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Laboratory Investigations

Volatile anaesthetics and the atmosphere: atmospheric lifetimes and atmospheric effects of halothane, enflurane, isoflurane, desflurane and sevoflurane

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The atmospheric lifetimes of the halogenated anaesthetics halothane, enflurane, isoflurane, desflurane and sevoflurane with respect to reaction with the hydroxyl radical (OH·) and UV photolysis have been determined from observations of OH· reaction kinetics and UV absorption spectra. Rate coefficients for the reaction with OH radicals for all halogenated anaesthetics investigated ranged from 0.44 to 2.7×10^{-14} cm^3 molec^{-1} s^{-1}. Halothane, enflurane and isoflurane showed distinct UV absorption in the range 200–350 nm. In contrast, no absorption in this wavelength range was detected for desflurane or sevoflurane. The total atmospheric lifetimes, as derived from both OH· reactivity and photolysis, were 4.0–21.4 yr. It has been calculated that up to 20% of anaesthetics enter the stratosphere. As a result of chlorine and bromine content, the ozone depletion potential (ODP) relative to chlorofluorocarbon CFC-11 varies between 0 and 1.56, leading to a contribution to the total ozone depletion in the stratosphere of approximately 1% for halothane and 0.02% for enflurane and isoflurane. Estimates of the greenhouse warming potential (GWP) relative to CFC-12 yield values of 0.02–0.14, resulting in a relative contribution to global warming of all volatile anaesthetics of approximately 0.03%. The stratospheric impact of halothane, isoflurane and enflurane and their influence on ozone depletion is of increasing importance because of decreasing chlorofluorocarbons globally. However, the influence of volatile anaesthetics on greenhouse warming is small.

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The atmosphere can be subdivided according to its temperature profile. The lowest layer where temperature decreases with altitude is called the troposphere. Its upper limit varies between an altitude of 8 and 18 km depending on geographical latitude. The troposphere is followed by the stratosphere, where temperature increases again up to approximately 50 km. Processes occurring in the upper layers (mesosphere, thermosphere and exosphere) are not of interest in this study. Therefore, in this article we use ‘atmosphere’ to refer to the troposphere and stratosphere.

The stratospheric ozone layer is now known to be damaged by long living chlorine- and bromine-containing compounds (chlorofluorocarbons (CFC) and halons) which are released into the atmosphere by human activity. Although the destructive potential of these compounds has been discussed since 1974,[1] this has become obvious only since the discovery of the Antarctic ozone hole in 1985.[2] As a consequence, the use of CFC and halons has been regulated according to the Montreal protocol in 1987 and its subsequent amendments in 1990 and 1992. In contrast with CFC in technical and industrial applications, their use in medical applications has been declared as ‘essential use’ without restrictions. The major use of CFC for medical purposes is as inhalation propellants in pulmonary diseases such as asthma. The total global use of CFC for this application is in the order of 10–12 kilotons per year and hence corresponds to a fraction of the approximate 1% of total CFC consumption before the Montreal protocol regulation.[3]

A second class of halogenated compounds which are used in medicine without regulatory restrictions are the anaesthetic gases halothane ($CF_3CHBrCl$, 2-bromo-2-chloro-1,1,1-trifluorethane), enflurane (CHF_2OCF_2CHFCl, 1-difluormethoxy-2-chloro-1,1,2-trifluorethane), isoflurane (CHF_2O-$CHClCF_3$, 1-difluormethoxy-1-chloro-2,2,2-trifluorethane), desflurane ($CHF_2OCHFCF_3$, 1-difluormethoxy-1,2,2,2-tetrafluorethane) and sevoflurane ($CH_2FOCH(CF_3)_2$, 1-monofluormethoxy-2,2-trifluormethyl-ethane). Although the total amount of these compounds used globally has not been assessed thoroughly, it may be estimated to be in the order of 10 kilotons per year. This scenario is based on the average annual consumption of anaesthetic gases at the University Hospital at Göttingen in the late 1980s (halothane 342 kg, enflurane 16.4 kg, isoflurane 52 kg in a total of 20 000 anaesthetics per year). From the number of hospitals in Germany (size weighted) and the population in developed countries, the total number of inhalation anaesthetics has been estimated at 2×10^8/yr globally. It is well known that more than 80% of inhalation anaesthetic agent is exhaled unchanged by the patient and therefore emitted into the lower atmosphere.[4]

The major atmospheric effects that may arise from emission of volatile anaesthetics are their contribution to ozone depletion in the stratosphere and to greenhouse warming in the troposphere. Atmospheric lifetimes of anthropogenic compounds are the primary basis of assessing these effects. The tropospheric lifetime determines the fraction of the total amount of a halogenated trace gas that enters the stratosphere and hence makes its halogen content available for ozone destruction. Concerning greenhouse warming, the tropospheric lifetime regulates the average concentration level for an anthropogenic compound that influences the infrared radiation balance of the Earth.

To date, little information is available on the ecotoxicological properties of inhalation anaesthetics. Brown and colleagues[5] determined the lifetime of these compounds from OH· reactivity, and the ozone depletion potential (ODP) and greenhouse warming potential (GWP) were estimated. In the present work, similar studies have been performed. In addition to OH·reactivity measurements, UV absorption spectra were detected to derive total photochemical lifetimes (tropospheric+stratospheric lifetimes). From these experiments ODP and GWP values were calculated. Our study also includes experiments with desflurane which have not been done previously.

The first step in our investigation was to determine the rate coefficient k_{OH} for the different anaesthetics. Moreover, we detected the absorption spectra of the anaesthetics in the ultraviolet range 200–350 nm. From the different experiments we derived the tropospheric and total atmospheric lifetimes of the anaesthetic gases to estimate the stratospheric input and influence on the destruction of the ozone layer. The contribution to the greenhouse effect was estimated from the tropospheric lifetimes and literature data of the infrared absorption bands.

Methods

Theory

Trace gases in the atmosphere can be removed by chemical reaction with radicals, by photolysis, and by wet or dry deposition. The atmospheric lifetime τ is the mean residence time of a molecule before it is removed by one of these processes. Note that in atmospheric research, the lifetime τ means the time that a concentration decreases to 1/e. For most reactive trace gases, τ is limited by its reactivity with the hydroxyl radical (OH·) and/or photolysis. It depends on the concentration of the molecule, concentration of the OH· radical and rate coefficient k_{OH} of the reaction in the former case, and on the concentration of the molecule and photodissociation coefficient or frequency of photodissociation j in the latter. While concentrations are measured or gained from models, the rate coefficient k_{OH} and the j values are determined in laboratory experiments. The atmospheric lifetime τ_{OH} is the chemical lifetime and τ_{photo} is the photochemical lifetime. If both processes are significant, a combination of τ_{OH} and τ_{photo} gives the total atmospheric lifetime τ. Details are given in the appendix.

From the atmospheric lifetime, the chemical structure and physical behaviour of a gas, its influence on stratospheric ozone depletion and greenhouse warming can be derived. Means of estimating the extent of this influence are the ozone depletion potential (ODP) and the greenhouse warming potential (GWP), which express the relative effect to other atmospheric trace gases. In our study we used the ODP value relative to CFC-11 and the GWP value relative to CFC-12. More details are given in the appendix.

Experimental method

In order to determine the rate coefficients k_{OH}, laboratory experiments were carried out in a tubular reaction chamber through which the gas mixtures were passed. Hydroxyl radicals were generated by photolysis of HNO_3 at a wavelength of 248 nm by use of an excimer laser (Lambda Physik, EMG 200) as a light source. Decay of the OH· concentration was followed by the laser long-path absorption technique (LLPA; ring-dye laser, Coherent CR 699–21) at 308.42 nm. All experiments were carried out at 298 K and under pseudo-first-order conditions (i.e. concentrations of the anaesthetics were always in excess in order to be considered constant while the concentration of OH· was measured). From more then 100 experiments the rate coefficients, k_{1st}, under first-order conditions were obtained and finally $k_{2nd} \approx k_{OH}$ derived. More experimental details are described in the appendix.

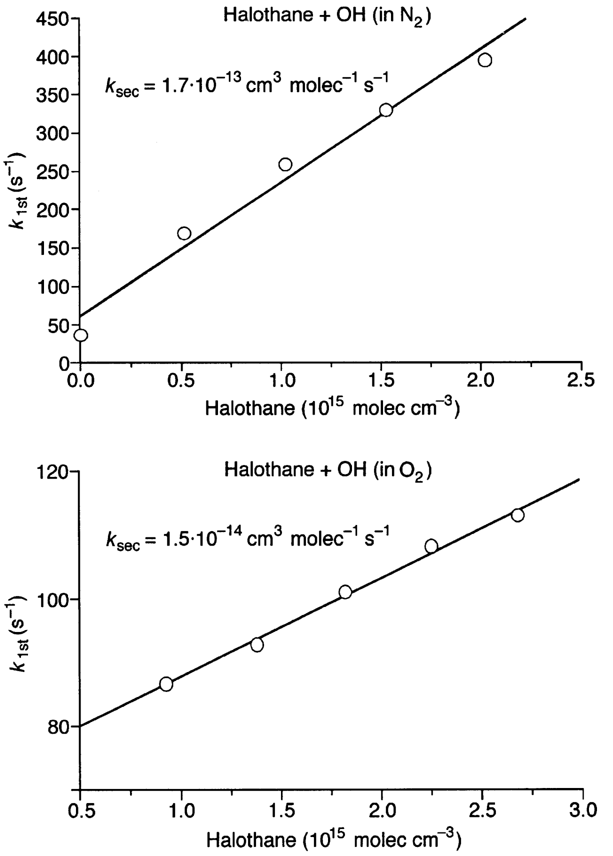

Fig 1 First-order decay constants for OH as a function of halothane concentration, as measured in nitrogen (top) and oxygen (bottom).

UV absorption spectra of the anaesthetics in the range 200–350 nm were detected with a deuterium lamp. Calibration of the deuterium lamp was performed with mercury bands.

Results

OH rate coefficients and chemical lifetimes

In the experimental reaction system, enflurane, isoflurane, desflurane and sevoflurane produced exponential OH· decay profiles, but the same was not true for halothane. At the photolysis wavelength of HNO_3 (248 nm), halothane showed absorption also (see also Fig. 6). Therefore, additional production of photofragments (Br atoms and/or CF_3CHCl-radicals) which consume OH radicals and/or an unexpected OH· generation process can occur. Indeed the measured OH· concentration as a function of time showed a biexponential profile in the experiments with halothane. Moreover, the time constants for the decay of OH· were also dependent on whether nitrogen or oxygen was used as the diluent. In experiments with oxygen, we have also observed, in the absence of HNO_3, OH radicals that must be produced from photolysis of halothane. We used the last part of the OH· decay profile to derive the rate coefficient k_{2nd}= 1.5×10^{-14} cm^3 molec^{-1} s^{-1}. From measurements made in nitrogen we analysed only the foremost part, when additional production of photofragments or OH radicals is negligible, and gained k_{2nd}=1.7×10^{-13} cm^3 molec^{-1} s^{-1} (Fig. 1). Although both sets of experiments gave reproducible results, we consider the result from the HNO_3-free experiment in oxygen as the more correct one. This conclusion is based on the recognition that it is additional radical production by photolysis of halothane which is responsible for enhanced OH· reactivity. However, in the presence of oxygen, this interference is expected to be suppressed because of formation of peroxy radicals which are less reactive towards OH· than the parent radicals.

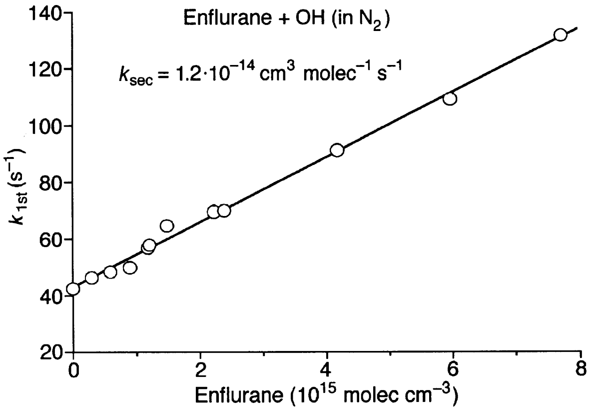

Fig 2 k_{1st} *vs* enflurane concentration for the reaction enflurane+OH in nitrogen (N_2).

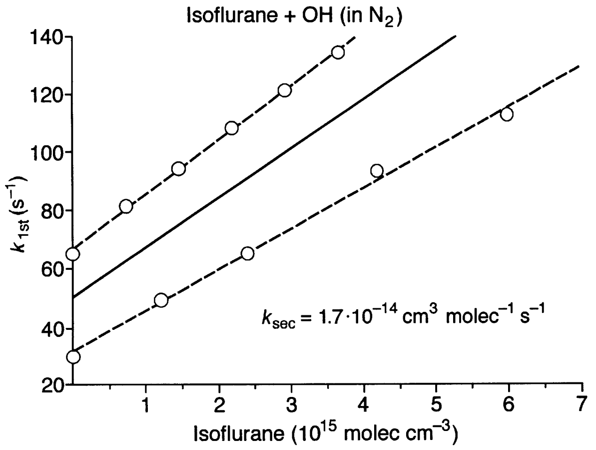

Fig 3 k_{1st} *vs* isoflurane concentration for the reaction isoflurane+OH in nitrogen (N_2). (Results from two different sets of measurements and their arithmethic mean.)

Figures 2–5 show the k_{1st} values as a function of concentration for the other anaesthetics, together with linear regression lines and the second-order rate coefficients $k_{2nd} \approx k_{OH}$ derived. Inspection of these values reveals that the OH· rate coefficients k_{OH} were not very different and ranged from 0.44 to 2.7×10^{-14} cm^3 molec^{-1} s^{-1} (Table 1).

From these experimental values, the chemical lifetime of the anaesthetics τ_{OH} was calculated. We assumed [OH·]= 4.5×10^5 molec cm^{-3} for the diurnal averaged OH· concentration at ground level, and $[OH\cdot]_z$, the variation of OH· with altitude, was obtained from a one-dimensional photo-

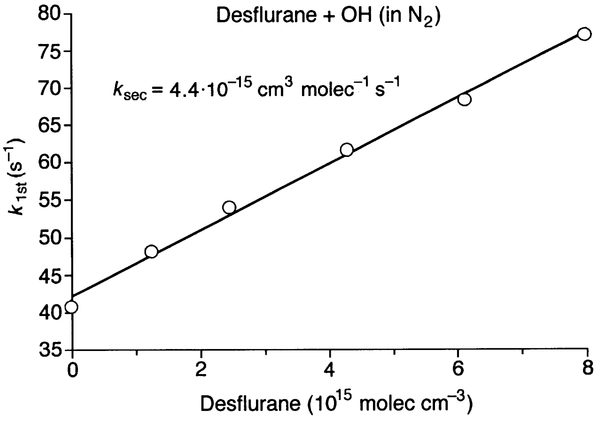

Fig 4 k_{1st} *vs* desflurane concentration for the reaction desflurane+OH in nitrogen (N_2).

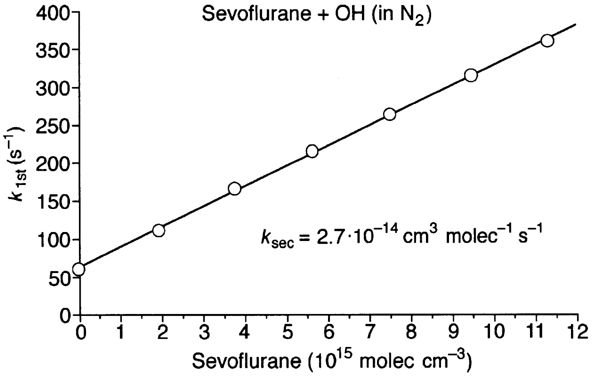

Fig 5 k_{1st} *vs* sevoflurane concentration for the reaction sevoflurane+OH in nitrogen (N_2).

Table 1 Measured rate coefficients at 298 K for the reactions of the OH radical with anaesthetics and resulting lifetimes (τ_{OH}). [1]Data from oxygen experiment only; [2]Lifetimes based on k_{OH} values from this work

	k_{OH} (10^{-14} cm^3 molec^{-1} s^{-1})		
Anaesthetic	**This work**	**Brown and colleagues[5]**	**Lifetime[2] τ_{OH} (yr)**
Halothane	1.5 (0.3)[1]	6.0 (0.4)	7.0
Enflurane	1.2 (0.2)	1.7 (0.5)	8.2
Isoflurane	1.7 (0.3)	2.1 (0.5)	5.9
Desflurane	0.44 (0.08)	–	21.4
Sevoflurane	2.7 (0.5)	7.3 (2.2)	4.0

chemical transport model.[6] Note, however, that a temperature dependence of k_{OH}, which would probably lower k_{OH} and hence increase $\tau_{OH,z}$ at higher altitudes, has been neglected. The resulting lifetimes ranged from 4 (sevoflurane) to 21 (desflurane) yr (Table 1). As a consequence, we may conclude that a considerable fraction (see below) of the anaesthetics emitted reach the stratosphere.

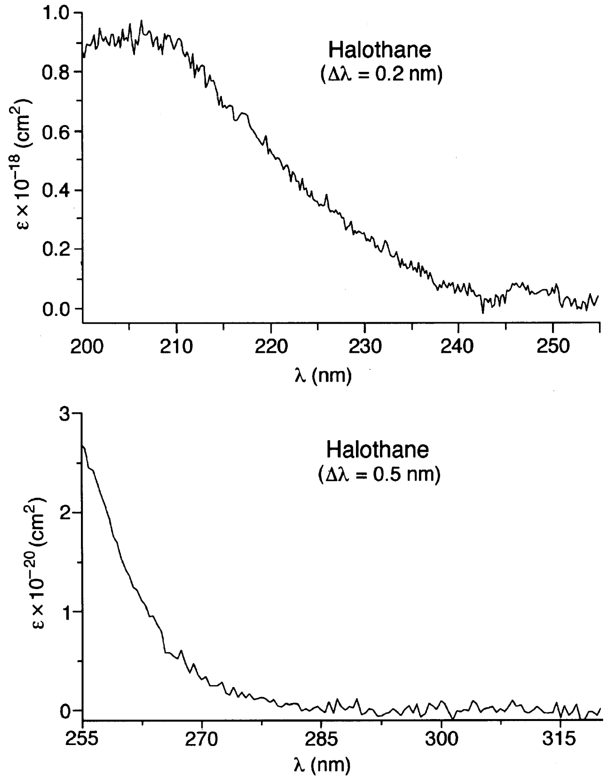

Fig 6 UV absorption spectra of halothane in the range 200–260 nm (top) and 255–315 nm (bottom).

UV absorption spectra and photochemical lifetimes

The UV absorption spectra of halothane, enflurane, isoflurane, desflurane and sevoflurane were measured in the range 200–350 nm. The gas phase spectra of halothane, enflurane and isoflurane are shown in Figures 6–8. All three anaesthetics had substantial UV absorption only below 250 nm. The long wavelength absorption onset, however, shifted from 270 nm to 250 nm and 215 nm for halothane, enflurane and isoflurane, respectively. As a consequence, the maximum UV absorptivity of halothane near 205 nm was nearly three orders of magnitude larger than that of enflurane or isoflurane in this wavelength range. No absorption was observed for desflurane or sevoflurane. The photophysical properties of halothane, enflurane and isoflurane are summarized in Table 2.

In order to asses the photochemical lifetimes τ_{photo} of the volatile anaesthetics, photolysis frequency and hence photochemical lifetime calculations were performed with models. The local photochemical lifetime was integrated over height up to 36 km. The resulting values of τ_{photo} are listed in Table 2. All photochemical lifetimes of the anaesthetics were extremely long, the only exception being halothane for which a lifetime of approximately 100 yr was determined. As a consequence, the anaesthetics must be considered stable with respect to photochemical degradation throughout the entire atmosphere.

Total lifetimes

Combination of τ_{OH} and τ_{photo} (eqn (7)) in Tables 1 and 2 gave total lifetimes τ of the anaesthetics which were identical to the chemical lifetimes, except for halothane where the relatively short photochemical lifetime reduced

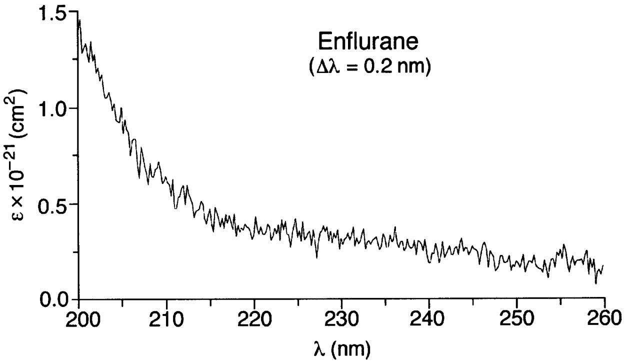

Fig 7 Absorption spectra of enflurane in the range 200–260 nm.

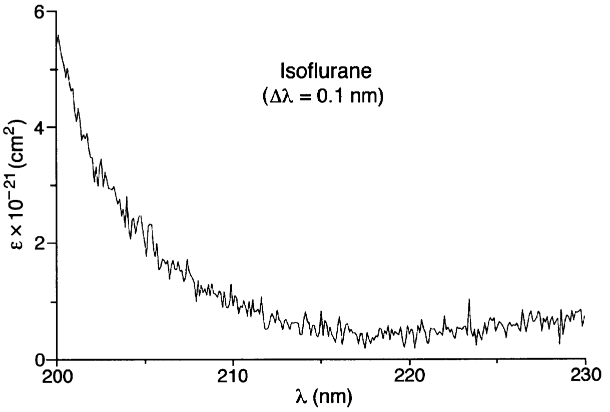

Fig 8 Absorption spectra of isoflurane in the range 200–230 nm.

the chemical lifetime from 7.0 yr to 6.6 yr. The values of τ ranged from 4 to 21.4 yr (Table 3).

ODP values

ODP values for the five volatile anaesthetics were calculated and are summarized in Table 3, together with those for CFC-11 and CFC-12. Despite its much shorter lifetime, halothane had an ODP value of 1.56 which is comparable with that of CFC-11 (1.0 by definition) and CFC-12 (1.55). This is because its lifetime is more than compensated for by its bromine content. However, the ODP values of the anaesthetics containing chlorine only are much lower than those of the CFC as a result of their shorter lifetimes.

GWP values

The infrared bandstrength S for halothane, enflurane, isoflurane and sevoflurane from conventional infrared experiments[5] and the lifetimes from our experiments were used to calculate GWP values according to equation (13). Corresponding bandstrength of desflurane was estimated from analogies in molecular structure and composition in the order of 3000 cm^{-2} atm^{-1}. As indicated by Brown and colleagues,[5] the infrared bandstrengths of enflurane, isoflurane and sevoflurane were larger than that of halothane because the former contain an ether group which is responsible for intense absorption features in the 8–10 μm region. In Table 3, GWP values are listed together with S values from the literature. They were smaller than 0.15 relative to CFC-12.

Table 2 UV absorption cross sections at 200 nm and calculated photochemical lifetimes (50°N, equinox) for anaesthetic gases. nd=Not determined

Anaesthetic	**λ_{max} (nm)**	**σ_{200} (cm²)**	**τ_{photo} (yr)**
Halothane	205	9×10^{-19}	105
Enflurane	$<$ 200	1.4×10^{-21}	5340
Isoflurane	$<$ 200	5.5×10^{-21}	3130
Desflurane	$\ll$ 200	$\leqslant 10^{-22}$	nd
Sevoflurane	$\ll$ 200	$\leqslant 10^{-22}$	nd

Stratospheric input

Table 3 also lists the relative fractions of the anaesthetics that do not degrade in the troposphere but enter the stratosphere. The percentages given were obtained from a one-dimensional model calculation and varied from 12% to 21%.

Discussion

We have presented measurements of OH· rate coefficients and UV absorption spectra for the five commonly used inhalation anaesthetics (halothane, enflurane, isoflurane, desflurane and sevoflurane). Although the rate coefficients for the different anaesthetics were similar (1.5 ± 1.0 10^{-14} cm^3 $molec^{-1}$ s^{-1}), a systematic variation in OH· reactivity was observed. Desflurane had the lowest rate coefficient, most likely because both abstractable H atoms of this compound have fluorine atoms in the α-position. This tends to decrease OH reactivity.[7] However, this is not the case for halothane, enflurane and isoflurane, where Cl atoms are also available in the α-position. In contrast, the relatively high OH· rate coefficient of sevoflurane is explained mainly by the presence of an abstractable H atom from a tertiary carbon atom.

Our results for enflurane and isoflurane are compatible with the earlier study of Brown and colleagues.[5] However, the rate coefficients for halothane and sevoflurane were larger by a factor of 4 and 2.7, respectively (Table 1). For halothane, the reason for this discrepancy might be because of the same experimental difficulties in their study when producing OH radicals (see results). However, Brown and colleagues' study did not contain a detailed experimental description and therefore this point remains unclear.

In the UV spectra, we found that the absorptivity of halothane was approximately three orders of magnitude stronger than that for the other anaesthetics (Table 2). This difference is probably a result of the bromine content of halothane for which the chromophore is red-shifted compared with chlorine. It should be noted that the spectra for enflurane and isoflurane were in good agreement with other observations reported in the literature.[8] [9] No UV absorption above 200 nm was observed for desflurane or sevoflurane because they contain only fluorine, the most blue-shifted chromophore of all halogens.

Table 3 Summary of atmospheric lifetimes, relative input into the stratosphere, and ODP and GWP values of CFC-11, CFC-12 and halogenated volatile anaesthetics. [1]WMO Report[18]; [2]this value is smaller compared with that of Table 1 (τ=7.0 yr) because of additional photochemical destruction. In all other cases the atmospheric lifetime is identical to the chemical lifetime only; [3]as obtained from a one-dimensional modelling calculation; [4]an efficiency of Br relative to Cl of α=50 was used; [5]integrated infrared absorption cross section; [6]Brown and colleagues[5]; [7]estimated from analogies in composition and structure relative to other anesthetics; [8]greenhouse warming potentials relative to CFC-12

Compound	M (g mol^{-1})	τ (yr)	Input into stratosphere[3] (%)	ODP[4]	S[5] (cm^{-2} atm^{-1})	GWP[8]
CFC-11	137.5	50[1]	100	1.00	2500[1]	0.33
CFC-12	121.0	102[1]	100	1.55	3300[1]	1.00
Halothane	197.4	6.6[2]	13.2	1.56	1400[6]	0.02
Enflurane	184.5	8.2	16.2	0.04	4800[6]	0.08
Isoflurane	184.5	5.9	14.6	0.03	3900[6]	0.05
Desflurane	168.0	21.4	21.4	0.00	3000[7]	0.14
Sevoflurane	200.0	4.0	12.6	0.00	2550[6]	0.02

Because solar radiation below 290 nm is completely filtered out by stratospheric ozone, any short wavelength absorption of anthropogenic compounds does not contribute to photochemical degradation in the troposphere. The reaction with OH radicals accounts for the majority of the total tropospheric lifetime of these compounds; UV photodissociation is only a minor contributor and only of importance in the stratosphere.

The atmospheric lifetimes derived by Brown and colleagues[5] were systematically lower than those determined in our study. Apart from the differences in OH· rate coefficients, this is a result of the assumed OH· concentration at ground level. When modelling the vertical distribution of OH·, Brown and colleagues started with 7.7×10^5 molec cm^{-3} at ground, a factor 1.7 larger than that used in our work.

From the tropospheric lifetimes it was derived that up to 20% of the anaesthetics may enter the stratosphere and hence contribute to halogen loading. The most noticeable example was halothane which had an ODP value of 1.56 relative to CFC-11 because of its bromine content. The dominant bromine containing compound in the stratosphere is methyl bromide (CH_3Br) with an annual source strength of 170 kilotons and an ODP value of 0.6.[10] If a total global halothane emission of 7000 tons/yr is assumed, then the total ODP weighted emission flux relative to CH_3Br is in the order of 10%. Because the relative stratospheric input of methyl bromide is of the same order of magnitude as halothane, the ratio at ground is the same in the stratosphere. Bromine in the stratosphere, however, is of increasing interest because it contributes 35–80 times more to ozone depletion than chlorine (see appendix). At present, the stratosphere contains 20 pptv bromine (including 10 pptv CH_3Br) and 3500 pptv chlorine.[10] (pptv=Parts per American trillion per volume and corresponds to a concentration of (2.46×10^7) molecules cm^{-3}=$(4.09\times10^{-5}\times$molecular weight) µg m^{-3} at 25°C and 1013 mbar.) If one assumes that Br destroys 50 times more ozone than chlorine, the bromine content of halothane contributes approximately 1% to ozone depletion. However, the chlorine content of halothane contributes only approximately 0.02% to total ozone depletion, while the contribution of enflurane and isoflurane is more than 100 times less based on their ODP values. In view of the likelihood that the atmospheric burden of CFC is decreasing as a result of the Montreal protocol, the importance of volatile anaesthetics in the future, in particular bromine containing halothane, must be emphasized.

Halocarbon global warming potentials have been derived based on our lifetime calculations and infrared bandstrengths from the literature. GWP values relative to CFC-12 were less than 0.15. If one assumes a total global emission of carbon dioxide from all anthropogenic sources in the order of 7.1 Gtons carbon/yr[11] and accept a relative GWP between carbon dioxide and CFC-12 of 1/7800[11] then the relative contribution to global warming of all volatile anaesthetics is in the order of 0.03%. Thus the total GWP-weighted emission fluxes of volatile anaesthetics is small compared with those of other greenhouse gases.

In our study, removal paths other than reaction with OH· and photolysis were neglected. Wet and dry deposition or uptake by soils, oceans or the biosphere may also play a role for volatile anaesthetics. This would reduce the lifetimes calculated in this study. If these processes are essential sinks for volatile anaesthetics, their fate and the fate of degradation products in the aqueous environment in addition to the biosphere should be investigated in the future.

Appendix

Gas phase chemistry in the atmosphere

In the following section, we describe some basic equations and common units for atmospheric processes that are essential in this article (for further reading see textbooks[12–14]).

The main removal process for many trace gases in the atmosphere that contain hydrogen (H) is the reaction with the hydroxyl radical (OH·) by abstraction of a H atom. Thus the primary degradation of volatile anaesthetics containing hydrogen atoms (An-H) is most likely the reaction with OH·:

$$\text{An-H}+\text{OH}\cdot\rightarrow\text{An}\cdot+H_2O \quad (1)$$

where An-H=volatile anaesthetic.

Furthermore, volatile anaesthetics containing halogen atoms (An-X, X= Br or Cl) may be subject to competitive photochemical destruction. The absorption of photons by An-X is described by:

$$\text{An-X}+h\nu\rightarrow\text{An}\cdot+\text{X} \quad (2)$$

where An-X=volatile anaesthetic; X=Br or Cl; hν=energy from sunlight, with h=Planck's constant; and ν=frequency of the radiation.

The bimolecular reaction (1) is a second-order reaction, whereas the unimolecular reaction (2) is a first-order reaction. The reaction rate R describes the speed of a reaction or the change in concentration of a compound with time. For reaction (1) it depends on the concentration of An-H and OH· and its units are molecules cm^{-3} s^{-1}:

$$R=k_{OH}\ [\text{An-H}][OH\cdot] \tag{3}$$

where R=reaction rate in molec cm^{-3} s^{-1} (molec= molecules); k_{OH}=rate coefficient for a bimolecular reaction in cm^3 $molec^{-1}$ s^{-1}; [An-H]= concentration of volatile anaesthetic in molec cm^{-3}; and [OH]=concentration of OH radical in molec cm^{-3}.

The constant of proportionality k_{OH} is called the rate coefficient (or rate constant). In this figure, concentrations are given in molec cm^{-3} and consequently the common unit for k in the bimolecular reaction is cm^3 $molec^{-1}$ s^{-1}. The rate coefficient k_{OH} is temperature dependent, but in a first approach this is neglected in our study.

For the unimolecular reaction (2), the reaction rate R depends on the concentration of [An-X], and the constant of proportionality is the photodissociation coefficient or frequency of photodissociation *j*, also called *j* value:

$$R=j\ [\text{An-X}] \tag{4}$$

where R=reaction rate in molec cm^{-3} s^{-1}; j=frequency of photodissociation or photodissociation coefficient in s^{-1}; and [An-X]=concentration of volatile anaesthetic in molec cm^{-3}.

The *j* value is a function of the incident radiation energy spectrum and thus changes with date, time of day, longitude, altitude and meteorological conditions (see below) (for more details on chemical kinetics see textbooks[12–14]).

For reaction (1) the chemical lifetime of a trace gas is determined by the rate coefficient k_{OH} and the average atmospheric OH· concentration:

$$\tau_{OH}=k_{OH}^{-1}\ [OH\cdot]^{-1}\ \text{(bimolecular reaction)} \tag{5}$$

where k_{OH}=rate coefficient in cm^3 $molec^{-1}$ s^{-1} for second-order reaction; and [OH·]=OH· concentration in molec cm^{-3}.

In addition, reaction (2) might limit the atmospheric lifetime of the volatile anaesthetic:

$$\tau_{photo}=j^{-1}\ \text{(unimolecular reaction)} \tag{6}$$

where j=frequency of photodissociation or photodissociation coefficient in s^{-1}.

If both processes limit the lifetime in the atmosphere the total lifetime τ is given by:

$$\tau=(1/\tau_{OH}+1/\tau_{photo})^{-1} \tag{7}$$

As the concentration of OH· varies with altitude, the average chemical lifetime τ_{OH} is the altitudinal mean, weighted by the local concentration of the OH radical:

$$\tau_{OH}=\frac{\int_0^z \tau_{OH,z}[OH]_z dz}{\int_0^z [OH]_z dz} \tag{8}$$

where $[OH]_z$=OH· concentration at altitude z; and $\tau_{OH,z}=(k_{OH}\ [OH]_z)^{-1}$ local chemical lifetime at altitude z, analogue to equation (5).

In our model the values were integrated from ground to 36 km altitude to calculate degradation by OH radicals in the troposphere and in the lower stratosphere.

The *j* value of a compound in the atmosphere is a function of atmospheric photon flux, absorption cross section and quantum yield, expressed by the following equation:

$$j=\int_0^\infty \Phi_\lambda \sigma_\lambda F_\lambda\ d\lambda \tag{9}$$

where σ_λ=absorption cross section in cm^2 $molec^{-1}$; Φ_λ=quantum yield, assumed to be 1 (see text); F_λ=atmospheric photon flux in cm^{-2}; and λ= wavelength in nm.

Numerically, integration in equation (9) is carried out only in the wavelength region, where the product $\Phi_\lambda \times \sigma_\lambda \times F_\lambda$ does not vanish.

With the quantum yield Φ_λ it is taken into account that the absorption of a photon does not always lead to dissociation or a single dissociation path. For instance, photodissociation occurs for some species at two different wavelengths, that is different bonds break at different energies. Fractional quantum yields account for these different pathways of destruction. However, here, Φ_λ is assumed to be unity under all conditions. The atmospheric photon flux F_λ is calculated from a model of radiation transfer.[6 16]

As mentioned above, *j* varies with the incident radiation energy spectrum. In the present calculation, a geographical latitude of 50°N and equinox have been chosen, and the obtained photolysis rates have been averaged over 24 h under clear sky conditions. The inverse of the local photolysis rate gives the local photochemical lifetime $\tau_{photo,z}$ at altitude z:

$$\tau_{photo,z}=\frac{24\ (h)}{\int_0^{24\ (h)} j_z dt} \tag{10}$$

where j_z=j value at altitude z.

In order to obtain the mean photochemical lifetime, the local photochemical lifetime weighted by the local anaesthetic concentration, must be averaged according to altitude.

$$\tau_{photo}=\frac{\int_0^z \tau_{photo,z}\ [An]_z dz}{\int_0^z [An]_z dz} \tag{11}$$

where $[An]_z$=concentration of anaesthetic at altitude z; and integration limits are from ground=0 km to z=36 km.

$[An]_z$ must be obtained from an independent one-dimensional model calculation of chemistry, photolysis and transport. In the present simulation a mixing ratio of 1 pptv at ground level was used as a lower boundary condition[6] and the integration was made over 36 km altitude.

Ozone depletion potential

The potential contribution of any anthropogenic compound to ozone depletion in the stratosphere is generally expressed by the ozone depletion potential (ODP). Although ODP values are genuinely obtained from model calculation, approximate estimates can also be made relative to a reference compound such as CFC-11 ($CFCl_3$, ODP=1.0) with the total atmospheric lifetime (τ), molecular weight (M) and number of Cl and Br atoms (n) in the anaesthetic (An-H).[5 15]

$$\text{ODP}=\frac{\tau_{An-H}}{\tau_{CFC-11}}\cdot\frac{M_{CFC-11}}{M_{An-H}}\cdot\frac{n_{Cl}+\alpha n_{Br}}{3} \tag{12}$$

The coefficient α accounts for the fact that Br atoms can destroy ozone between 35 and 80 times more effectively than Cl atoms.[15] In our calculations α=50 has been chosen. Equation (12) does not account for the number of fluorine atoms as fluorine is not known to destroy stratospheric ozone. Therefore, desflurane and sevoflurane containing no other halogens than fluorine have an ODP value of zero.

Greenhouse warming potential

A second atmospheric concern of volatile anaesthetics is their contribution to greenhouse warming, as expressed by the greenhouse warming potential (GWP). GWP values are normally derived from radiative transfer models that account for the infrared absorptivity of a compound in the region of the terrestrial radiation window (9–13 µm). However, as for ODP, approximate equations have been derived in which GWP are calculated relative to a reference compound such as CFC-12 (CF_2Cl_2). We follow the notation used by Brown and colleagues[5]:

$$\text{GWP}=\frac{\tau_{An-H}}{\tau_{CFC-12}}\cdot\frac{M_{CFC-12}}{M_{An-H}}\cdot\frac{S_{An-H}}{S_{CFC-12}} \tag{13}$$

As in equation (12), the contribution of an anaesthetic (An-H) to the relative GWP is determined by its lifetime τ and molecular weight M. In addition, GWP depends on the infrared bandstrength S, which is integrated over the range of the atmospheric window. In our calculations S was obtained from the literature.[5]

Experimental method

To determine the second-order rate coefficient k_{OH}, experiments were performed under pseudo-first-order conditions. In pseudo-first-order conditions, one of the reactants (in our case the anaesthetic gas) is always in excess (at least 10-fold). During the reaction An+OH·, the concentration of An changes at most by 10% and can be considered to be constant. Then the decay of OH· with time is like a first-order reaction and therefore called pseudo-first-order reaction. The logarithmic plot of the observed OH concentration at the y-axis *vs* time at the x-axis at a certain concentration of the anaesthetic gas [An] gives a straight line, and from the slope k_{1st} is derived (not shown in this article). The coefficient k_{1st} varies with [An]. From the plot of k_{1st} *vs* [An] we have gained k_{2nd} that is considered to be identical to k_{OH} (slope).

The experiments were performed in a black-anodized aluminium tube (1200 mm length, 50 mm diameter), through which the gas mixture slowly flows. The centre part of this reactor extends into four arms which are perpendicular to each other and to the main axis of the reactor. Whereas the main axis represents the direction of the absorption path, the perpendicular axis is used for fluorescence excitation. Each light path is multiple folded by the use of mirror systems in White configuration. The reaction studies are initiated by laser pulse photolysis of HNO_3 at 248 nm along the main axis of the reactor (excimer laser, Lambda Physik, EMG 200) to produce OH radicals. Detection of OH· was achieved at 308.42 nm using a narrow band ring-dye laser (Coherent, CR 699–21) pumped by an Ar^+ laser. The detection limit for OH· concentration is 10^9 molec cm^{-3} at 50 mbar.

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