

The indirect determination of chlorine atom concentration in the troposphere from changes in the patterns of non-methane hydrocarbons

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ABSTRACT

About 200 measurements of C₂–C₉ hydrocarbons were made during a ship cruise (NATAC 91) in the western Mediterranean Sea, the eastern Mid- and North Atlantic and the North Sea in April and May 1991. The changes in the ratios of several pairs of hydrocarbons are used to investigate the possible impact of Cl-atom reactions on the atmospheric removal processes of hydrocarbons. In order to minimize the potential bias from atmospheric mixing processes, a careful selection of suitable hydrocarbon sets is essential. The NMHC mixing ratios observed during NATAC 91 are generally well above those typical for air in the remote marine background and the observed changes in the hydrocarbon patterns agree very well with those predicted from OH-radical chemistry. No significant evidence for an impact of chlorine atoms could be found in this data set. The best estimate for the average [Cl]/[OH] ratio is in the range of 10^{–3}. However, within the various uncertainties associated with such estimates, this value is not significantly different from zero. The upper limit is in the range of 2–7·10^{–3}. Based on an average OH-radical concentration of 10⁶ cm^{–3}, this corresponds to some 10³ Cl-atoms cm^{–3}. This is far below the Cl-atom concentrations found during the tropospheric ozone depletion events in arctic spring. Our values are also far below those derived in some other studies for the marine boundary layer but are still compatible with recent model calculations. Our findings support the conclusion of Rudolph and coworkers that on average, Cl-atoms are of limited importance for the chemistry of the troposphere. It is important that the major part of the uncertainty of the Cl-atom concentration estimates results from errors in the rate constants for the reactions of the hydrocarbons with OH-radicals. A reliable and consistent set of the relevant rate constants would further improve the accuracy of the Cl-atom concentration estimates or their upper limits derived from changes in the hydrocarbon patterns.

1. Introduction

There is convincing evidence that the sporadic occurrence of very low concentrations of ozone in the lower troposphere of the arctic in spring is the result of a Cl- and Br-atom catalyzed ozone

decomposition (Barrie et al., 1988; Bottenheim et al., 1990; Kieser et al., 1993; Yokouchi et al., 1994; Jobson et al., 1994; Hausmann and Platt, 1994; Solberg et al., 1996; Ramacher et al., 1996). However, the temporal and spatial extent of these “low ozone events” is limited (Hopper and Hart, 1994; Anlauf et al., 1994) and on a global average halogen atom concentrations observed during such events can only have a minor impact on the

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chemistry of the troposphere. Comparably strong evidence for the occurrence of high halogen atom concentrations in other regions of the troposphere is still missing.

In a number of papers, it has been discussed that halogen atoms may be of considerable importance for the chemistry of the troposphere. They may affect the oxidizing capacity of the atmosphere, especially the atmospheric removal rate of volatile organic compounds (Singh and Kasting, 1988; Pszenny et al., 1993; Jobson et al., 1994; Hemming et al., 1994; Finlayson-Pitts, 1994; Wingenter et al., 1996). However, presently there is no method which would allow the direct measurement of Cl-atoms in the troposphere. Consequently, the evidence for the existence of relevant levels of Cl-atoms in the troposphere is only indirect (Pszenny et al., 1993; Parrish et al., 1993; Jobson et al., 1994a; Hemming et al., 1994; Finlayson-Pitts, 1993; Singh et al., 1996a; Blake et al., 1996; Wingenter et al., 1996; Maben et al., 1996) and sometimes subject to controversial discussions (Finlayson-Pitts, 1993; Parrish et al., 1993).

Singh and Kasting (1988) suggested that Cl-atoms generated by the reaction of gaseous HCl with OH-radicals may affect the turnover of volatile organic compounds in the marine atmosphere. However, due to the low HCl concentrations in the marine atmosphere, this process cannot maintain relevant levels of Cl-atoms (Graedel and Keene, 1995). In a model study of a heavily polluted urban air mass entering the marine atmosphere, Sander and Crutzen (1996) calculated that Cl-atom concentrations may peak for a short period of a few hours at values of roughly 10^4 cm^{-3} , but generally, the calculated Cl-atom concentrations were much lower, mostly below 10^3 cm^{-3} . Vogt et al. (1996) presented a mechanism for halogen release in the remote marine boundary layer and calculated that during daytime Cl-atom concentrations of some 10^3 cm^{-3} can occur.

Based on measured distributions of ethane and tetrachloroethene and estimates of their global budgets an upper limit of $5 \cdot 10^2 \text{ Cl atoms cm}^{-3}$ was derived by Rudolph et al. (1996) as tropospheric average. Based on a comparison of model calculations with the tropospheric C_2Cl_4 measurements of Wang et al. (1995) Singh et al. (1996b) very recently derived a somewhat higher upper

limit of $5\text{--}50 \cdot 10^3 \text{ cm}^{-3}$ for the marine boundary layer. Both studies found no evidence that the average tropospheric Cl-atom concentrations are significantly different from zero.

Strong evidence for a significant impact of Cl- and Br-atoms on the chemistry of the lower troposphere was found for the tropospheric ozone depletion events in Arctic spring (Barrie et al., 1988; Bottenheim et al., 1990; Kieser et al., 1993; Yokouchi et al., 1994; Jobson et al., 1994; Hausmann and Platt, 1994; Solberg et al., 1996; Ramacher et al., 1996). From changes in the concentration patterns of nonmethane hydrocarbons Jobson et al. (1994) and Ramacher et al. (1996) estimated that during the depletion events the Cl- and Br-atom concentrations range around $3\text{--}8 \cdot 10^4 \text{ cm}^{-3}$ and $3\text{--}6 \cdot 10^7 \text{ cm}^{-3}$, respectively.

There is some evidence that high Cl-atom concentrations may be found in the remote marine boundary layer. Based on changes in the hydrocarbon patterns Wingenter et al. (1996) estimated marine boundary layer concentrations of $3\text{--}6 \cdot 10^4 \text{ Cl-atoms cm}^{-3}$ for one of the flights performed as part of the ASTEX/MAGE experiment in the vicinity of the Azores in June 1992. In a similar approach Singh et al. (1996a) deduced Cl-atom concentrations around 10^5 cm^{-3} for the marine boundary layer over the tropical Pacific from day/night measurements of some selected organic compounds.

Plots of the logarithmic ratios of hydrocarbon concentrations have been used to gain insight into their removal reactions and atmospheric mixing processes (cf. Roberts et al., 1984; Rudolph and Johnen, 1990; McKeen et al., 1991, 1996; Parrish et al., 1992). Rudolph and Johnen (1990) and Parrish et al. (1992) found that the slope of a log-log plot of the *n*-butane/ethane versus the propane/ethane ratios is about 1.6 for remote oceanic regions. If the slope of such a plot is determined by the reaction of nonmethane hydrocarbons with OH-radicals, it can be calculated from the known rate constants for these reactions. Finlayson-Pitts (1993) interpreted the deviation of the slope of the observed curve from the theoretical value of 2.77 as an indication for a contribution of Cl-atoms to the atmospheric removal of hydrocarbons. However, in a number of studies, it was pointed out that atmospheric mixing processes or the existence of significant background concentrations of hydrocarbons also can explain such devi-

ations (Parrish et al., 1993; McKeen and Liu, 1993; McKeen et al., 1991, 1996).

The validity of conclusions drawn from such log-log plots of hydrocarbon ratios, and related procedures, critically depends on the validity of a few key assumptions (Rudolph and Johnen, 1990). In this paper we will use measurements of non-methane hydrocarbons (NMHC) we made over the Mediterranean Sea, the Atlantic and the North Sea to estimate upper limits for Cl-atom concentrations. It will be demonstrated that by the selection of suitable NMHC pairs for the log-log plots allows reliable insight into possible contributions of Cl-atoms to the NMHC turnover in the troposphere can be obtained.

2. Experiment

The NMHC measurements were made during a cruise of the Ukrainian research vessel Ernst Krenkel in spring 1991 (NATAC 91). The cruise started on 5 April in Marseilles (France) and ended on 22 May in Hamburg (Germany). The cruise track covered the western part of the Mediterranean Sea, the eastern part of the Mid and North Atlantic, and the North Sea. A detailed description of the cruise track can be found in Ratte et al. (1995).

About 200 in situ measurements of C₂-C₉ hydrocarbons were made by a gas chromatographic method. The experimental setup was nearly identical to the one described by Koppmann et al. (1992), the instrument followed closely the design described by Rudolph et al. (1989) and Koppmann et al. (1992). The chromatograph was installed in a container on the front deck of the ship. The air was sampled through a stainless steel inlet line (10 mm i. d.) which was permanently flushed with outside air at a flow rate of 30 dm³ min⁻¹. The air intake was located on a mast at the bow of the ship at a height of 15 m above the water line.

The detection limits (3σ) were between 5 and 10 ppt for the C₂-C₄ hydrocarbons and about 1 ppt for the >C₄ compounds. The reproducibility of the measurements was about 10%, the accuracy of the calibration is estimated to 10–20%, depending on the individual compound.

3. Results and discussion

Under ideal conditions, there is a linear relationship between the logarithms of the ratios of the atmospheric concentrations of NMHC (cf. Rudolph and Johnen, 1990):

$$\ln([c/jc]_t) = a \ln([k/c]_t) + b. \quad (1)$$

C is the concentration of the hydrocarbons measured in the same air sample. The slope, *a*, can be calculated from the rate constants for the atmospheric removal processes of the individual hydrocarbons. From our current understanding the reaction with OH-radicals is the dominant atmospheric removal process for most NMHC and thus the slope can be calculated from the rate constants (*k*_{OH}) for the reaction of the hydrocarbons with OH-radicals:

$$a_{OH} = (i k_{OH} - j k_{OH}) / (k k_{OH} - l k_{OH}). \quad (2)$$

To include reactions with Cl-atoms, eq. (2) has to be modified:

$$a_{Cl,OH} = (j k_{OH} + r j k_{Cl} - i k_{OH} - r i k_{Cl}) / (i k_{OH} + r i k_{Cl} - k k_{OH} - r k k_{Cl}). \quad (3)$$

The slope depends on the ratio, *r*, of the Cl-atom and OH-radical concentrations (*r* = [Cl]/[OH]). Rearrangement of eq. (3) yields:

$$[Cl]/[OH] = (a(i k_{OH} - k k_{OH}) - j k_{OH} + i k_{OH}) / (a(k k_{Cl} - l k_{Cl}) + j k_{Cl} - i k_{Cl}). \quad (4)$$

From this expression, no absolute concentrations can be derived, but we can calculate the [Cl]/[OH] ratio from the slopes of the log-log plots and reaction rate constants from laboratory studies.

As already pointed out by Rudolph and Johnen (1990), a few basic assumptions have to be made to justify the simple algebraic expressions given above. The air masses contributing to the NMHC concentration in an individual air sample must have a reasonably similar photochemical age. Although the treatment considers dilution effects, the NMHC concentrations in the diluting air must be small compared to the actually measured concentrations. This is an immediate consequence of the previously mentioned condition. Finally, it is assumed that on average the air masses sampled

had initially the same relative hydrocarbon composition.

It is obvious that these conditions are not always met by arbitrarily selected field observations. However, in the case of the measurements presented here, neglecting the background hydrocarbon mixing ratios is reasonably well justified. The NMHC mixing ratios observed during NATAC 91 are generally well above typical mixing ratios found in the remote marine atmosphere. E.g., *n*-butane mixing ratios average around 200 ppt, with only 5% of all values below 40 ppt. The average propane mixing ratio is around 500 ppt and less than 5% of the propane mixing ratios are below 200 ppt. These values by far exceed their concentrations in clean marine background air (cf. Rudolph, 1988; Koppmann et al. 1992; Donahue and Prinn, 1993; Blake et al., 1996). Even for ethane the mixing ratios are with an average of 2300 ppt and less than 5% of the measurements below 1800 ppt well above levels typical for marine background conditions.

As an example Fig. 1 shows the log-log plot of the *n*-butane/ethane versus propane/ethane ratios. The slope of a linear least square fit considering errors of both *x*- and *y*-values (Press et al. 1992) is 2.48 ± 0.05 . This is slightly less than the slope of about 2.64 expected for OH-radical chemistry but significantly higher than the slope of 1.96 calculated for removal by Cl-atoms only. The $[Cl]/[OH]$ ratio calculated according to eq. (4) is $3.3 \cdot 10^{-3} \pm 1.4 \cdot 10^{-3}$. Based on an average OH-radical concentration of $1 \cdot 10^6 \text{ cm}^{-3}$ the cor-

responding Cl-atom concentration is around $3 \cdot 10^3 \text{ cm}^{-3}$. This is substantially lower than the Cl-concentrations derived by Wingenter et al. (1996) and Singh et al. (1996a), but due to the high reactivity such Cl-atom levels may still be of some relevance for the chemistry of the troposphere.

It should be noted that the observed slope of roughly 2.5 is significantly different from observations by Rudolph and Johnen (1990), Parrish et al. (1992) and Blake et al. (1996). In the subset of their measurements which was ascribed to air masses influenced by outflow from North America, Blake et al. (1996) observed a significantly steeper slope, roughly comparable to the theoretical slope derived from the rate constants for OH-radical reactions. They explain this observation by different initial ratios of the hydrocarbon concentrations for the different regions. However, as shown by Rudolph and Johnen (1990), the emission pattern does not affect the slope of the log-log ratio plots, it determines the axis intercept. A more likely explanation is that for this subset of the data, the effect of mixing with non zero background air is less strong and thus the observed slope closer to the ideal behavior. This explanation agrees with the observation that the air masses classified by Blake et al. as "Continental North American" had on average the highest ethane mixing ratios. Also their data characterized as "Continental Iberian" show relatively high ethane mixing ratios and a steeper slope in the $\ln n$ -butane/ethane versus $\ln$ propane/ethane plot. The largest deviations from ideal theoretical behaviour were found for measurements made in marine background air. This supports the concept that eq. (2) is applicable only if the NMHC mixing ratios used for this type of analysis are well above the mixing ratios in marine background air.

To further test this hypothesis we reanalyze the results presented by Rudolph and Johnen (1990). For the latitude range north of 25°N , the reported ethane mixing ratios nearly always exceed 1000 ppt, by far most values exceed 1500 ppt. Likewise most of the propane and values in this data set are above 200 ppt and 50 ppt, respectively. Indeed, the slope of this log-log plot is 2.84 ± 0.2 , in very good agreement with theoretical predictions.

It has been pointed out by McKeen et al. (1996), that the existence of a significant background

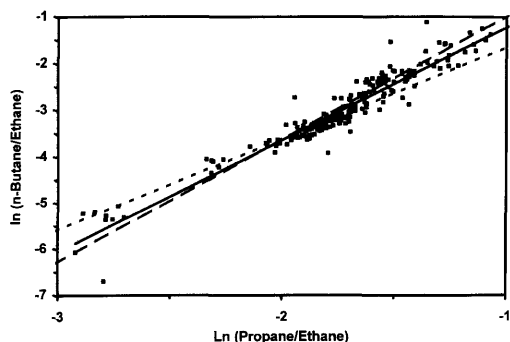


Fig. 1. Plot of $\ln n$ -butane/ethane versus $\ln$ propane/ethane. The solid line is a linear least square fit to the data points. The long dashed line is the theoretical slope for reactions with OH-radicals only, the short dashed line for reactions with Cl-atoms only.

concentration for the hydrocarbons can result in systematic changes of the slope of the log-log plots. Depending on the ethane mixing ratios even moderate changes of about 100 ppt in the ethane background may result in a change of the calculated $[Cl]/[OH]$ ratio of about 10^{-3} , roughly equivalent to 10^3 Cl-atoms cm^{-3} . Consequently uncertainties of the ethane background mixing ratio reduces the usefulness of ethane in ratio plots for a reliable calculation of Cl-atom concentrations. However, if we exclude the unlikely coincidence that background effects by mere chance cancel the effects of reactions of NMHC with Cl-atoms, we can use such a plot to derive an upper limit of the Cl-atom concentrations. Including the uncertainty of the calculated slope of the log-log ratio plot, the upper limit of the $[Cl]/[OH]$ ratio is $4.3 \cdot 10^{-3}$, if we also include the uncertainties of the rate constants, the upper limit is $11 \cdot 10^{-3}$. This upper limit is quite high, mainly the consequence of the relatively small difference between the theoretical slopes for OH-radical and Cl-atom reactions.

To reduce this uncertainty we can select hydrocarbons sets for the plots which have large differences of the theoretical OH- and Cl-kinetics slopes. Table 1 lists the experimentally observed slopes of a number of log-log plots for the measurements made during NATAC 91. Also included are the theoretical slopes for OH-radical removal and

Cl-atom reactions only and the $[Cl]/[OH]$ ratio calculated according to eq. (3). The rate constants used for these calculations are listed in Table 2. A detailed analysis of the uncertainties is given in Table 3.

The slopes derived from observations agree in general very well with the theoretical slopes for OH-radical chemistry only. With the exception of one value, all experimental slopes agree within their statistical uncertainties with the predicted OH-chemistry only dependencies. It should be noted that, due to the temperature dependence of the reaction rate constants, the theoretical slopes depend on temperature. Our calculations for the theoretical OH-slope are made for an average temperature of 283 K. A rather high uncertainty of the average temperature of 20 K would result in a change of these slopes by less than 30%, in most case by less than 10%. This is less than the uncertainty due to the errors of the rate constants (see also Parrish et al., 1993).

All observed slopes differ significantly from the theoretical Cl-atom chemistry slopes. It is very unlikely that for these different hydrocarbon sets with their very different rate constants the good agreement between observed and OH-kinetics slope is due to a fortuitous compensation of atmospheric Cl-atom reactions by non ideal dilution and mixing effects which are not considered in eq. (1).

Table 1. Comparison of theoretical and experimental slopes of the log-log ratio plots and derived $[Cl]/[OH]$ ratios

Ln		Slope of linear least square fit			
Y-axis	X-axis	Observed	OH-chemistry ^a	Cl-chemistry ^a	$[Cl]/[OH]$ ratio ^a
<i>n</i> -butane/ benzene	pentane/ benzene	0.58 ± 0.02	0.38 ± 0.13	0.76 ± 0.08	$1.2 \cdot 10^{-2}$
<i>n</i> -butane/ ethane	propane/ ethane	2.48 ± 0.05	2.64 ± 0.34	1.96 ± 0.28	$3.4 \cdot 10^{-3}$
benzene/ <i>n</i> -butane	propane/ <i>n</i> -butane	0.77 ± 0.08	0.72 ± 0.25	2.67 ± 0.29	$5.0 \cdot 10^{-4}$
toluene/ benzene	<i>n</i> -pentane/ <i>n</i> -butane	3.16 ± 0.18	3.32 ± 0.86	0.19 ± 0.15	$3.4 \cdot 10^{-4}$
<i>n</i> -butane/ benzene	toluene/ benzene	0.33 ± 0.02	0.18 ± 0.07	4.09 ± 0.35	$4.5 \cdot 10^{-3}$
<i>n</i> -hexane/ benzene	toluene/ benzene	0.94 ± 0.04	0.85 ± 0.23	6.62 ± 0.63	$1.7 \cdot 10^{-3}$

^a The reaction rate constants and their uncertainties are taken from Hooshiyar et al. (1995), Talukdar et al. (1994), Atkinson (1994), Atkinson and Aschmann (1986), Atkinson et al. (1989 and 1992).

Table 2. Rate constants for the reaction of hydrocarbons with OH-radicals and Cl-atoms^a

Compound	$k_{\text{OH}} \cdot 10^{12}$, molecules $\text{cm}^{-3} \text{s}^{-1}$	$k_{\text{Cl}} \cdot 10^{12}$, molecules $\text{cm}^{-3} \text{s}^{-1}$
ethane	0.21	57
propane	0.98	127
<i>n</i> -butane	2.2	194
<i>n</i> -pentane	3.7	250
<i>n</i> -hexane	5.6	305
benzene	1.3	15
toluene	6.3	59

^a The reaction rate constants and their uncertainties are taken from Hooshiyar et al. (1995), Talukdar et al. (1994), Atkinson (1994), Atkinson and Aschmann (1986), Atkinson et al. (1989 and 1992). As far as the temperature dependencies of the rate constants are known, they are calculated for 283 K.

Table 3. $[\text{Cl}]/[\text{OH}]$ ratios derived from the observed slopes of log-log hydrocarbon ratio plots and their uncertainties

Hydrocarbon pairs		Uncertainties due to					
Y-axis	X-axis	$[\text{Cl}]/[\text{OH}]$ ratio [§]	Slope	OH-rate constants ^a	Cl-rate constants ^a	Total	Upper limit $[\text{Cl}]/[\text{OH}]$
<i>n</i> -butane/ benzene	pentane/ benzene	$1.2 \cdot 10^{-2}$	$2.4 \cdot 10^{-3}$	$8.6 \cdot 10^{-3}$	$4.8 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$	$2.2 \cdot 10^{-2}$
<i>n</i> -butane/ ethane	propane/ ethane	$3.4 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$7.2 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$	$7.6 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
benzene/ <i>n</i> -butane	propane/ <i>n</i> -butane	$5.0 \cdot 10^{-4}$	$9.4 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	$2.9 \cdot 10^{-4}$	$3.0 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$
toluene/ benzene	<i>n</i> -pentane/ <i>n</i> -butane	$3.4 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$7.1 \cdot 10^{-7}$	$1.9 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
<i>n</i> -butane/ benzene	toluene/ benzene	$4.5 \cdot 10^{-3}$	$4.9 \cdot 10^{-4}$	$2.4 \cdot 10^{-3}$	$3.6 \cdot 10^{-4}$	$2.5 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$
<i>n</i> -hexane/ benzene	toluene/ benzene	$1.7 \cdot 10^{-3}$	$7.9 \cdot 10^{-4}$	$4.6 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	$4.7 \cdot 10^{-3}$	$6.4 \cdot 10^{-3}$

^a The reaction rate constants and their uncertainties are taken from Hooshiyar et al. (1995), Talukdar et al. (1994), Atkinson (1994), Atkinson and Aschmann (1986), Atkinson et al. (1989 and 1992).

Based on these observations we can confidently derive upper limits for the Cl-atom concentrations. The upper limits which include the uncertainties derived from the error of the slope and the reaction rate constants are included in Table 3. They range from about 0.01 to $3 \cdot 10^{-4}$.

A possibility to minimize the effect of mixing and dilution is to look at hydrocarbon pairs with identical rate constants for their reaction with OH-radicals. In this specific case, the removal by OH-radicals proceeds at the same relative rate for both compounds and their relative concentrations do not change as result of OH-chemistry

(Jobson et al., 1994; McKeen et al., 1990 and 1993). Consequently, such hydrocarbon pairs do not carry any information about the OH-radical concentration. We can test this by looking at the slopes of plots of benzene versus propane and of toluene versus *n*-hexane. For each pair the rate constants for their reaction with OH-radicals are very similar (Table 2) and we find nearly ideal linear dependencies with slopes of 0.124 ± 0.024 and 0.545 ± 0.011 . Also the intercepts with the axis of 5 ± 1 ppt and 0.1 ± 0.05 ppt, respectively, are marginal compared to the average mixing ratios (see above). However, these substances have sub-

stantially different reactivities towards Cl-atoms and thus are very sensitive indicators for Cl-atom reactions.

Parrish et al. (1993) and Jobson et al. (1994) used *n*- and *i*-butane as such a hydrocarbon pair. Their reactivities towards OH and Cl differ by 10% and 50%, respectively. However, as mentioned above, propane and benzene, and *n*-hexane and toluene, are also pairs. Their reactivities towards OH differ in both cases by only about 20%, but their rate constants for reactions with Cl-atoms by a factor of about 10 and 6, respectively.

In Figs. 2, 3 log-log plots based on these two hydrocarbon pairs are shown. In a general sense these plots compare two indicators for the amount of photochemical aging of an air mass which have the same sensitivity towards OH-radicals but very different sensitivities towards Cl-atoms. As can be seen, even for these selected hydrocarbon pairs with a high sensitivity towards Cl-atom chemistry there is no indication of a significant impact of Cl-chemistry. The slopes for these two hydrocarbon sets correspond to a [Cl]/[OH] ratio of

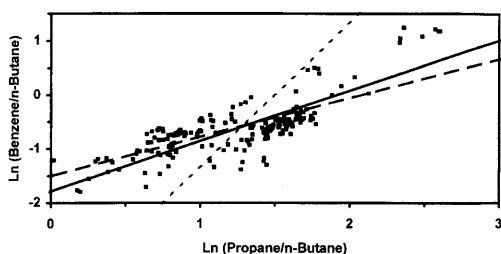


Fig. 2. Same as Fig. 1 but for $\ln$ benzene/*n*-butane versus $\ln$ propane/*n*-butane.

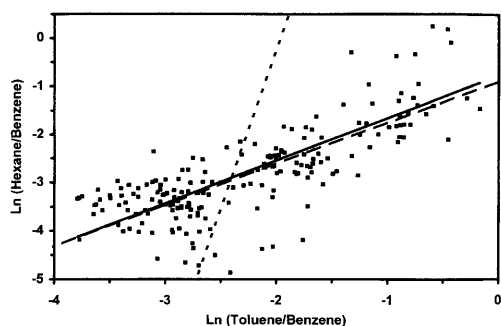


Fig. 3. Same as Fig. 1 but for $\ln$ *n*-hexane/benzene versus $\ln$ toluene/benzene.

slightly less than $5 \cdot 10^{-4}$ and $2 \cdot 10^{-3}$ (Table 1, 3). However, within the uncertainty of the estimates none of these values is significantly different from zero.

As can be seen from Table 3, the main source for the rather high uncertainty of the derived upper limits of the [Cl]/[OH] ratios is the error of the rate constants. It should be noted that the uncertainty due to errors of the rate constants for reactions with Cl-atoms is much lower than for OH-radical rate constants. This is the result of the relatively small impact of Cl-atom reactions on the removal of nonmethane hydrocarbons which is evident from the good agreement between the experimental slopes and the slopes calculated for OH-reactions only.

The total error of the upper limit of the [Cl]/[OH] ratio is calculated from the absolute error of the rate constants. As can be seen from eqs. (2) and (4) systematic errors which would have a comparable affect for all rate constants would at least partly compensate each other, especially if the slope (a) is close to unity. For this reason also the effect of temperature for the theoretical slopes etc. is quite small (see above) and the errors caused by uncertainties of the actual temperatures is small compared to those resulting from the uncertainties of the rate constants.

4. Summary and conclusions

Measurements of hydrocarbons can be very powerful tools to gain insight into atmospheric removal processes of these compounds. Specifically very sensitive estimates of the upper limit of the impact of Cl-atoms can be derived from log-log plots of hydrocarbon ratios. However, care must be taken in the selection of suitable hydrocarbon pairs in order to avoid the potential bias arising from mixing processes and non zero background concentrations. Only then can meaningful and unambiguous results be obtained.

The Cl-atom concentrations derived from the hydrocarbon measurements are very low. The best estimates of an [Cl]/[OH] ratio in the range of $3 \pm 4 \cdot 10^{-3}$ is statistically not significantly different from zero. The upper limit of this ratio derived from the NMHC pairs most sensitive to Cl-atom chemistry is in the range of $0.5\text{--}5 \cdot 10^{-3}$. Based on

an average OH-radical concentration of roughly 10^6 cm^{-3} (Prinn et al., 1995) this corresponds to Cl-atom concentrations in the range of a few 10^3 cm^{-3} . Such low Cl-atom concentrations can only have a small impact on the chemistry of the marine boundary layer. These findings agree with the low average Cl-atom concentrations of less than 10^3 cm^{-3} derived from the global budgets of ethane and tetrachloroethene (Rudolph et al., 1996) and the model predictions of Sander and Crutzen (1996). Also the model estimates of Vogt et al. (1996) are still within the upper limits of our estimates. However, the Cl-atom concentrations derived by Singh et al. (1996a) and Wingenter et al. (1996) are not compatible with our results. Our measurements cover a reasonably extensive ocean area and a period of 2 months. Nevertheless, our results do not rule out that in other regions of the marine boundary layer or in another season higher Cl-atom concentrations may occur.

Our upper limit is valid only as an average for the whole cruise. Therefore it cannot be excluded that for short time periods and limited regions higher Cl-atom concentrations may have occurred in the area investigated here. However, Cl-atom concentrations in the range of several 10^4 cm^{-3} to 10^5 cm^{-3} as deduced by Wingenter et al. (1996)

and Singh et al. (1996a) could only have persisted for very short time periods and limited areas.

The results of this study indicate that, with the exception of specific situations such as the tropospheric ozone depletion episodes during Arctic spring, Cl-atoms are probably of minor importance for the chemistry of the troposphere. Surprisingly enough, the largest uncertainties of our calculated Cl-atom concentrations result from uncertainties of the rate constants, especially for the reactions of hydrocarbons with OH. A consistent and precise set of the relevant rate constants would greatly reduce the uncertainty of the derived upper limits of Cl-atom concentrations.

5. Acknowledgments

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