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# Gas-phase reactions of Cl atoms with hydrochloroethers: relative rate constants and their correlation with substituents' electronegativities

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**Rate constants for the reactions of Cl atoms with $CH_3OCHCl_2$ and $CH_3OCH_2CH_2Cl$ were determined at (296 ± 2) K and atmospheric pressure using synthetic air as bath gas. Decay rates of these organic compounds were measured relative to the following reference compounds: $CH_2ClCH_2Cl$ and *n*-$C_5H_{12}$. Using rate constants of $1.33 \times 10^{-12}$ and $2.52 \times 10^{-10}$ $cm^3$ molecule$^{-1}$ sec$^{-1}$ for the reaction of Cl atoms with $CH_2ClCH_2Cl$ and *n*-$C_5H_{12}$, respectively, the following rate coefficients were derived: $k(Cl + CH_3OCHCl_2) = (1.05 \pm 0.11) \times 10^{-12}$ and $k(Cl + CH_3OCH_2CH_2Cl) = (1.14 \pm 0.10) \times 10^{-10}$, in units of $cm^3$ molecule$^{-1}$ $s^{-1}$. The rate constants obtained were compared with previous literature data and a correlation was found between the rate coefficients of some $CH_3OCHR^1R^2 + Cl$ reactions and ΔElectronegativity of —$CHR^1R^2$. Copyright © 2008 John Wiley & Sons, Ltd.**

**Keywords:** relative rate constants, hydrochloroethers, chlorine atoms, electronegativity

## INTRODUCTION

Recent years have seen a marked increase in awareness of environmental issues in general, and particularly in issues relating to air quality. Large quantities of oxygenated hydrocarbons, especially haloethers, are emitted into the atmosphere each year from anthropogenic sources, and the potential atmospheric significance of such pollutants is dependent on the transformations which they undergo in the troposphere, the nature of the products of these transformations, and the atmospheric lifetimes of each species.[1]

The reaction with OH radicals is a main mechanism for removing oxygenated volatile compounds in the atmosphere. Nevertheless, the reaction of chlorine atom with organic compounds is considered of potential relevance in the marine troposphere where significant chlorine atom concentration may be present.[2,3]

The objectives of the present work have been:

(i) To extend the existing scant data base of rate constants for the reactions of chlorine atoms with hydrochloroethers (HCEs) as part of ongoing work in our laboratory regarding the atmospheric impact of these compounds as acceptable candidates to replace the harmful CFCs and their derivatives in industrial uses.

(ii) To determine the rate coefficients for the following gas-phase reactions:

$$Cl + CH_3OCHCl_2 \rightarrow \text{Products} \qquad (1)$$

$$Cl + CH_3OCH_2CH_2Cl \rightarrow \text{Products} \qquad (2)$$

(iii) To evaluate reactivity trends of HCEs.

A relative rate technique was used to study the kinetics of the reactions (1) and (2) at room temperature and atmospheric pressure (~750 Torr), using synthetic air as diluent gas. To our best knowledge, only one study has been carried out previously for these reactions by McLoughlin *et al.*,[4] who measured the rate coefficient for the reaction of Cl atoms with $CH_3OCH_2CH_2Cl$ using a relative technique.

The results obtained will be presented and compared with those obtained previously for the same and related reactions of Cl atoms. A correlation of the rate constants with the electronegativities of the substituent groups will be analyzed. The atmospheric implications for the studied HCEs are considered briefly.

## EXPERIMENTAL

### Relative rate measurements

The reaction rate coefficients for the reactions (1) and (2) were determined by using the relative rate method

$$Cl + HCE \rightarrow \text{Products} \qquad (3)$$

$$Cl + \text{Reference} \rightarrow \text{Products} \qquad (4)$$

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The principle of this method is to measure the decay rate of the Cl-induced oxidation of the HCE relative to a reference compound for which the Cl oxidation rate constant is well known.

Assuming that the HCE and the reference compound are lost solely via reaction with Cl atoms and that they are not reformed in any process, the relative rate coefficient, $k_{rel}$, can be obtained by the following relation:

$$\ln\left\{\frac{[HCE]_0}{[HCE]_t}\right\} = \frac{k_3}{k_4}\ln\left\{\frac{[Reference]_0}{[Reference]_t}\right\}, \quad k_{rel} = \frac{k_3}{k_4} \qquad (5)$$

where $[HCE]_0$, $[Reference]_0$, $[HCE]_t$, and $[Reference]_t$ are the concentrations of the HCE and reference compound at times $t = 0$ and $t$, respectively and $k_3$ and $k_4$ are the rate constants of reactions (3) and (4), respectively. Thus, a plot of $\{\ln[HCE]_0/[HCE]_t\}$ *versus* $\{\ln[Reference]_0/[Reference]_t\}$ should be linear with a slope equal to $k_{rel}$.

Rate constants were measured at (296 ± 2) K and atmospheric pressure (~750 Torr) using synthetic air as bath gas. The experimental setup used to determine these relative rate constants consisted of a greaseless vacuum system, an 80 L collapsible Tedlar bag and a gas chromatograph (Shimadzu GC-14B) coupled with a flame ionization detector (GC-FID). Measured amounts of the reagents were flushed from calibrated Pyrex bulbs into the collapsible reaction chamber by a stream of synthetic air and it was then filled to its full capacity at atmospheric pressure with synthetic air. Periodically, gas samples were removed from the Tedlar bag using calibrated gas syringes (Hamilton gas tight) and analyzed using the GC-FID. A Porapak Q column (100–120 Mesh, 2.5 m, 1/8″ i.d.) was used, and the temperature varied from 303 to 483 K during the chromatographic runs. $N_2$ was used as the carrier gas.

### Chemicals

The concentration ranges used in the experiments were 132–162 ppm for the HCEs, 109–148 ppm for $CH_2ClCH_2Cl$ and $n$-$C_5H_{12}$ used as reference compounds, where 1 ppm = $2.46 \times 10^{13}$ molecule $cm^{-3}$ at 298 K and 760 Torr of total pressure. $CH_3OCHCl_2$, $CH_3OCH_2CH_2Cl$, and $CH_2ClCH_2Cl$ were obtained from Aldrich, with a manufacturer's stated purity of 98, 98, and 99%, respectively. $n$-$C_5H_{12}$ (purity 99.9%) was obtained from Mallinckrodt. All reagents were degassed by repeated freeze–pump–thaw cycling before their use.

Cl atoms were generated *in situ* in the collapsible Tedlar bag by the UV photolysis of molecular chlorine, using a set of blacklamps (Philips 30W) with a $\lambda$ maximum around 360 nm. In the present work, typically between 2 and 5 of these lamps were used to produce atomic chlorine and the time of photolysis varied from 2 to 30 min. Molecular chlorine was prepared in our laboratory using the reaction between HCl and $KMnO_4$ and was purified by repeated trap to trap distillation until a sample of 99% purity was obtained, confirmed by IR and UV spectroscopy. The initial concentrations of $Cl_2$ were typically in the range 193–209 ppm.

Synthetic air (purity 99.999%) and chromatographic gases ($N_2$, $H_2$, and chromatographic air) were obtained from AGA.

## RESULTS

The rate constants for the reactions of Cl atoms with the two HCEs studied here were determined at (296 ± 2) K and atmospheric pressure, using the relative rate method. The rate constant of reaction (1) was measured relative to the following:

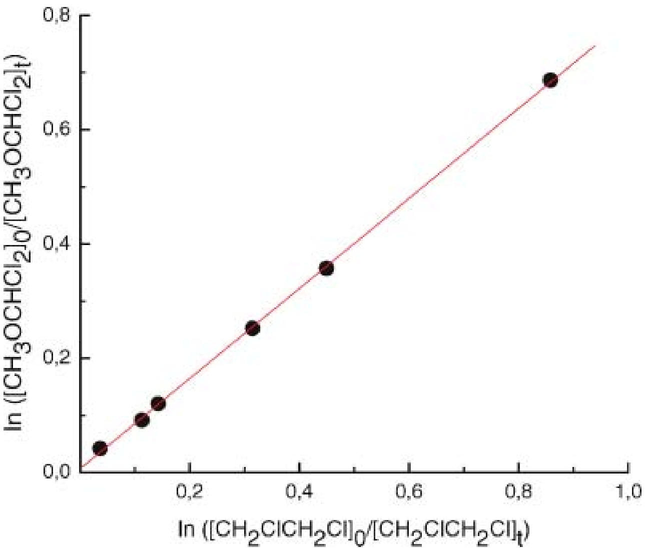

**Figure 1.** Plot of $\ln([CH_3OCHCl_2]_0/[CH_3OCHCl_2]_t)$ *versus* $\ln([CH_2ClCH_2Cl]_0/[CH_2ClCH_2Cl]_t)$ for the reaction of Cl atoms with $CH_3OCHCl_2$

$$Cl + CH_2ClCH_2Cl \rightarrow Products \qquad (6)$$

where $k_6 = (1.33 \pm 0.13) \times 10^{-12}$.[5–7] For reaction (2), the reference reaction was

$$Cl + n - C_5H_{12} \rightarrow Products \qquad (7)$$

with $k_7 = (2.52 \pm 0.12) \times 10^{-10}$,[8,9] with $k$ values in units of $cm^3$ $molecule^{-1}$ $s^{-1}$.

The relative rate method relies on two assumptions: (1) both the reactant and reference compounds are removed solely via reaction with Cl atoms; and (2) both the reactant and reference compound have the same exposure to Cl atoms. To verify these assumptions, several experiments were performed to check unwanted loss of the HCE or references via photolysis, dark chemistry, and wall reactions. In all cases, none were observed. Moreover, due to the UV irradiation field used in this study, the exposure of HCE/reference compounds to atomic chlorine is considerably uniform.[10]

Figure 1 shows a plot of ln $([Reactant]_0/[Reactant]_t)$ *versus* ln $([Reference]_0/[Reference]_t)$, for the reaction (1) using $CH_2ClCH_2Cl$ as the reference compound. A similar plot for reaction (2) using $n$-$C_5H_{12}$ as the reference compound is shown in Fig. 2. For each HCE studied, at least three runs were carried out to determine the rate coefficients and to test the internal consistency of the rate constant ratios. The ratio of the rate constants $k_{rel}$ was calculated from the experimental data using Eqn (3) from the slopes of the plots shown in Figs 1 and 2. The rate constants for the reactions (1) and (2), $k_1$ and $k_2$, were obtained from the $k_{rel}$ as the value of reference rate constant $k_4$ was known. Thus, the value obtained for $k_1$ is $(1.05 \pm 0.11) \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, which was derived using the rate constant ratio $k_1/k_6 = (0.79 \pm 0.01)$ and the literature value for $k_6$. Taking into account the values of $k_7$ and $k_2/k_7 = (0.45 \pm 0.01)$, the derived $k_2$ is $(1.14 \pm 0.10) \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The errors quoted are twice the standard deviation, arising from the least squares analysis of the data, and include the corresponding error in the reference rate constant.

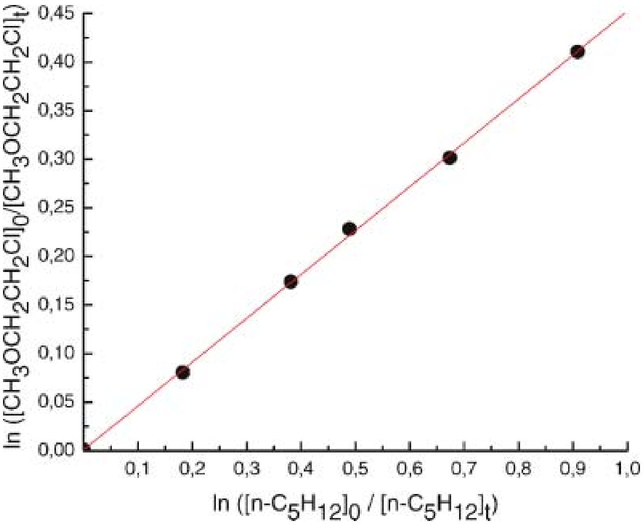

**Figure 2.** Plot of ln($[CH_3OCH_2CH_2Cl]_0/[CH_3OCH_2CH_2Cl]_t$) *versus* ln($[n\text{-}C_5H_{12}]_0/[n\text{-}C_5H_{12}]_t$) for the reaction of Cl atoms with $CH_3OCH_2CH_2Cl$

# DISCUSSION

## Cl + HCE rate constants

The rate coefficients determined for the reactions of Cl atoms with the two HCEs of the present work at 298 K are presented in Table 1, along with the rate constants for other related ethers obtained from the literature for comparison purposes. To the best of our knowledge, this kinetic work represents the first experimental measurement of the rate constant for the reaction of Cl atoms with $CH_3OCHCl_2$, whereas for $CH_3OCH_2CH_2Cl$ there is only one other previous determination.[4]

Under our experimental conditions, OH radical formation is possible via secondary reactions involving $O_2$,[11,12] and thus the relative rate measurements would represent only an upper limit to the rate of the HCE/Cl reaction. In a previous study carried out at (298 ± 2) K and atmospheric pressure, and using $N_2$ as diluent gas, we determined for $k_1$ and $k_2$ values equal to $(1.04 \pm 0.30) \times 10^{-12}$ and $(1.11 \pm 0.20) \times 10^{-10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$, respectively.[16] These values indicate that there is no discernable difference between results obtained in air or $N_2$ diluent. Within the experimental uncertainties, there is no evidence for any effect of the presence of $O_2$ on $k_1$ and $k_2$. Therefore, the absence of changes suggests that interference by OH formation is not significant for any of the HCEs and that the presence of systematic errors due to OH reacting with the HCEs on both rate constants is negligible under our experimental conditions.

## Correlation of Cl + HCE reactivity with substituent electronegativities

The reactivity of HCEs is expected to depend on several factors, such as the number and position of H-atoms, the strength of the C—H bonds and the degree and position of Cl substitution.[17] Likewise, it is accepted that the ether linkage —O— activates the neighboring C—H bonds since the reaction rates for the haloethers are higher than those of the corresponding haloalkanes.[17]

The kinetic information on Cl + HCE reactions that is available is particularly well suited to observe a large inductive effect on reactivity. The set of Cl + HCE reactions chosen involve R substitutions directly at $CH_3OCHR^1R^2$ (where $R^1$ and $R^2$ are equal to H-atoms, Cl atoms, methyl group, or chlorinated methyl group). In order to investigate further this inductive effect, we examined the possibility of a linear relationship between the logarithm of the room temperature rate coefficients of the Cl + HCE reactions and the difference between the sum of electronegativities of the atoms or groups in the substituted $—CHR^1R^2$ and the sum of electronegativities of the three hydrogen atoms in $—CH_3$ ($\Delta\text{Electronegativity} = E_{CHR^1R^2} - E_{CH_3}$). This kind of relationship was previously observed by Seetula and Gutman[18]; likewise in this work the same correlation was found which is shown in Fig. 3. Pauling electronegativities of H and Cl were taken to be 2.20 and 3.16, respectively.[19] A Pauling electronegativity of 1.82 for the $CH_3$ group was used, taken from the work of Seetula and Gutman.[18] The electronegativity values for $CH_2Cl$ (2.78) and $CHCl_2$ (3.74) were calculated using an 'effective' electronegativity of carbon equal to 4.78, which was derived from the $CH_3$ group electronegativity value.

It is clear from the data in Table 1 and from the correlation between rate constants of the Cl reactions *versus* ΔElectronegativity of $CHR^1R^2$ that the inductive effect would be responsible for the differences in reactivity between the Cl + HCE rate constants. Reactivity is enhanced by adding electron-donating methyl groups and is reduced by replacing H-atoms on $—CH_3$ by electron-withdrawing halogen atoms or halogenated methyl groups. Considering that HCEs are expected to react with Cl atoms via an H-atom abstraction mechanism, the qualitative

**Table 1.** Rate constants for the reactions of Cl atoms with HCEs at (296 ± 2) K and ΔElectronegativity

| Ether | $k_{Cl(296K)}$ ($cm^3$ $molecule^{-1}$ $s^{-1}$) | Ref. | Electronegativity $CHR^1R^2$ | ΔElectronegativity |
|---|---|---|---|---|
| $CH_3OCH_3$ | $1.81 \times 10^{-10a}$ | [13] | 6.60 | 0.00 |
| $CH_3OCH_2Cl$ | $2.91 \times 10^{-11}$ | [14] | 7.56 | 0.96 |
| $CH_3OCHCl_2$ | $1.05 \times 10^{-12}$ | This work | 8.52 | 1.92 |
| $CH_3OCH_2CH_3$ | $3.49 \times 10^{-10}$ | [15] | 6.22 | −0.38 |
| $CH_3OCH_2CH_2Cl$ | $1.14 \times 10^{-10}$ | This work | 7.18 | 0.58 |
|  | $1.44 \times 10^{-10}$ | [4] | — | — |
| $CH_3OCH_2CHCl_2$ | $4.4 \times 10^{-11}$ | [4] | 8.14 | 1.54 |

[a] This value is the average between all the experimental values given in Reference [13].

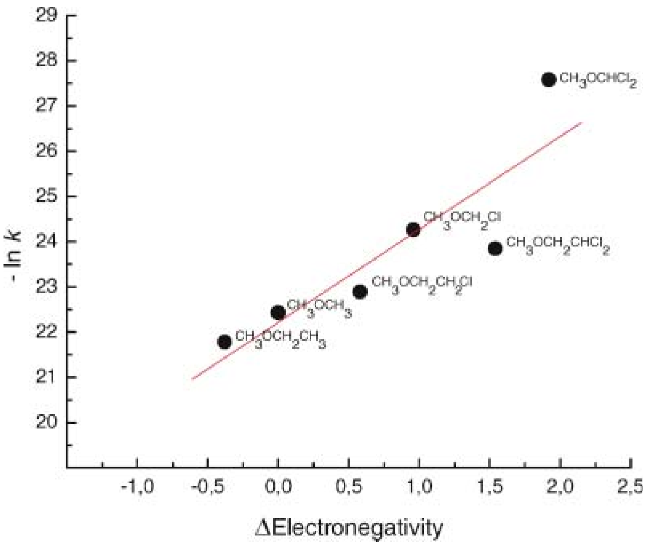

**Figure 3.** Plot of −ln *k versus* ΔElectronegativity. *k* is the rate constant for the reaction of Cl atoms with a certain HCE at (296 ± 2) K

observations above could be rationalized taking into account that the reaction transition state in the Cl + HCE reactions would involve an H-atom with a partial positive charge located between the Cl atom and the $CH_3OCR^1R^2$ group $[CH_3OCR^1R^2$---H---Cl]. Enhanced electron density (R = methyl group) would stabilize such a transition state and facilitate reaction, while diminished electron density (R = halogen atom or halogenated methyl group) would reduce its stability due to repulsive forces between the electrophilic attacking Cl atom and the relative positive charge density over the H-atom.

### Atmospheric implications

Atmospheric lifetimes, $\tau_X$, of the HCEs studied were estimated using the following expressions: $\tau_{Cl} = 1/k_{Cl}$ [Cl] and $\tau_{OH} = 1/k_{OH}$ [OH], where $k_{Cl}$ and $k_{OH}$ are the bimolecular rate constants for reaction of Cl atoms or OH radicals with a certain HCE at (296 ± 2) K in units of $cm^3\,molecule^{-1}\,s^{-1}$, respectively. [Cl] and [OH] are the average tropospheric concentrations of atomic chlorine and hydroxyl radicals, which have been deduced to be $1 \times 10^4$ atoms $cm^{-3}$ [20] and $5 \times 10^5$ radicals $cm^{-3}$,[21] respectively. Tropospheric lifetimes of 10 days for $CH_3OCH_2CH_2Cl$ and 3 years for $CH_3OCHCl_2$ were calculated for the reactions with chlorine atoms taking into account the rate constant values determined in the present work for both ethers ($1.14 \times 10^{-10}$ and $1.05 \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$, respectively). The corresponding lifetimes for the reactions with OH radicals were estimated as 5 and 93 days, respectively; considering rate constants for the reactions of $CH_3OCH_2CH_2Cl$ and $CH_3OCHCl_2$ with OH to be $4.92 \times 10^{-12}\,cm^3\,molecule^{-1}\,s^{-1}$ [4] and $2.5 \times 10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$,[22] respectively.

The removal of both HCEs studied in this work by $NO_3$ radicals or $O_3$ molecules is expected to be of negligible importance.[23,24] Photolysis is another potential loss process, but the UV absorption of the HCEs lies at wavelengths short enough that the photolytic decomposition will not be of any significance in the lower troposphere.

In conclusion, the atmospheric lifetimes of both ethers are determined by the OH-initiated oxidation. The relatively short lifetimes of the HCEs studied will hinder the transport of these organic compounds into the stratosphere, making a minor or negligible contribution to the ozone depletion through $ClO_x$ catalytic cycles.

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## REFERENCES

[1] B. J. Finlayson-Pitts, J. N. Pitts, Jr., *Chemistry of the upper and lower atmosphere*, Academic Press, New York, **2000**.
[2] C. W. Spicer, E. G. Chapman, B. J. Finlayson-Pitts, R. A. Plastidge, J. M. Hubbe, J. D. Fast, C. M. Berkowitz, *Nature* **1998**, *394*, 353–356.
[3] M. J. Ezell, W. Wang, A. A. Ezell, G. Soskin, B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.* **2002**, *4*, 5813–5820.
[4] P. McLoughlin, R. Kane, I. Shanahan, *Int. J. Chem. Kinet.* **1993**, *25*, 137–149.
[5] T. J. Wallington, M. Bilde, T. E. Mogelberg, J. Sehested, O. J. Nielsen, *J. Phys. Chem.* **1996**, *100*, 5751–5760.
[6] E. Tschuikow-Roux, F. Faraji, J. Niedzielski, *Int. J. Chem. Kinet.* **1986**, *18*, 513–528.
[7] E. W. Kaiser, T. J. Wallington, *J. Phys. Chem.* **1996**, *100*, 4111–4119.
[8] R. Atkinson, S. M. Aschmann, *Int. J. Chem. Kinet.* **1985**, *17*, 33–41.
[9] P. A. Hooshiyar, H. Niki, *Int. J. Chem. Kinet.* **1995**, *27*, 1197–1206.
[10] K. Takahashi, Y. Matsumi, T. J. Wallington, M. D. Hurley, *Chem. Phys. Lett.* **2002**, *352*, 202–208.
[11] J. V. Michael, D. G. Keil, R. B. Klemm, *J. Chem. Phys.* **1985**, *83*, 1630–1636.
[12] G. S. Tyndall, T. A. Staffelbach, J. J. Orlando, J. G. Calvert, *Int. J. Chem. Kinet.* **1995**, *27*, 1009–1020.
[13] *NIST Chemical Kinetics Database on the Web Public Beta Release 1.4-*Standard Reference Database 17, Version 7.1, NIST Standard Reference Data, NIST, Gaithersburg, MD, 2007 (Web Version).
[14] M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, T. Ellermann, *J. Phys. Chem.* **1993**, *97*, 11712–11723.
[15] D. P. Starkey, K. A. Holbrook, G. A. Oldershaw, R. W. Walker, *Int. J. Chem. Kinet.* **1997**, *29*, 231–236.
[16] P. R. Dalmasso, R. A. Taccone, J. D. Nieto, M. A. Teruel, S. I. Lane, *Int. J. Chem. Kinet.* **2005**, *37*, 420–426.
[17] K. G. Kambanis, Y. G. Lazarou, P. Papagiannakopoulos, *J. Phys. Chem. A* **1998**, *102*, 8620–8625.
[18] J. A. Seetula, D. Gutman, *J. Phys. Chem.* **1991**, *95*, 3626–3630.
[19] P. W. Atkins, *Physical Chemistry*, 6th edn, OUP, Oxford, **1998**.
[20] O. W. Wingenter, M. K. Kubo, N. J. Blake, T. W. Smith, D. R. Blake, F. S. Rowland, *J. Geophys. Res.* **1996**, *101*, 4331–4340.
[21] T. Brauers, U. Aschmutat, U. Branderburger, H. P. Dorn, M. Hausmann, M. Hessling, A. Hofzumahaus, F. Holland, C. Plas-Dulmer, D. H. Ehhalt, *Geophys. Res. Lett.* **1996**, *23*, 2545–2548.
[22] P. R. Dalmasso, J. D. Nieto, P. M. Cometto, R. A. Taccone, S. I. Lane, in press.
[23] A. C. Brown, C. E. Canosa-Mas, A. D. Parr, R. P. Wayne, *Atmos. Environ.* **1990**, *24*, 2499–2511.
[24] R. P. Wayne, I. Barnes, P. Biggs, J. P. Burrows, C. E. Canosa-Mas, J. Hjorth, G. Le Bras, G. K. Moortgat, D. Perner, G. Poulet, G. Restelli, H. Sidebottom, *Atmos. Environ.* **1991**, *25*, 1–203.