deposition than are the gas-phase PCDDs and PCDFs, analogous to the case for the PCBs.

\textbf{Dry Deposition of PCBs, PCDDs and PCDFs}

The flux of chemicals to the Earth’s surface due to dry deposition, \(F_{\text{dry}}\), is given by

\[
F_{\text{dry}} = V_{dg} C_a + V_{dp} C_p
\]

where \(V_{dg}\) and \(V_{dp}\) are the deposition velocities for the gas- and particle-phase chemicals, respectively (and hence \(V_{dp}\) is the deposition velocity for the particles with which the chemical is associated), and \(C_a\) and \(C_p\) are the atmospheric concentrations of the chemical in the gas and particle phases, respectively. The deposition velocities depend on the atmospheric stability, nature of the surface, nature of the chemical (for a gas-phase chemical) and (for a particle or particle-phase chemical) the size of the particle.\(^{76}\) For particle deposition, the deposition velocity is a minimum for particles with mean diameter \(\sim 0.3–0.5\) \(\mu\)m, and increases with both increasing and decreasing particle size.\(^{72,76}\) Ambient atmospheric deposition studies have concluded that the deposition of PCBs, PCDDs and PCDFs is largely due to deposition of the particle-phase compounds.\(^{45,71,84}\) Because of the preferential deposition of larger particles, the average deposition velocity may well decrease with distance from the source region (for example, \(V_{dp}\) may be larger for particles in an urban area compared to

---


\(^{80}\) M. P. Ligocki, C. Leuenberger and J. F. Pankow, \textit{Atmos. Environ.}, 1985, 19, 1609.


Atmospheric Chemistry of PCBs, PCDDs and PCDFs

those in more remote areas). Values of $V_{dp}$ of $0.1-1$ cm s$^{-1}$ for particle-phase organics (including PCBs), 0.2 cm s$^{-1}$ for particle-phase PCBs and 0.06–0.6 (average 0.2) cm s$^{-1}$ for particle-phase PCDDs and PCDFs have been reported. With a value of $V_{dp} = 0.2$ cm s$^{-1}$, the calculated residence time of particles and particle-associated chemicals due to dry deposition in the well-mixed troposphere is $\sim 30$ days. It may be noted that modelling of the transport of particle-associated $^{210}$Pb leads to an estimated residence time of particles in the atmosphere of $\sim 5–15$ days due to combined wet and dry deposition, reasonably consistent with the above calculations.

The available data therefore indicate that deposition of PCBs, PCDDs and PCDFs from the atmosphere is dominated by wet and dry deposition of the particle-phase congeners.

4 Chemical Transformations

Gas- and particle-phase organic compounds can undergo chemical change via a number of routes. For gas-phase chemicals, these involve photolysis and reaction with the hydroxyl (OH) radical, reaction with the nitrate (NO$_3$) radical and reaction with ozone (O$_3$). The formation of OH radicals, NO$_3$ radicals and O$_3$ in the troposphere, and the requirements for photolysis to occur in the troposphere, are briefly discussed below, prior to presenting the experimental data for the PCBs, PCDDs and PCDFs for these processes.

Photolysis in the Troposphere

Absorption of solar radiation by molecular oxygen and ozone in the stratosphere limits the transmission of ultraviolet radiation into the troposphere to wavelengths $\geq 290$ nm. Any depletion of stratospheric ozone will lead to an increase in the intensity of UV radiation, and to shorter wavelength radiation, entering the troposphere. For photolysis to occur, the chemical must absorb radiation in the ‘actinic’ region [between $\sim 290$ nm (the short-wavelength cut-off imposed by absorption of shorter wavelengths in the stratosphere) and $\sim 800$ nm (the longest wavelength that can lead to breakage of chemical bonds)]. Furthermore, having absorbed radiation, the chemical must undergo change. The photolysis rate, $k_{\text{phot}}$, is given by

$$k_{\text{phot}} = \int_{290}^{800} J_{\lambda} \sigma_{\lambda} \phi_{\lambda} d\lambda$$

where $J_{\lambda}$ is the radiation flux at wavelength $\lambda$, $\sigma_{\lambda}$ is the absorption cross-section at wavelength $\lambda$ and $\phi_{\lambda}$ is the quantum yield for chemical change at wavelength $\lambda$.

**Ozone in the Troposphere**

The presence of O$_3$ in the troposphere is due to downward transport from the stratosphere with dry deposition at the Earth’s surface$^{84,87}$ and in situ chemical formation and destruction.$^{87,88}$ Mixing ratios of O$_3$ in the ‘ocean’ remote lower troposphere are in the range $(10–40) \times 10^{-9},^{87,89}$ and increase with increasing altitude.$^{87}$ A 24 h average troposphere O$_3$ concentration of $7 \times 10^{11}$ molecule cm$^{-3}$ appears reasonable for lifetime calculations.

**OH Radicals in the Troposphere**

The presence of O$_3$ in the troposphere leads to the formation of OH radicals, by the photolysis of O$_3$ at wavelengths $290–320$ nm to form the electronically excited oxygen atom, O($^1$D), which either reacts with water vapor or is deactivated by reaction with O$_2$ and N$_2$ to the ground state oxygen atom, (O$^3$P), which then rapidly recombines with O$_2$ to reform O$_3$.\(^{84,90}\)

$$O_3 + h \nu \rightarrow O_2 + O(^1D) \ (\lambda < 320 \text{ nm}) \quad (8)$$

$$O(^1D) + H_2O \rightarrow 2 \text{OH} \quad (9)$$

$$O(^1D) + M \rightarrow O(^3P) + M \ (M = \text{N}_2, \text{O}_2) \quad (10)$$

A diurnally, seasonally and annually averaged global tropospheric concentration of the OH radical has been derived from the emissions, atmosphere concentrations and OH radical reaction rate constant for methyl chloroform (CH$_3$CCl$_3$), resulting in a 24 h average OH radical concentration of $9.7 \times 10^5$ molecule cm$^{-3}$.\(^{91}\) Because of the fairly long lifetimes of the PCBs, PCDDs and PCDFs (see below), for lifetime calculations this globally averaged tropospheric OH radical concentration is more relevant than ground-level direct measurements of OH radical concentrations.

**NO$_3$ Radicals in the Troposphere**

Emissions of NO from combustion processes and soils and in situ formation of NO from lightning are followed by reactions leading to the formation of the NO$_3$ radical.$^{84,90}$

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (11)$$

$$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (12)$$

---


Because the NO$_3$ radical photolyses rapidly, NO$_3$ radical concentrations are low during daylight hours, but can become elevated during nighttime. Measured ground-level NO$_3$ radical concentrations range up to $1 \times 10^{10}$ molecule cm$^{-3}$, and a 12 h nighttime average concentration of $\sim 5 \times 10^{8}$ molecule cm$^{-3}$, uncertain by a factor of $\sim 10$, has been proposed.

5 Transformations of Gas-phase PCBs, PCDDs and PCDFs

Reactions with O$_3$

To date, the kinetics of the gas-phase reactions of O$_3$ with biphenyl, 2,2'-dichlorobiphenyl, dibenzo-p-dioxin, 1-chlorodibenzo-p-dioxin and dibenzofuran have been studied at room temperature. In all cases, no reactions were observed and the measured upper limits to the rate constants are given in Table 1. The observed lack of reaction of O$_3$ with gas-phase PCBs, PCDDs and PCDFs is expected, based on literature data for other aromatic compounds, and it is anticipated that the room temperature rate constants for the gas-phase reactions of O$_3$ with PCBs, PCDDs and PCDFs are all $\leq 10^{-20}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

Reactions with the NO$_3$ Radical

The gas-phase reactions of the NO$_3$ radical with biphenyl, 2,2'-dichlorobiphenyl, dibenzo-p-dioxin, 1-chlorodibenzo-p-dioxin and dibenzofuran have been studied at room temperature. While no reactions of the NO$_3$ radical with biphenyl, 2,2'-dichlorobiphenyl or dibenzofuran were observed, dibenzo-p-dioxin and 1-chlorodibenzo-p-dioxin were observed to react, with the measured reaction rate constants increasing with increasing NO$_2$ concentration. As discussed in detail by Atkinson and Kwok et al., the reactions of the NO$_3$ radical with the PCBs, PCDDs and PCDFs appear to proceed by initial addition of the NO$_3$ radical to form an NO$_3$ adduct, which either thermally decomposes back to reactants or reacts with O$_2$ and/or NO$_2$ (Scheme 1).

The measured rate constant, $k_{obs}$, is then given by

$$k_{obs} = k_d[k_r[NO_2] + k_d[O_2]]/(k_b + k_c[NO_2] + k_d[O_2])$$  \hspace{1cm} (13)

The experimental data for dibenzo-p-dioxin, 1-chlorodibenzo-p-dioxin and polycyclic aromatic hydrocarbons show that under the experimental conditions employed, $k_r[NO_2] > k_d[O_2]$ and that equation (13) simplifies to

$$k_{obs} = k_r k_r[NO_2]/(k_b + k_c[NO_2])$$  \hspace{1cm} (14)
Table 1 Rate constants \( k \) for the gas-phase reactions of \( \text{O}_3 \) with PCBs, PCDDs and PCDFs at room temperature

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>( 10^{20} \times k ) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>( T/(\text{K}) )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biphenyl</td>
<td>&lt; 20</td>
<td>294 ± 1</td>
<td>Atkinson et al.(^93)</td>
</tr>
<tr>
<td>2,2'-Dichlorobiphenyl</td>
<td>&lt; 2</td>
<td>297 ± 2</td>
<td>Kwok et al.(^95)</td>
</tr>
<tr>
<td>PCDDs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzo-( p )-dioxin</td>
<td>&lt; 5</td>
<td>297 ± 2</td>
<td>Kwok et al.(^94)</td>
</tr>
<tr>
<td>1-Chlorodibenzo-( p )-dioxin</td>
<td>&lt; 7</td>
<td>297 ± 2</td>
<td>Kwok et al.(^95)</td>
</tr>
<tr>
<td>PCDFs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>&lt; 8</td>
<td>297 ± 2</td>
<td>Kwok et al.(^94)</td>
</tr>
</tbody>
</table>

Scheme 1

In addition, a direct reaction pathway (for example, involving H-atom abstraction) should be considered (although the experimental data do not show any evidence for this pathway, nor is it expected\(^92\)):

\[
\text{NO}_3 + \text{aromatics} \rightarrow \text{products} \tag{15}
\]

where the rate constant for reaction (15) is referred to as \( k_{\text{abs}} \).

For biphenyl, 2,2'-dichlorobiphenyl and dibenzofuran, no reactions were observed\(^93,95,98,99\) and only upper limits to the rate constants \( k_{\text{abs}} \) and rate constant ratios \( k_k/k_b \) are available, and these are given in Table 2. In contrast, reactions of dibenzo-\( p \)-dioxin and 1-chlorodibenzo-\( p \)-dioxin with the \( \text{NO}_3 \) radical were observed\(^95,99\) with the measured reaction rate constants \( k_{\text{obs}} \) increasing with increasing \( \text{NO}_3 \) concentration in accord with equations (13) and (14). The rate constant ratios \( k_k/k_b \) obtained from the experimental data are given in Table 2. The measured rate constants in the absence of \( \text{NO}_3 \) allow upper limits to the rate constants \( k_{\text{abs}} \) to be obtained,\(^95,99\) and these are also given in Table 2. For dibenzo-\( p \)-dioxin, an upper limit to the rate constant ratio \( k_d/k_c \) has also been derived (Table 2),\(^99\) showing that the reaction of the \( \text{NO}_3 \)-dibenzo-\( p \)-dioxin adduct with \( \text{NO}_2 \) dominates over reaction with \( \text{O}_2 \) for \( \text{NO}_2 \) mixing ratios \( \geq 8 \times 10^{-8} \) (and possibly much lower since only an upper limit to the rate constant ratio \( k_d/k_c \) was obtained). Rate constants \( k_{\text{abs}} \) for the initial addition of the \( \text{NO}_3 \) radical to dibenzo-\( p \)-dioxin\(^95\) and 1-chlorodibenzo-\( p \)-dioxin can also be
Table 2 Rate constants $k_{\text{obs}}$ and rate constant ratios $k_d/k_c$ and $k_d/k_f$ for the gas-phase reactions of the NO$_3$ radical with PCBs, PCDDs and PCDFs at room temperature

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>$k_{\text{obs}}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$k_d/k_c$ (cm$^6$ molecule$^{-2}$ s$^{-1}$)</th>
<th>$k_d/k_f$</th>
<th>$T$(K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PCBs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biphenyl</td>
<td>$&lt;6 \times 10^{-16}$</td>
<td>$&lt;5 \times 10^{-30}$</td>
<td></td>
<td>298 ± 2</td>
<td>Atkinson et al.$^{92,98}$</td>
</tr>
<tr>
<td>2,2'-Dichlorobiphenyl</td>
<td>$&lt;8 \times 10^{-16}$</td>
<td>$&lt;3 \times 10^{-30\text{a}}$</td>
<td></td>
<td>297 ± 2</td>
<td>Kwok et al.$^{95}$</td>
</tr>
<tr>
<td><strong>PCDDs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzop-dioxin</td>
<td>$&lt;8 \times 10^{-15}$</td>
<td>$3.9 \times 10^{-27\text{b}}$</td>
<td>$&lt;4 \times 10^{-7}$</td>
<td>297 ± 2</td>
<td>Kwok et al.$^{99}$</td>
</tr>
<tr>
<td>1-Chlorodibenzo-p-dioxin</td>
<td>$&lt;1.6 \times 10^{-14}$</td>
<td>$5.7 \times 10^{-28\text{b,c}}$</td>
<td></td>
<td>297 ± 2</td>
<td>Kwok et al.$^{95}$</td>
</tr>
<tr>
<td><strong>PCDFs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>$&lt;1.6 \times 10^{-15}$</td>
<td>$&lt;7 \times 10^{-30}$</td>
<td></td>
<td>297 ± 2</td>
<td>Kwok et al.$^{99}$</td>
</tr>
</tbody>
</table>

$^{a}$Rate constant ratio cited in Kwok et al.$^{95}$ was erroneously a factor of 10 low.

$^{b}$Uncertain to a factor of ~2.

$^{c}$Reanalysis of the experimental data of Kwok et al.$^{95}$
derived, with values at 297 ± 2 K of $6.8 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $2.7 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, both with overall uncertainties of a factor of ~2.

The rate constants presented in Table 2 suggest that the NO$_3$ radical reactions with the gas-phase PCBs and PCDFs have upper limits to the rate constants for any reaction of $k_{abs} < 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (NO$_2$ concentrations in the troposphere are sufficiently low that the contribution of any NO$_2$-dependent reaction is encompassed within the upper limit to the bimolecular reaction rate constant $k_{abs}$). While dibenzo-$p$-dioxin and 1-chlorodibenzo-$p$-dioxin react with the NO$_3$ radical by the NO$_2$-dependent mechanism shown in Scheme 1 and equation (13), the NO$_2$ concentrations in the troposphere are sufficiently low that the effective bimolecular rate constants, $k_d(k_c[NO_2] + k_d[O_2])/k_{bp}$, are below the upper limits to the rate constants $k_{abs}$.

Reactions with the OH Radical

The experimentally measured rate constants for the gas-phase reactions of the OH radical with PCBs, PCDDs and PCDFs are given in Table 3. The majority of the rate constants measured have been for the PCBs, with the measurements of Anderson and Hites$^{104,105}$ providing rate constants for a number of trichloro-, tetrachloro- and pentachlorobiphenyls. It should be noted that Anderson and Hites$^{104,105}$ measured rate constants for the PCBs at elevated temperatures in the range 322–366 K, with the minimum temperature at which measurements were made being 322 or 323 K apart from 4,4@-dichlorobiphenyl (329 K) and the three pentachlorobiphenyls (343 K). Arrhenius expressions were obtained from these data and used to calculate the rate constants at 298 K by extrapolation.$^{104,105}$ The rate constants measured by Anderson and Hites$^{104,105}$ in the temperature range 322–366 K all show a decrease in rate constant with decreasing temperature, corresponding to values of $B$ in the Arrhenius expression $k = A \exp(-B/T)$ ranging from 20 ± 150 K for biphenyl to 1950 ± 470 K for 2,2@,3,5,6-pentachlorobiphenyl (where the indicated errors are one standard deviation).

Table 3 shows that the room temperature rate constants for biphenyl reported by Zetzsch, Atkinson et al., Atkinson and Aschmann, Klöpffer et al.$^{101,103}$ and Anderson and Hites$^{104}$ are in good agreement. Furthermore, the room temperature rate constants reported by Atkinson and Aschmann$^{101,102}$ and Anderson and Hites$^{104}$ for the monochlorobiphenyls are in excellent agreement, as are those of Kwok et al.$^{95}$ and Anderson and Hites$^{104}$ for 2,2@-dichlorobiphenyl. Table 3 shows that in general the rate constants for the biphenyls decrease with increasing chlorination, and this also appears to be the case for the PCDDs based on the rate constants for dibenzo-$p$-dioxin and 1-chlorodibenzo-$p$-dioxin. The data for the PCBs also show that for a given degree of chlorination, the rate constant depends on the substitution pattern around the aromatic rings (Table 3).

As also concluded previously, reaction with the OH radical may be the only important tropospheric loss process for the gas-phase PCBs, PCDDs and PCDFs. It is therefore necessary to know the rate constants for the gas-phase
Table 3 Rate constants for the gas-phase reactions of the OH radical with PCBs, PCDDs and PCDFs at room temperature

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>((10^{12} \times k_{cm^3 \text{ molecule}^{-1} \text{ s}^{-1}}))</th>
<th>(T(\text{K}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PCBs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biphenyl</td>
<td>5.8 ± 0.8</td>
<td>296</td>
<td>Zetzsch(^{100})</td>
</tr>
<tr>
<td></td>
<td>7.61 ± 0.67</td>
<td>294 ± 1</td>
<td>Atkinson et al.(^{93,101})</td>
</tr>
<tr>
<td></td>
<td>8.32 ± 0.75</td>
<td>295 ± 1</td>
<td>Atkinson and Aschmann(^{101,102})</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>300</td>
<td>Klöpffer et al.(^{101,103})</td>
</tr>
<tr>
<td></td>
<td>6.7 ± 1.0a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Chlorobiphenyl</td>
<td>2.82 ± 0.38</td>
<td>295 ± 1</td>
<td>Atkinson and Aschmann(^{101,102})</td>
</tr>
<tr>
<td></td>
<td>2.7 ± 0.7a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>3-Chlorobiphenyl</td>
<td>5.28 ± 0.82</td>
<td>295 ± 1</td>
<td>Atkinson and Aschmann(^{101,102})</td>
</tr>
<tr>
<td></td>
<td>5.0 ± 0.7a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>4-Chlorobiphenyl</td>
<td>3.86 ± 0.67</td>
<td>295 ± 1</td>
<td>Atkinson and Aschmann(^{101,102})</td>
</tr>
<tr>
<td></td>
<td>3.4 ± 0.6a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,2'-Dichlorobiphenyl</td>
<td>2.0 ± 0.5</td>
<td>297 ± 2</td>
<td>Kwok et al.(^{95})</td>
</tr>
<tr>
<td></td>
<td>2.2 ± 0.5a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,4-Dichlorobiphenyl</td>
<td>2.6 ± 0.7a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>3,3'-Dichlorobiphenyl</td>
<td>4.1 ± 1.2</td>
<td>297 ± 2</td>
<td>Kwok et al.(^{95})</td>
</tr>
<tr>
<td></td>
<td>4.2 ± 1.1</td>
<td>297 ± 2</td>
<td>Kwok et al.(^{95})</td>
</tr>
<tr>
<td>4,4'-Dichlorobiphenyl</td>
<td>2.0 ± 0.5</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2',3,4-Trichlorobiphenyl</td>
<td>1.0 ± 0.4a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,4,4'-Trichlorobiphenyl</td>
<td>1.1 ± 0.3a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,4,5-Trichlorobiphenyl</td>
<td>1.3 ± 0.2a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,4,5-Trichlorobiphenyl</td>
<td>1.2 ± 0.3a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,2',3,5'-Tetrachlorobiphenyl</td>
<td>0.8 ± 0.4a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,2',4,4'-Tetrachlorobiphenyl</td>
<td>1.0 ± 0.5a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,2',3,5',6-Pentachlorobiphenyl</td>
<td>0.4 ± 0.3a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,3,3',4,6-Pentachlorobiphenyl</td>
<td>0.6 ± 0.5a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td>2,3,4,5,6-Pentachlorobiphenyl</td>
<td>0.9 ± 0.9a</td>
<td>298</td>
<td>Anderson and Hites(^{104})</td>
</tr>
<tr>
<td><strong>PCDDs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzo-p-dioxin</td>
<td>14.8 ± 3.5</td>
<td>297 ± 2</td>
<td>Kwok et al.(^{94})</td>
</tr>
<tr>
<td>1-Chlorodibenzo-p-dioxin</td>
<td>4.7 ± 1.6</td>
<td>297 ± 2</td>
<td>Kwok et al.(^{95})</td>
</tr>
<tr>
<td><strong>PCDFs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzofuran</td>
<td>3.9 ± 0.9</td>
<td>297 ± 2</td>
<td>Kwok et al.(^{94})</td>
</tr>
</tbody>
</table>

\(^{a}\)Rate constants calculated at 298 K from measurements carried out at elevated temperatures in the range 322–366 K.
reactions of the OH radical with the various PCB, PCDD and PCDF congeners in order to estimate the lifetimes of these compounds. However, because of experimental limitations, rate constants have been measured for only a few of the large number of PCB, PCDD and PCDF congeners, and then only for the more volatile and less chlorinated congeners (Table 3).

Atkinson and Kwok et al. have proposed and discussed methods for the estimation of OH radical reaction rate constants for the PCBs, PCDDs and PCDFs, based on the correlation of the rate constants for OH radical addition to aromatic rings, $k_{OH}^R$, with the sum of the electrophilic substituent constants, $\Sigma \sigma^+$. Based on a review of the literature rate constants for OH radical addition to a wide range of aromatic compounds, Atkinson derived the correlation,

$$\log k_{OH} (\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}) = -11.71 - 1.34 \Sigma \sigma^+$$ \hspace{1cm} (16)

and no new data have been reported which change this correlation. $\Sigma \sigma^+$ is calculated by assuming that (a) steric hindrance can be neglected, (b) $\Sigma \sigma^+$ is the sum of the electrophilic substituent constants of all of the substituent groups attached to the aromatic rings, (c) the OH radical adds to the position yielding the most negative value of $\Sigma \sigma^+$ and (d) if all positions are occupied, the ipso position is treated as a meta position. Atkinson used the rate constants for the reactions of the OH radical with biphenyl and the monochlorobiphenyls and the literature values of the electrophilic substituent constants for the Cl and phenyl groups to derive electrophilic substituent constants for the $\text{C}_6\text{H}_x\text{Cl}_y$ $(x = 1 - 4)$ groups, and the relevant electrophilic substituent constants are given in Table 4. A comparison of estimated (using equation (16) and the electrophilic substituent constants given in Table 4) and measured (Table 3) room temperature rate constants $k_{OH}^R$ for the PCB congeners for which rate constants have been measured is shown in Figure 2, where the solid line denotes perfect agreement between the estimated and experimentally measured rate constants and the dashed lines denote disagreement by a factor of 2. Figure 2 shows that the estimated rate constants are in good agreement with the experimental data, with the estimated values possibly being low by $\sim 25\%$. This generally good agreement for the PCBs containing up to five chlorine atoms indicates that this estimation method can be used to reliably calculate (to within a factor of $\sim 2$) the room temperature rate constants $k_{OH}^R$ for the PCB congeners for which experimental measurements are not yet available. The estimated room temperature rate constants for PCBs containing up to six chlorine atoms are given in Table 5; as noted above, for a given degree of chlorination the rate constant depends on the Cl atom substitution pattern around the aromatic rings.

Table 4 Electrophilic substituent constants $\sigma^+_{o,p}$ and $\sigma^+_m$ used in the estimation of OH radical reaction rate constants for PCBs, PCDDs and PCDFs

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\sigma^+_{o,p}$</th>
<th>$\sigma^+_m$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>0.114</td>
<td>0.399</td>
<td>Brown and Okamoto\textsuperscript{106}</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{5}</td>
<td>-0.179</td>
<td>0.109</td>
<td>Brown and Okamoto\textsuperscript{106}</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{4}Cl</td>
<td>-0.039</td>
<td>0.207</td>
<td>Atkinson\textsuperscript{77}</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{3}(Cl\textsubscript{2})</td>
<td>0.101</td>
<td>0.305</td>
<td>Atkinson\textsuperscript{77}</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{2}(Cl\textsubscript{3})</td>
<td>0.241</td>
<td>0.403</td>
<td>Atkinson\textsuperscript{77}</td>
</tr>
<tr>
<td>C\textsubscript{6}HCl\textsubscript{4}</td>
<td>0.381</td>
<td>0.501</td>
<td>Atkinson\textsuperscript{77}</td>
</tr>
<tr>
<td>C\textsubscript{6}Cl\textsubscript{5}</td>
<td>0.521</td>
<td>0.599</td>
<td>Atkinson\textsuperscript{77}</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{3}(O)</td>
<td>-0.30</td>
<td>0.00</td>
<td>Kwok et al.\textsuperscript{95}</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{2}Cl\textsubscript{3}O</td>
<td>-0.20\textsuperscript{a}</td>
<td>0.07\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{2}Cl\textsubscript{4}O</td>
<td>-0.10\textsuperscript{a}</td>
<td>0.14\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{4}Cl\textsubscript{2}O</td>
<td>0.00\textsuperscript{a}</td>
<td>0.21\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{2}Cl\textsubscript{4}O</td>
<td>0.10\textsuperscript{a}</td>
<td>0.28\textsuperscript{a}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Derived from $\sigma^+$(C\textsubscript{6}H\textsubscript{5}O) assuming that the effect of increasing Cl atom substitution on the C\textsubscript{6}H\textsubscript{5}O group is 70\% of the effect of increasing Cl atom substitution on the C\textsubscript{6}H\textsubscript{5} group.

Figure 2 Comparison of the experimentally measured and estimated room temperature rate constants $k^{\text{exp}}_{\text{OH}}$ and $k^{\text{OH}}_{\text{calc}}$ respectively, for the gas-phase reactions of the OH radical with PCBs. Solid line denotes perfect agreement of $k^{\text{exp}}_{\text{OH}}$ and $k^{\text{OH}}_{\text{calc}}$, while the dashed lines denote disagreement by a factor of 2.0. The rate constants are tabulated in Table 3: ○, Anderson and Hites\textsuperscript{104,105}; ●, Atkinson et al.,\textsuperscript{93,101} Atkinson and Aschmann\textsuperscript{101,102} and Kwok et al.\textsuperscript{95}; △, Zetzsch;\textsuperscript{100} ▽, Klöpffer et al.\textsuperscript{101,103}

Analogous estimation methods have been proposed for the PCDDs and PCDFs\textsuperscript{77,95} with the most recent study of Kwok et al.\textsuperscript{95} proposing that the PCDDs be viewed as two benzene rings with Cl and phenoxy (C\textsubscript{6}H\textsubscript{5}Cl\textsubscript{x}O, with $x = 0\sim4$) substituent groups, and that the PCDFs be viewed as two benzene rings with Cl, phenoxy (C\textsubscript{6}H\textsubscript{5}Cl\textsubscript{x}O, with $x = 0\sim4$) and phenyl (C\textsubscript{6}H\textsubscript{5}Cl\textsubscript{x}, with $x = 0\sim4$) substituent groups. Kwok et al.\textsuperscript{95} used the measured room temperature rate constants for dibenzo-p-dioxin, dibenzofuran and diphenyl ether (C\textsubscript{6}H\textsubscript{5}OC\textsubscript{6}H\textsubscript{4}) to derive electrophilic substituent constants for the C\textsubscript{6}H\textsubscript{3}O group and then...
Table 5 Estimated room temperature rate constants $k_{\text{OH}}$ for the gas-phase reactions of the OH radical with gas-phase PCBs, PCDDs and PCDFs

<table>
<thead>
<tr>
<th>No. Cl atoms</th>
<th>PCBs</th>
<th>PCDDs$^a$</th>
<th>PCDFs$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.8</td>
<td>9.8</td>
<td>7.0</td>
</tr>
<tr>
<td>1</td>
<td>3.2–4.6</td>
<td>6.4 (4.7 ± 1.6)$^b$</td>
<td>4.3–4.4</td>
</tr>
<tr>
<td>2</td>
<td>1.4–3.1</td>
<td>2.7–4.2</td>
<td>1.8–2.8</td>
</tr>
<tr>
<td>3</td>
<td>1.0–2.1</td>
<td>1.7–2.7</td>
<td>1.0–1.7</td>
</tr>
<tr>
<td>4</td>
<td>0.35–1.7</td>
<td>0.7–1.7</td>
<td>0.4–1.0</td>
</tr>
<tr>
<td>5</td>
<td>0.3–0.9</td>
<td>0.45–0.75</td>
<td>0.25–0.45</td>
</tr>
<tr>
<td>6</td>
<td>0.16–0.5</td>
<td>0.2–0.4</td>
<td>0.1–0.2</td>
</tr>
</tbody>
</table>

$^a$Using the $\sigma^+$ ($\text{C}_6\text{H}_{5-x}\text{Cl}_x$) values given in Table 4.

$^b$Experimental values (see Figure 2 for a comparison between the measured and calculated rate constants for the PCBs).

calculated room temperature rate constants for PCDDs and PCDFs containing up to five chlorine atoms, assuming that the electrophilic substituent constants of $\text{C}_6\text{H}_{5-x}\text{Cl}_x\text{O}$ groups ($x = 1–4$) were identical to those for the $\text{C}_6\text{H}_5\text{O}$ group. However, it is expected that the electrophilic substituent constants for the $\text{C}_6\text{H}_{5-x}\text{Cl}_x\text{O}$ group will depend on the value of $x$, and the rate constants calculated by Kwok et al.$^95$ for the PCDDs and PCDFs were probably too high, being increasingly overestimated as the degree of chlorination increases. The phenoxy group may exhibit a somewhat lesser effect of Cl substitution on the electrophilic substituent constant than is the case for the phenyl group (because the Cl atoms are further from the attachment point to the aromatic ring). Electrophilic substituent constants for the $\text{C}_6\text{H}_{5-x}\text{Cl}_x\text{O}$ group have been derived assuming that the decrease in $\sigma^+$ ($\Delta\sigma^+$) per additional Cl atom on the phenoxy group is $\sim 0.7$ of that for the phenyl group, and these values of $\sigma^+$ are given in Table 4. It should, of course, be noted that this is all very empirical and that the rate constants estimated for the PCDDs and PCDFs (Table 5) are quite uncertain, the more so the higher the degree of chlorination. For example, if the decrease in $\sigma^+$ ($\Delta\sigma^+$) per additional Cl atom on the phenoxy group is the same as that for the phenyl group, then the calculated rate constants for the PCDDs and PCDFs are lower than those given in Table 5 by a factor which increases with the number of chlorine atoms (with this factor being 1.1–1.3 for the PCDDs and PCDFs containing two chlorine atoms and 1.4–1.7 for those containing five chlorine atoms).

Photolysis

While there have been a number of studies concerning the absorption cross-sections, photolysis rates and photolysis quantum yields of PCBs,$^{107–109}$ PCDDs$^{107,109–117}$

Atmospheric Chemistry of PCBs, PCDDs and PCDFs

and PCDFs in the solution phase, there have been few studies dealing with the absorption cross-sections or photolysis rates of chlorinated biphenyls, dibenzo-<i>p</i>-dioxins or dibenzofurans in the gas phase. Berman <i>et al.</i> measured the absorption spectra and cross-sections of the first absorption band of 3,3′,4,4′-tetrachlorobiphenyl at 250, 300 and 350°C, and observed that the long-wavelength threshold of this band was red-shifted with increasing temperature, from 302 nm at 250°C to 306 nm at 350°C. Extrapolation of these long-wavelength thresholds to lower temperatures results in a long-wavelength threshold for 3,3′,4,4′-tetrachlorobiphenyl of 293 nm at 298 K, with marginal overlap of the absorption spectrum with the tropospheric solar spectrum. In the study of Orth <i>et al.</i>, 2,3,7,8-tetrachlorodibenzo-<i>p</i>-dioxin was photolysed at 150°C over the wavelength range <i>\lambda</i> 250−340 nm. While photolysis was observed, this could have been due to photolysis at wavelengths <i>\lambda</i> 290 nm (shorter than those in the troposphere) and the effect of elevated temperature may also have been significant. Funk <i>et al.</i> measured the absorption spectra and cross-sections of three PCDDs and two PCDFs at elevated temperatures (120−300°C), and observed the peak wavelengths and approximate long-wavelength thresholds of the first absorption band to be at 303 nm and ~340 nm for both 2,3,7,8-tetrachlorodibenzo-<i>p</i>-dioxin and 1,2,3,7,8-pentachlorodibenzo-<i>p</i>-dioxin, at 305 nm and ~360 nm for octachlorodibenzo-<i>p</i>-dioxin, at 300 nm and ~340 nm for 2,3,7,8-tetrachlorodibenzo furan and at 333 nm and ~365 nm for octachlorodibenzofuran, with no evidence for shifts of the peak wavelength with temperature over the limited ranges employed. It should be noted that the long-wavelength threshold for absorption of dibenzofuran in the gas phase at room temperature is at ~299−300 nm, indicating that the chlorinated dibenzofurans will absorb radiation within the actinic region in the troposphere.

6 Transformations of Particle-phase PCBs, PCDDs and PCDFs

Few direct data are available concerning the chemical and photochemical degradations of PCBs, PCDDs and PCDFs present in the particle phase. Tysklind and Rappe irradiated fly-ashes containing PCDDs and PCDFs from incineration plants with artificial UV light (at wavelengths ≥300 nm) for up to 288 h. After 288 h the fly-ash samples showed ~10−15% losses of the tetrachloro- to octachlorodibenzo-<i>p</i>-dioxins and ~0−20% losses of the tetrachloro- to octachlorodibenzo furans. Similar results were obtained for sunlight absorption in the gas phase.

irradiation for 28 h. Koester and Hites used a rotary photoreactor to irradiate fly-ashes containing PCDDs and PCDFs at wavelengths >295 nm (with the light intensities at 295–305 nm and 310–315 nm being higher than natural sunlight at 50° zenith angle). Within the experimental uncertainties of ±35%, Koester and Hites observed no photodegradation of the tetrachloro- to octachlorodibenzo- \( p \)-dioxins or dibenzofurans upon irradiating four fly-ashes (ranging in colour from black to grey to yellow) for up to 200 h. Furthermore, irradiation of pre-cleaned black fly-ash spiked with selected tetrachloro- to hexachlorodibenzo- \( p \)-dioxins and dibenzofurans for 100 h led to no photodegradation of the spiked PCDDs or PCDFs within the experimental uncertainties. These data indicate that photolysis of fly-ashes containing PCDDs and PCDFs is of negligible or minor importance in the atmosphere, and this conclusion may also hold for particle-phase PCDDs, PCDFs and PCBs in general.

7 Tropospheric Lifetimes of PCBs, PCDDs and PCDFs

Gas-phase PCBs, PCDDs and PCDFs

The little information available (see above) suggests that photolysis of gas-phase PCBs in the troposphere will be negligible for those PCBs with \( \leq 4 \) chlorine atoms, and this may also be the case for the more chlorinated PCBs. However, it appears that the PCDDs and PCDFs will absorb radiation in the actinic region in the troposphere, and hence the importance of photolysis will depend on the photodissociation quantum yields in the gas phase, which are, however, not presently known.

The measured rate constants, or upper limits thereof, for the gas-phase reactions of OH radicals, NO\(_3\) radicals and O\(_3\) can be combined with the estimated ambient tropospheric concentrations of OH radicals, NO\(_3\) radicals and O\(_3\) to calculate the tropospheric lifetimes of the gas-phase PCBs, PCDDs and PCDFs due to each of these reactions. The lifetime, \( \tau_x \), for reaction with species X is given by \( \tau_x = (k_x[X])^{-1} \). Ambient concentrations (molecule cm\(^{-3}\)) of: OH radicals, a 24 h, seasonal, annual and global tropospheric average of \( 9.7 \times 10^5 \); NO\(_3\) radicals, a 12 h nighttime average of \( 5 \times 10^8 \); and O\(_3\), a 24 h average of \( 7 \times 10^{11} \) (30 \( \times 10^{-9} \) mixing ratio) are used to calculate lifetimes due to these gas-phase reactions.

The upper limits to the O\(_3\) reaction rate constants given in Table 1, and the expected upper limit to the rate constants for the gas-phase reactions of O\(_3\) with PCB, PCDD and PCDF congeners of \( < 2 \times 10^{-20} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (see above), lead to a calculated lower limit to the tropospheric lifetimes of PCB, PCDD and PCDF congeners due to gas-phase reaction with O\(_3\) of \( > 2 \) years. Similarly, the upper limit to the measured bimolecular rate constants \( k_{abs} \) for reactions of the NO\(_3\) radical with PCBs, PCDDs and PCDFs under tropospheric conditions, of \( k_{abs} < 1 \times 10^{-15} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), leads to a lower limit to the tropospheric lifetimes of PCB, PCDD and PCDF congeners due to gas-phase reaction with the NO\(_3\) radical of \( > 45 \) days.

In contrast, reactions of the PCBs, PCDDs and PCDFs with the OH radical
Table 6 Calculated tropospheric lifetimes of gas-phase PCBs, PCDDs and PCDFs due to reaction with the OH radical

<table>
<thead>
<tr>
<th>No. Cl atoms</th>
<th>PCBs</th>
<th>PCDDs</th>
<th>PCDFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.8</td>
<td>1.2 (0.8)(^b)</td>
<td>1.7 (3.1)(^b)</td>
</tr>
<tr>
<td>1</td>
<td>2.6–3.7</td>
<td>1.9 (2.5)(^b)</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>3.8–9</td>
<td>2.8–4.4</td>
<td>4.3–6.6</td>
</tr>
<tr>
<td>3</td>
<td>5.7–12</td>
<td>4.4–7</td>
<td>7–12</td>
</tr>
<tr>
<td>4</td>
<td>7–34</td>
<td>7–17</td>
<td>12–30</td>
</tr>
<tr>
<td>5</td>
<td>13–40</td>
<td>16–27</td>
<td>27–48</td>
</tr>
<tr>
<td>6</td>
<td>24–75</td>
<td>30–60</td>
<td>60–120</td>
</tr>
</tbody>
</table>

\(^a\)Calculated using the estimated OH radical reaction rate constants given in Table 5 and assuming a 24 h average OH radical concentration of \(9.7 \times 10^5\) molecule cm\(^{-3}\). \(^b\)Using the experimentally measured reaction rate constants.

lead to calculated lifetimes, using the measured and estimated OH radical reaction rate constants given in Tables 3 and 5, ranging from 1.7 days for biphenyl, 0.8 days for dibenzo-\(\mu\)-dioxin and 3 days for dibenzofuran to \(\sim 13–40\) days for the pentachlorobiphenyls, \(\sim 16–27\) days for the pentachlorodibenzo-\(\mu\)-dioxins and \(\sim 27–48\) days for the pentachlorodibenzofurans. The calculated lifetimes for the OH radical reactions are given in Table 6. Within the PCBs, PCDDs and PCDFs the calculated lifetimes increase with increasing chlorination, by a factor of \(\sim 1.7\) per extra chlorine atom for each class of organochlorine compound. The lifetimes for the PCB congeners are expected to be reasonably reliable, because of the existence of measured rate constants for a fairly large number of PCBs, including pentachlorobiphenyls (Table 3). In contrast, apart from dibenzo-\(\mu\)-dioxin, 1-chlorodibenzo-\(\mu\)-dioxin and dibenzofuran, the estimated lifetimes for the OH radical reactions with the PCDD and PCDF congeners are quite uncertain, and as discussed above the uncertainties increase with increasing chlorination. It should be recognized that in all cases the calculated lifetimes are inversely proportional to the tropospheric OH radical concentration assumed.

Particle-phase PCBs, PCDDs and PCDFs

As discussed above, the PCBs, PCDDs and PCDFs present in the atmosphere in the particle phase will be removed from the troposphere by wet and dry deposition of the particles, and potentially also by photolysis and/or reaction of the particle-phase PCBs, PCDDs and PCDFs. At the present time, insufficient data are available to assess the importance of photolysis and/or chemical reactions of the particle-phase congeners, although the studies of Tysklind and Rappe\(^{122}\) and Koester and Hites\(^{123}\) suggest that photolysis is not important. Upper limits to the lifetimes of the particle-phase PCBs, PCDDs and PCDFs are given by those for wet and dry deposition of the particles, with these lifetimes depending on a number of factors, as discussed above. Based on the approximate calculations given above for the lifetimes of particles due to wet and dry deposition, and the data of Balkanski \textit{et al.}\(^{83}\) for aerosol-phase \(^{210}\)Pb, the lifetimes of particle-associated PCBs, PCDDs and PCDFs due solely to wet and dry deposition are expected to be in the range \(\sim 5–30\) days, depending on particle
8 Conclusions

In the atmosphere, the PCBs, PCDDs and PCDFs are distributed between the gas and particle phases, with the more chlorinated congeners partitioning more into the particle phase. In general, the PCBs, PCDDs and PCDFs containing \( \leq 5 \) chlorine atoms are present largely in the gas phase, with the congeners containing \( \geq 6 \) chlorine atoms being present mainly in the particle phase (although this gas/particle partitioning is a function of the atmospheric temperature, with lower temperatures favouring partitioning into the particle phase, and on the particle loading in the atmosphere). The available laboratory and ambient air data indicate that the dominant tropospheric loss processes for the PCBs, PCDDs and PCDFs are wet and dry deposition for those PCBs, PCDDs and PCDFs present in the atmosphere in the particle phase, and reaction with the OH radical for those PCBs, PCDDs and PCDFs present in the atmosphere in the gas phase. However, photolysis of gas-phase PCDDs and PCDFs and reaction of gas-phase PCDDs with the \( \text{NO}_3 \) radical cannot presently be ruled out as being of importance as PCDD and/or PCDF loss processes in the troposphere. The estimated lifetimes of the gas-phase PCBs, PCDDs and PCDFs increase with increasing chlorination, from \( \sim 0.8\text{–}3 \) days for biphenyl, dibenzo-p-dioxin and dibenzofuran to \( \sim 15\text{–}50 \) days for the pentachloro-biphenyls, dibenzo-p-dioxins and -dibenzofurans (with the calculated lifetimes being inversely dependent on the OH radical concentration assumed). The lifetimes for the particle-phase and more highly chlorinated PCBs, PCDDs and PCDFs appear to be determined by wet and dry deposition of the ‘host’ particles, with estimated lifetimes of \( \sim 5\text{–}30 \) days, depending on a number of factors including the frequency of precipitation events. The lifetimes of the chlorinated biphenyls, dibenzo-p-dioxins and dibenzofurans are \( >1 \) day and therefore allow (especially for the congeners containing \( \geq 3 \) chlorine atoms) long-range transport of these organochlorine compounds into remote areas of the world.

There are clearly several areas of significant uncertainty, including the role of photolysis in both the gas and particle phases and the identities and formation yields of the products of the gas-phase OH radical reactions.

9 Acknowledgements

Drs. R. A. Hites and P. N. Anderson are gratefully thanked for communicating their rate constant data for the gas-phase reactions of the OH radical with PCBs prior to publication, and Dr. J. Arey is thanked for helpful discussions.