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Atmospheric oxidation of halogenated aromatics: comparative analysis of reaction mechanisms and reaction kinetics

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Atmospheric transport is the major route for global distribution of semi-volatile compounds such as halogenated aromatics as well as their major exposure route for humans. Their major atmospheric removal process is oxidation by hydroxyl radicals. There is very little information on the reaction mechanism or reaction-path dynamics of atmospheric degradation of halogenated benzenes. Furthermore, the measured reaction rate constants are missing for the range of environmentally relevant temperatures, *i.e.* 230–330 K. A series of recent theoretical studies have provided those valuable missing information for fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene. Their comparative analysis has provided additional and more general insight into the mechanism of those important tropospheric degradation processes as well as into the mobility, transport and atmospheric fate of halogenated aromatic systems. It was demonstrated for the first time that the addition of hydroxyl radicals to monohalogenated as well as to perhalogenated benzenes proceeds indirectly, *via* a prereaction complex and its formation and dynamics have been characterized including the respective transition-state. However, in fluorobenzene and chlorobenzene reactions hydroxyl radical hydrogen is pointing approximately to the center of the aromatic ring while in the case of hexafluorobenzene and hexachlorobenzene, unexpectedly, the oxygen is directed towards the center of the aromatic ring. The reliable rate constants are now available for all environmentally relevant temperatures for the tropospheric oxidation of fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene while pentachlorophenol, a well-known organic micropollutant, seems to be a major stable product of tropospheric oxidation of hexachlorobenzene. Their calculated tropospheric lifetimes show that fluorobenzene and chlorobenzene are easily removed from the atmosphere and do not have long-range transport potential while hexafluorobenzene seems to be a potential POP chemical and hexachlorobenzene is clearly a typical persistent organic pollutant.

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Environmental impact

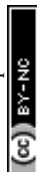
A study on the atmospheric fate and degradation of semi-volatile halogenated aromatics is of high environmental relevance as well as of broad interest for several areas of environmental research such as atmospheric chemistry, environmental modeling, degradation/transformation of chemicals, secondary pollution, *etc.* The atmospheric transport is the major route for their global distribution as well as a major exposure route to humans. The major atmospheric removal process of halogenated aromatics is their oxidation by hydroxyl radicals. This comparative study will provide additional and more general insight into the mechanism of this important tropospheric process as well as into the mobility, transport and atmospheric fate of halogenated aromatic systems. The reported results will also be important for modeling their environmental behavior and fate.

1. Introduction

A large amount of volatile and semivolatile organic chemicals (10^8 tons) are released annually into the atmosphere from a variety of anthropogenic sources.¹ The primary removal route of anthropogenic pollutants from the atmosphere is their

oxidation by various oxidizing species present in the atmosphere.^{2,3} The most effective atmospheric degradation process is oxidation by hydroxyl radicals^{4–7} due to their high reactivity as well as their significant and constant tropospheric concentration, *i.e.* 9.7×10^5 radicals cm^{-3} .⁸ It is of interest to note here that oxidation by hydroxyl radicals is also important for (bio) degradation of organic pollutants in aquatic and terrestrial systems.^{9–12} Other oxidation species that effectively contribute to the removal of anthropogenic pollutants from the atmosphere are ozone (O_3), the nitrate radical (NO_3) and halogen

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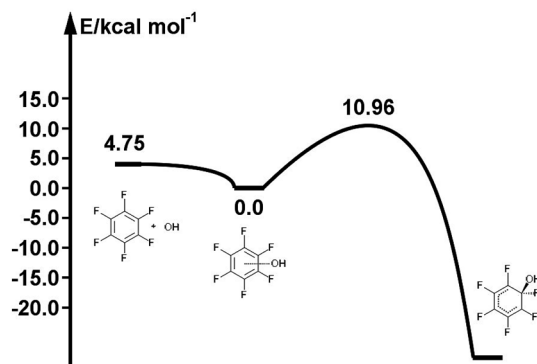


Fig. 1 Schematic energy path for the addition of hydroxyl radicals to hexafluorobenzene. The values obtained by the G3 method are enthalpies at room temperature (298.15 K) relative to the pre-reaction complex in kcal mol⁻¹. Reprinted from ref. 83 with the permission of Croatian Chemical Society according to CC BY license (<https://creativecommons.org/licenses/by/4.0/>).

between hydroxyl radical oxygen and the aromatic ring are somewhat larger for hexafluorobenzene and hexachlorobenzene, *i.e.* 2.76 and 2.89 Å, respectively. The higher stabilization energies of pre-reaction complexes with perhalogenated benzenes (4.75 or 6.6 kcal mol⁻¹) seem to be a consequence of electrostatic interaction between the partially negatively charged oxygen atom and a positive electrostatic potential of the aromatic ring due to the strong electron withdrawing effect of six halogen atoms (Fig. 3).⁹⁷ An analogous complex was published also for hexafluorobenzene and hydrogen fluoride.⁹⁸ In the case of monohalogenated benzenes, the lower stabilization energies of pre-reaction complexes (2.98 or 2.99 kcal mol⁻¹) are a result of electrostatic interaction between the partially positively charged hydrogen atom and a negative electrostatic potential of the aromatic ring (Fig. 3).⁹⁷

The formation of pre-reaction complexes proceeds across loose transition states^{79,81,83,84,95,96} which are favorable for the

formation of pre-reaction complexes since those transition states reduce the dissociation rate of pre-reaction complexes (eqn (1)). The loose transition states seem to be analogous to the outer transition state suggested for the addition of the hydroxyl radical to ethylene.⁹⁹ Each pre-reaction complex has several low vibrational frequencies (35–90 cm⁻¹) corresponding to the relative motions of the OH radical and halogenated benzene which are critical for the oxidation of halogenated benzenes. One degree of freedom corresponds to receding of the hydroxyl radical from the corresponding halogenated benzene while two degrees of freedom correspond to the nearly free movement of the hydroxyl radical across the plain of the aromatic ring. By the last two motions, the hydroxyl radical can approach all aromatic carbons and interact with them. The normal mode which corresponds to the receding motion of the hydroxyl radical is responsible for the dissociation of the pre-reaction complex.

3.2. Rearrangement of pre-reaction complexes into the “hot” adducts

In the pre-reaction complexes, the hydroxyl radical is almost perpendicular to the aromatic ring and points approximately to the center of the aromatic ring. It has a flat potential energy surface (Fig. 4) which makes possible the large amplitude motions of the hydroxyl radical. For example, in the case of a hexachlorobenzene pre-reaction complex the change in its potential energy is only 8 meV (0.185 kcal mol⁻¹) while the OH radical slides from the center of the ring to one of the carbon atoms which compares favorably with the room temperature thermal energy of about 25 meV (0.577 kcal mol⁻¹). These large amplitude motions enable the hydroxyl radical to approach all carbon atoms in the benzene ring and interact with them.

Once the hydroxyl radical approaches one of the carbon atoms in halogenated benzenes, it starts to change its orientation from perpendicular to parallel with respect to the benzene ring. At the same time, the oxygen atom and a specific carbon

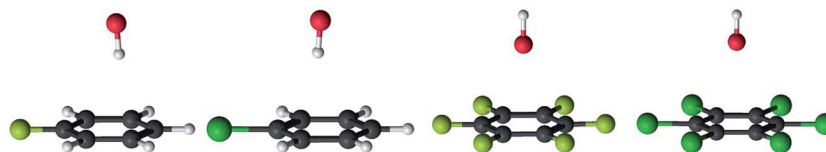


Fig. 2 The pre-reaction complexes of the OH radical with fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene. Carbon atoms are black, hydrogens are white, oxygens are red, fluorine atoms are yellow and chlorine atoms are green.



Fig. 3 Plots of electrostatic potential of fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene calculated at the MP2/6-31G(d,p) level. Blue color corresponds to the negative electrostatic potential areas while red color corresponds to the positive electrostatic potential areas. Green color describes areas with principally neutral electrostatic potential.



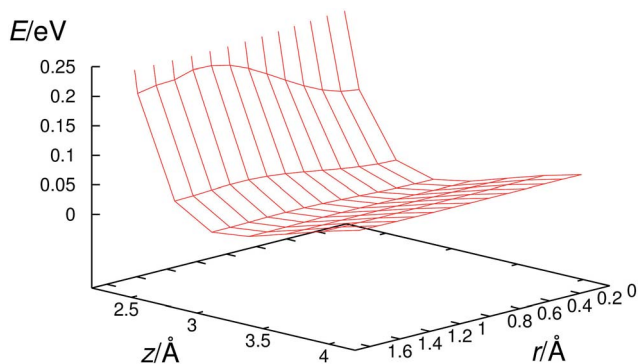


Fig. 4 Potential energy surface of the hexachlorobenzene prereaction complex obtained at the MP2/6-311+G(d,p) level while using the reduced basis set 6-31+G(d,p) for chlorine atoms. The OH radical was translated parallel (r axis) and perpendicular (z axis) with respect to the benzene ring. The origin of r and z axes is in the center of the benzene ring. $0.1 \text{ eV} = 2.31 \text{ kcal mol}^{-1}$.

atom start to attract each other and, consequently, the carbon atom at the reaction center moves from the aromatic ring plain toward the oxygen atom. The range of displacements of such carbon atoms from planarity is between 0.2 and 0.4 Å for tested halogenated benzenes. All these processes result in a significant increase in the potential energy of the reacting system and the transition state is formed at that stage (Fig. 5). In the transition state, the hydroxyl radical is approximately parallel to the aromatic ring. The oxygen atom is located directly above the interacting carbon atom while the hydrogen atom is pointing towards the ring center. The separation between hydroxyl radical oxygen and reacting carbons is almost identical, *i.e.* 1.96–1.97 Å, for all ten transition states of fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene oxidation by the hydroxyl radical. The C–O bond formation and concurrent relaxation of the aromatic ring lower the energy of the reacting molecular system and it slides into a deep well producing a “hot” adduct with a large amount of excess energy (20–40 kcal mol⁻¹). The detailed reaction pathway dynamics,

from the prereaction complexes to the formation of adducts, for chlorobenzene and hexachlorobenzene are shown in the video files published as freely accessible supplement material in the source publications (<http://dx.doi.org/10.1016/j.chemosphere.2013.04.041> and <http://dx.doi.org/10.1016/j.chemosphere.2016.06.026>).^{81,84}

3.3. Reaction thermodynamics

All oxidation reactions of halogenated benzenes by hydroxyl radicals are highly exothermic and have reaction enthalpies from -14.5 to $-32.8 \text{ kcal mol}^{-1}$ (Table 1) and, at its first step, produce “hot” adducts with large amounts of excess energy. However, all those reactions also have high reaction barriers which range from 5.2 up to 7.3 kcal mol⁻¹ (Table 1) and consequently the rearrangement of prereaction complexes into “hot” adducts seems to be kinetically driven. Unfortunately, there is no simple correlation between calculated reaction barriers and measured reaction rates although the slowest reaction for hexachlorobenzene also has the highest reaction barrier. Thus, it is fair to conclude that the rate control for the oxidation reactions of halogenated benzenes by the hydroxyl radical is most probably an intricate interplay between the depth of the prereaction complex well, *i.e.* the amount of excess energy present in the prereaction complex, and the height of the reaction barrier for the individual reaction.

3.4. Reaction rates and atmospheric lifetimes

There is an exceptional correspondence between the calculated and measured rate constants for all four oxidation reactions of halogenated benzenes by hydroxyl radicals^{79,81,83,84} (Table 2) and it holds for the whole temperature range of available measured data. Thus, for the first time, reliable rate constants are available for the whole range of environmentally relevant temperatures for atmospheric degradation of important halogenated benzenes, *i.e.* fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene. Furthermore, the unusual and different temperature trends were nicely reproduced for all four oxidation reactions of halogenated benzenes by hydroxyl radicals, *i.e.* no or

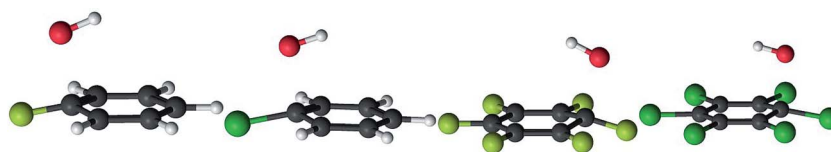


Fig. 5 The transition states for addition of OH radicals to fluorobenzene (*ipso*-isomer), chlorobenzene (*ipso*-isomer), hexafluorobenzene and hexachlorobenzene. Carbon atoms are black, hydrogens are white, oxygens are red, fluorine atoms are yellow and chlorines are green.

Table 1 Thermodynamic data and rate constants of fluorobenzene (C₆H₅F), chlorobenzene (C₆H₅Cl), hexafluorobenzene (C₆F₆) and hexachlorobenzene (C₆Cl₆) oxidation by the hydroxyl radical

Properties	C ₆ H ₅ F	C ₆ H ₅ Cl	C ₆ F ₆	C ₆ Cl ₆
Prereaction complex binding energy (kcal mol ⁻¹)	2.98	2.99	4.75	6.59
Reaction barrier (kcal mol ⁻¹)	5.21	4.69	6.21	7.30
Reaction enthalpy (kcal mol ⁻¹)	14.49–20.61	14.90–17.76	32.78	24.58
Rate constant × 10 ¹³ (298 K)	7.90	6.02	1.52	0.28



Table 2 Comparison of calculated (k_{calc})^{79,81,83,84} and experimental (k_{exp}) rate constants (cm^3 per molecule per s) for the addition of hydroxyl radicals to fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene

T/K	$k_{\text{calc}} \times 10^{13}$	T/K	$k_{\text{exp}} \times 10^{13}$
Fluorobenzene^a			
230–310	9.46–7.60	230–310	6.90 ± 1.38
295	7.76	296	7.9 ± 2.2^b
Chlorobenzene^a			
230–300	7.98–3.15	230–300	7.7 ± 3.1
300	3.15	299	$5.83\text{--}6.17^c$
Hexafluorobenzene^d			
330	0.81	327	2.15 ± 0.12
290–300	0.60–0.64	294	1.52 ± 0.09
270–280	0.46–0.52	275	1.36 ± 0.08
260	0.42	260	1.09 ± 0.06
240–250	0.27–0.33	244	0.79 ± 0.04
Hexachlorobenzene^e			
380	2.10	386	2.45 ± 0.07
360	1.30	367	1.75 ± 0.05
340	1.07	347	1.05 ± 0.03
300	0.31	298	$0.20\text{--}0.38^f$

^a Ref. 100. ^b Ref. 101. ^c Ref. 80. ^d Ref. 102. ^e Ref. 103. ^f Estimated in ref. 103.

very weak temperature dependence for fluorobenzene and chlorobenzene, weak but significant positive temperature dependence for hexafluorobenzene and positive, nonlinear temperature dependence for hexachlorobenzene.

However, in order to obtain such a good correspondence between the calculated and measured rate constants, it was

necessary to introduce two critical approximations in the procedure for calculating reaction rate constants. First of all, we had to apply a two-dimensional particle-in-the-box approximation to correctly describe the relative translation of the hydroxyl radical with respect to individual halobenzene in the pre-reaction complex since the harmonic oscillator approximation poorly describes this low frequency motion which has a very flat potential as shown for hexachlorobenzene in Fig. 4. In order to demonstrate even more clearly the poor performance of harmonic oscillator approximation in describing this translational motion, we have plotted in Fig. 6 the 2D potential energy of harmonic oscillator vs. two-dimensional particle-in-the-box approximation for the translation of the hydroxyl radical over hexachlorobenzene. Even a brief inspection of Fig. 6 clearly shows that the particle-in-the-box approximation provides far more adequate description of flat potential presented in Fig. 4. It should be also indicated here that, besides the major difference in the shape of those two potential curves, there is a large difference in the zero point energies, 2.28 (0.053) vs. 0.153 (0.0035) meV (kcal mol^{-1}), as well as in the density of states. Thus, the particle-in-the-box approximation facilitates the rearrangement of pre-reaction complexes into adducts and significantly increases all reaction rates, up to several orders of magnitude for hexachlorobenzene (Table 3).

For reactions of fluorobenzene, chlorobenzene and hexafluorobenzene, it was also necessary to adjust the level of the reaction barrier and pre-reaction complex well in order to reproduce the measured reaction rate constants. This correction facilitates the formation of pre-reaction complexes as well as the rearrangement of pre-reaction complexes into adducts. However, although this correction also has a significant effect on reaction rates, its magnitude is relatively constant and about

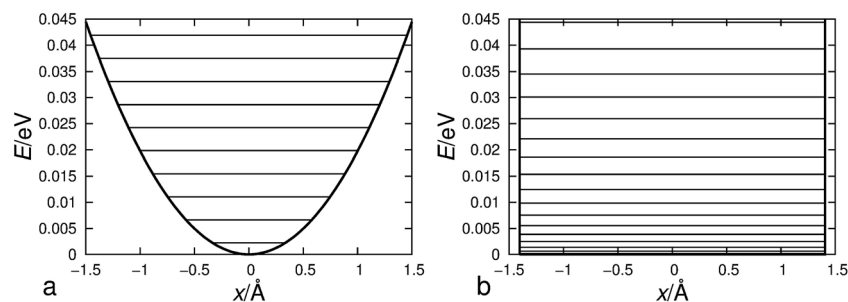


Fig. 6 The potential energy plots of harmonic approximation (a) and a two-dimensional particle-in-the-box approximation (b) for the translation of the hydroxyl radical over hexachlorobenzene. $1 \text{ meV} = 0.023 \text{ kcal mol}^{-1}$.

Table 3 The correction factor of calculated reaction rates for the addition of the hydroxyl radical to halogenated benzenes due to the two-dimensional particle-in-the-box approximation and the lowering of energies of the pre-reaction complex well and reaction barrier^a

Correction factors	$\text{C}_6\text{H}_5\text{F}$	$\text{C}_6\text{H}_5\text{Cl}$	C_6F_6	C_6Cl_6
Two-dimensional particle-in-the-box approximation (cm^3 per molecule per s)	29.6	1.80	22.0	749
Lowering of the reaction barrier and pre-reaction complex well (cm^3 per molecule per s)	23.7	12.8	12.1	na
Energy correction (kcal mol^{-1})	0.7	1.07	0.7	None
Rate constant $\times 10^{13}$ (300 K)	7.70	3.15	0.64	0.31

^a na – not applied.



an order of magnitude for all three reactions (Table 3). It should be noted that the energy correction applied for those three oxidation reactions is smaller or equal to the uncertainty (1.07 kcal mol⁻¹) in G3 results obtained for a representative set of 376 test molecules.⁸⁸ Furthermore, by energy corrections of reaction barriers and prereaction complex wells, the whole potential energy profiles between them have been shifted and, thus, the energy gaps between those two most important stationary points were unaltered.

The high quality of calculated reaction rate constants for the whole range of environmentally relevant temperatures^{79,81,83,84} enabled the calculation of accurate tropospheric lifetimes for fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene. Their tropospheric lifetimes were calculated by

$$\tau = 1/(k_{\text{calc}} \times [\text{OH}]) \quad (2)$$

where k_{calc} is the calculated reaction rate at 277 K, the average temperature of the Earth's troposphere,¹⁰⁴ and [OH] is the global tropospheric hydroxyl radical concentration averaged over 24 h period (9.7×10^5 radicals per cm³).⁸ The calculated tropospheric lifetimes and calculated reaction rates at 277 K for oxidation by hydroxyl radicals are shown in Table 4. The calculated reaction rates at 277 K were interpolated from the calculated rate constants at 270 and 280 K.

The calculated tropospheric lifetimes of fluorobenzene and chlorobenzene show that those chemicals are relatively easily removed from the atmosphere and do not have potential for a long-range transport. For hexafluorobenzene the calculated tropospheric lifetime is 237 days which indicates its status as a potential POP chemical. Finally, the calculated tropospheric lifetime of hexachlorobenzene is 522 days which supports its status of a classical POP chemical as well as its observed long-range transport.^{105,106} Namely, today hexachlorobenzene is regularly detected all over the world in the air, soil, water, sediment, biota and human tissue samples including the remote areas.¹⁰⁵⁻¹⁰⁸ Furthermore, in the recent study it was detected in 99.9% of human serum samples of the US population.¹⁰⁹

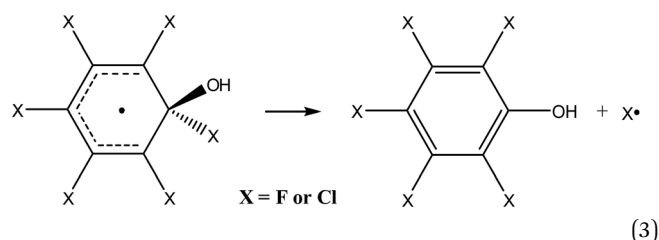
3.5. Stable oxidation products of halogenated benzenes

There is little or no information on the reaction products of hydroxyl radical addition to halogenated benzenes and in particular for perhalogenated derivatives, hexafluorobenzene and hexachlorobenzene. The reaction with O₂ has been identified as the main reaction channel in the troposphere for aromatic adducts (X-C₆H₅-OH, X = H, CH₃, OH, etc.)^{74,110,111} and

major stable products are phenols.^{110,112-114} Glowacki *et al.*⁷³ examined the product formation channels for hydroxyl radical addition to benzene. It was found out that phenol and HO₂ are formed predominantly by direct *ipso*-hydrogen abstraction by O₂ from the HO-benzene adduct. Their high yield (55%) was in agreement with the recent experimental results.^{112,113,115}

For fluorobenzene, the yield of 4-fluorophenol was 10% following the reaction of the hydroxyl radical and fluorobenzene while the yield of 2-fluorophenol or 3-fluorophenol was below the detection limits (>3%).¹⁰¹ Consequently, we have calculated the reaction barriers for the elimination of fluorine atom from an *ipso*-adduct, product phenol, as well as for the elimination of hydrogen atom from the *para*-adduct, product 4-fluorophenol.⁷⁹ The G3 reaction barrier for elimination of fluorine atom was 22.4 kcal mol⁻¹ but, since the excess energy of the "hot" *ipso*-adduct was 27.6 kcal mol⁻¹, this reaction channel seems to be feasible. However, since the *ipso*-adduct is only a minor primary product, this reaction channel may contribute only a small fraction of total phenols. The G3 reaction barrier for elimination of hydrogen atom was similar, *i.e.* 23.8 kcal mol⁻¹ while the excess energy of the "hot" *para*-adduct was 19.7 kcal mol⁻¹ and this reaction channel may be feasible too. Since the *para*-adduct is a major primary product, it seems that the direct elimination of hydrogen atom also contributes to the formation of 4-fluorophenol. It was also evaluated for chlorobenzene⁸⁰ and bromobenzene¹¹⁶ that phenol can be produced by the direct elimination of halogen atoms from their *ipso*-adducts.

By analogy to the tropospheric oxidation of monosubstituted benzenes, it may be assumed for perhalogenated derivatives that the major ring-retaining product will be pentafluorophenol or pentachlorophenol, produced by direct elimination of halogen atoms from the respective adduct (eqn (3)).



In order to prove that this process is thermodynamically and kinetically feasible, the transition state was optimized for the direct elimination of chlorine atom from the "hot" hexachlorobenzene adduct. The optimized geometry shows that the separation between the quaternary carbon atom and the leaving chlorine in the transition state is 3.31 Å and that the reaction barrier for the direct elimination of chlorine atom and formation of pentachlorophenol is quite low, only 4.1 kcal mol⁻¹.⁸⁴ Since the excess energy of the "hot" hexachlorobenzene adduct is huge with respect to this reaction barrier, *i.e.* 32 kcal mol⁻¹, the above results unambiguously demonstrate that the formation of pentachlorophenol is thermodynamically and kinetically feasible and that it should proceed easily. An analogous product, *i.e.* pentafluorophenol, was also recently postulated for the reaction of the hydroxyl radical with hexafluorobenzene⁸³

Table 4 Tropospheric lifetimes and calculated rate constants at 277 K for the oxidation of fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene by hydroxyl radicals

Properties	C ₆ H ₅ F	C ₆ H ₅ Cl	C ₆ F ₆	C ₆ Cl ₆
Rate constant × 10 ¹³ (277 K)	7.94	3.947	0.502	0.229
Tropospheric lifetime (days)	15	30	237	522



since for its “hot” adduct excess energy is also more than 30 kcal mol⁻¹.

Since the tropospheric concentration of hexachlorobenzene is fairly constant and uniform,^{117,118} the atmospheric production of pentachlorophenol seems to be a global phenomenon that will proceed at a constant pace for a long time due to the steady-state concentration of atmospheric hexachlorobenzene. Once produced, pentachlorophenol, due to its lower hydrophobicity, will be transported by the wet or dry deposition into the Earth's aquatic and solid systems since both compartments have a much higher affinity for pentachlorophenol than the air. Those results reveal that the troposphere may be an undisclosed global secondary source of pentachlorophenol relevant for all environmental compartments as well as a new exciting research area.

4. Conclusions

Direct and detailed insight was obtained into the complete reaction mechanism and reaction dynamics of OH radical addition to four halogenated benzenes, *i.e.* fluorobenzene, chlorobenzene, hexafluorobenzene and hexachlorobenzene. The presented studies have shown for the first time that the addition of OH radicals to all halogenated benzenes proceeds *via* a prereaction complex. The structure and reaction dynamics of prereaction complexes of monohalogenated benzenes are substantially different from those of perhalogenated benzenes. Namely, in the prereaction complexes of fluorobenzene and chlorobenzene hydrogen atoms of hydroxyl radicals are pointing approximately to the center of the aromatic ring while in the case of hexafluorobenzene and hexachlorobenzene the oxygen atom is unexpectedly directed towards the center of the aromatic ring. The substantial structural difference in the pre-reaction complexes is a consequence of a positive electrostatic potential of the aromatic ring in hexafluorobenzene and hexachlorobenzene due to the strong electron withdrawing effect of six halogen atoms. All oxidations of halogenated benzenes by hydroxyl radicals are highly exothermic and produce “hot” adducts with large amounts of excess energy. It was also demonstrated that pentachlorophenol, a well-known organic micropollutant, may be a major stable product of tropospheric oxidation of hexachlorobenzene and that atmosphere seems to be its hidden global secondary source. The reliable rate constants are now determined for the whole range of environmentally relevant temperatures (230–330 K) for the oxidation of fluorobenzene, chlorobenzene hexafluorobenzene and hexachlorobenzene by hydroxyl radicals and calculated rate constants are in excellent agreement with available experimental data. However, for such a good correspondence between the calculated and experimental results it was necessary to use two-dimensional particle-in-the-box approximation for the translation of the hydroxyl radical in prereaction complexes. Furthermore, it is now also possible to calculate the reliable tropospheric lifetimes of those halogenated benzenes for the whole range of environmentally relevant temperatures. The calculated tropospheric lifetimes clearly show that fluorobenzene and chlorobenzene are relatively easily removed

from the atmosphere and do not have potential for a long-range transport while hexafluorobenzene with a calculated tropospheric lifetime of 237 days indicates its status as a potential POP chemical and the calculated tropospheric lifetime of hexachlorobenzene, *i.e.* 522 days, supports its status of a classical persistent organic pollutant.

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