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Carbon kinetic isotope effect in the reaction of CH_4 with Cl atoms

G. Saueressig, P. Bergamaschi, J.N. Crowley, and H. Fischer
Max-Planck-Institut für Chemie, Mainz, Germany

G. W. Harris
York University, Ontario, Canada

Abstract. The carbon kinetic isotope effect in the reaction between Cl and CH_4 (KIE_{Cl}) has been measured using tunable diode laser absorption spectroscopy to determine $^{13}CH_4/^{12}CH_4$ ratios. Cl atoms were generated by the irradition of Cl_2 in static mixtures of $Cl_2/CH_4/N_2$ or $Cl_2/CH_4/N_2/O_2$. Both methods resulted in a (KIE_{Cl}) of 1.066 ± 0.002 at 297 K. The KIE_{Cl} displayed a slight temperature dependence, increasing to 1.075 ± 0.005 at 223 K. This result suggests a significant influence of the title reaction on the stratospheric CH_4 isotopic composition and may help to resolve discrepancies between measurements of stratospheric $^{13}CH_4/^{12}CH_4$ profiles and laboratory measurements of KIE_{OH}.

Introduction.

Methane is ubiquitous in the atmosphere and may be regarded as one of the most important trace constituents in the chemistry of both the troposphere and the stratosphere [*Cicerone and Oremland*, 1988]. CH_4 is an important greenhouse gas [*Lelieveld et al.*, 1993] that is lost mainly by reaction with OH radicals in the troposphere [*Crutzen*, 1973] and by reaction with OH, $O(^1D)$ and Cl atoms in the stratosphere [*Crutzen and Schmailzl*, 1983; *Garcia and Solomon*, 1994].

It is clearly important to identify the various natural and anthropogenic sources of methane and to assess their strengths. The various CH_4 sources are known to possess characteristic isotopic fingerprints, or mean $^{13}CH_4/^{12}CH_4$ ratios, which are clearly distinguishable for sources with different CH_4 formation processes. The comparison of these isotopic signatures with the mean isotopic signature of atmospheric CH_4 allows conclusions to be drawn about the relative contributions of the various sources to the global CH_4 budget [*Stevens and Engelkemeir*, 1993; *Wahlen*, 1993]. This approach requires knowledge of the isotopic fractionation of CH_4 through its sinks, of which reaction with OH is the most important.

Several laboratory studies have addressed the isotopic fractionation of CH_4 due to reaction with OH [*Cantrell et al.*, 1990] and a KIE_{OH} of 1.0054 ± 0.0009 is the best available value to date. Recent measurements of stratospheric CH_4 have identified a higher $^{13}CH_4$ enrichment [*Wahlen et al.*, 1989; C.A.M. Brenninkmeijer, D.C. Lowe, R.J. Sparks, M.R. Manning, and P. van Velthoven, ^{13}C, ^{14}C and ^{18}O isotopic composition of CO, CH_4 and CO_2 in the higher southern latitudes, lower stratosphere, submitted to *J. Geophys. Res.*, 1995] than expected from fractionation due to reaction with OH alone. This may indicate either that the experimental KIE_{OH} is incorrect or that other unconsidered reactions contribute to the fractionation observed in the stratosphere. One potential process is the reaction with Cl atoms:

$$Cl + CH_4 \rightarrow HCl + CH_3 \qquad (1)$$

which contributes significantly to CH_4 destruction in the lower stratosphere [*Crutzen and Schmailzl*, 1983] and is believed to have a large KIE [*Xiao et al.*, 1993]. The present study is the first experimental investigation of the isotopic fractionation in the Cl + CH_4 reaction.

Experimental

The reaction between Cl atoms and CH_4 was initiated by the broad band irradition (310-410 nm) of Cl_2 in static gas mixtures comprising of either $Cl_2/CH_4/N_2/O_2$ or $Cl_2/CH_4/N_2$ in a thermostatted 1.3 l pyrex vessel. Nine radially mounted TL08 lamps provided a homogeneous light flux over the entire length of the reaction volume.

The gases were thoroughly mixed by circulation around a closed loop and a sample was withdrawn from the cell prior to photolysis by expansion into a pre-evacuated 100 ml glass bulb. This sample was used to establish the initial CH_4 mixing ratio by gas chromatography (GC). The closed loop includes a glass spiral held at liquid nitrogen temperature which serves to remove Cl_2 from the sample.

Following the reaction, in which between 25% and 60% of the CH_4 is destroyed over a photolysis time of typically 3 minutes, the gas mixture was circulated through the loop and cold spiral again (to remove condensible, corrosive gases such as Cl_2 and HCl and thus protect the White cell mirrors of the TDLAS instrument, see below) before a second sample was extracted into a 1000 ml glass bulb.

This sample was first analysed for CH_4 mixing ratio using GC and then for isotopic composition using tunable diode laser absorption spectroscopy (TDLAS) [*Bergamaschi et al.*, 1994].

In the absence of O_2 a catalytic reaction sequence leads to CH_4 destruction:

$$Cl_2 + h\nu \rightarrow Cl + Cl \qquad (2)$$
$$Cl + CH_4 \rightarrow CH_3 + HCl \qquad (1)$$
$$CH_3 + Cl_2 \rightarrow CH_3Cl + Cl \qquad (3)$$

Under our conditions, 99.9% of the Cl atoms are generated photocatalytically via R3. On the other hand, in the presence of O_2, the chain is broken since CH_3 is rapidly scavenged to

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methylperoxy radicals, CH_3O_2:

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (4)$$

and Cl atom production is purely photolytic (R2). In this case the rate of CH_4 depletion is governed by the photolysis rate of Cl_2, the Cl_2 concentration and the rate of loss of Cl atoms with the various products of the oxidation of CH_4, i.e. HCHO, CH_3OH, CH_3OOH [*Lightfoot et al.*, 1992].

Experimental conditions were CH_4: 4200 ppm; Cl_2: 1800-6200 ppm at total pressures of 500 mbar with N_2 or N_2/O_2 bath gas.

The change in isotopic composition of a sample of CH_4 following reaction with Cl atoms was measured by the TDLAS technique. This part of the experiment has been described in detail elsewhere [*Bergamaschi et al.*, 1994] and only essential details are given here. The emission of the tunable diode laser was scanned over a wavenumber interval of ~0.2 cm^{-1} and the absorption due to a $^{13}CH_4/^{12}CH_4$ line pair measured over a 81 m pathlength in a White cell. All measurements were made at 30 mbar total pressure and room temperature. The line pair chosen was at 3007.078 cm^{-1} ($^{12}CH_4$) and 3007.145 cm^{-1} ($^{13}CH_4$).

A major secondary product in our reaction system is CH_3Cl which exhibits absorption lines near this region and is thus a potential interferent. However virtually all the product CH_3Cl is removed in the 77 K cold spiral prior to CH_4 isotopic analysis and the remaining CH_3Cl (< 1 ppm) had no discernible effects in the spectral region near our $^{12}CH_4/^{13}CH_4$ line pair.

The isotopic ratio of the sample is expressed in the δ-notation:

$$\delta^{13}C = (R_{sample}/R_{standard} - 1) \cdot 1000 \ [‰] \quad (I)$$

where R is equal to the ratio $[^{13}CH_4]/[^{12}CH_4]$. $\delta^{13}C$-values given in this study are expressed against our reference standard ($\delta = \delta^{13}C^{ref}$; $\delta^{13}C^{PDB}(ref) = -27.8$ ‰). CH_4 samples used for the reaction were taken from the same cylinder as the reference gas.

In combination with measurements of d[CH_4], (the reduction of CH_4 in the sample during the reaction period) the change in isotopic composition can be converted to KIE_{Cl} using the Rayleigh equation :

$$\delta_f - \delta_i = (\delta_i + 1000) \cdot (1/KIE_{Cl} - 1) \cdot \ln(c_f/c_i) \quad (II)$$

where δ_i and δ_f describe the initial and final isotopic composition [$\delta_i = \delta^{13}C^{ref}(ref) = 0$]. c_i and c_f are the respective concentrations of CH_4.

Results

Experiments without O_2 were carried out at 297 K (n=12), 263 K (n=2), 243 K (n=2) and 223 K (n=4) and the results are shown in Table 1. The KIE_{Cl} obtained at 297 K in N_2 (n=12) and in N_2/O_2 bath gas (n=4) are indistinguishable, ruling out a significant contribution to fractionation by excited $Cl(^2P_{1/2})$ atoms, which cannot be important in the N_2 system where almost all the Cl atoms are produced chemically in R3. In addition, the quenching rates of $Cl(^2P_{1/2})$ in N_2 or O_2 are sufficiently large to preclude its involvement in this chemical system [*Clark and Husain*, 1994].

Table 1. Temperature dependence of KIE_{Cl}

T/K	KIE_{CL}	n	n_0	bath gas
223	1.075 ± 0.005	4	1	N_2
243	1.069 ± 0.004	2	2	N_2
263	1.070 ± 0.004	2	1	N_2
297	1.066 ± 0.002	12	6	N_2
297	1.065 ± 0.003	4	1	N_2/O_2

Errors are at the 95 % confidence level. n refers to experiments with photolysis, n_0 are control experiments without photolysis.

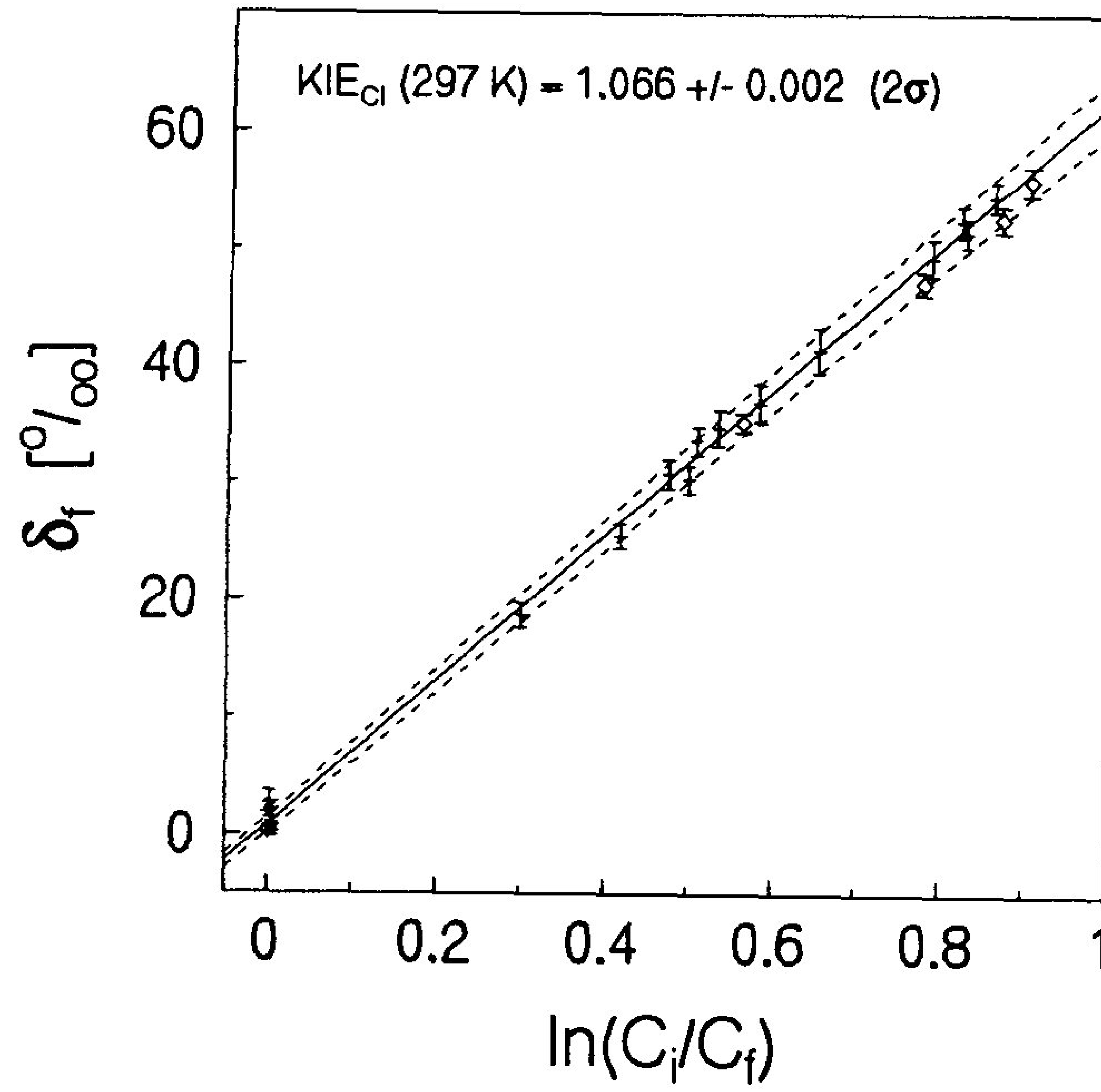

Figure 1. Plot of isotopic composition $\delta_f = (\delta^{13}C^{ref})_f$ versus degree of conversion of CH_4 $\ln(c_f/c_i)$ at 297 K. The diamonds are results with O_2 present. The dashed lines represent the 95% confidence limits of the fit.

As check of our methodology, control experiments were carried out in which the gas mixing and sampling procedures were identical to that described above, but the gas mixture was not irradiated (number n_0 in Table 1). The unchanged isotopic composition in the control experiments (data at $\ln(c_i/c_f)=0$ in Figure 1) precludes significant fractionation due to processes other than gas-phase reaction with Cl.

Figure 1 displays a plot of δ_f against $\ln(c_i/c_f)$ at 297 K, from which a KIE_{Cl} of 1.066 ± 0.002 was obtained (from n=12 experiments carried out without O_2). The temperature dependence of KIE_{Cl} (Table 1) can be expressed in Arrhenius form as a plot of $\ln(KIE_{Cl})$ versus 1/T as shown in Figure 2 and is given by $KIE_{Cl} = 1.043 \cdot \exp(6.455/T)$.

Application of a second line pair at 3002.853 and 3003.1 cm^{-1} pair to two samples (T=297 K, $Cl_2/CH_4/N_2$) yielded KIE_{Cl} = 1.064 ± 0.006. This confirms that the measurements of $^{13}CH_4/^{12}CH_4$ ratios were not influenced by interferences from CH_3Cl or other absorbing species.

Discussion

In the presence of O_2, Cl atoms are generated photolytically (R2), while in the absence of O_2 Cl is generated mainly photocatalytically (R1-R3). That both methods yield the same result gives us confidence that CH_4 is destroyed exclusively by reaction with $Cl(^2P_{3/2})$ (ground state Cl) and that other potential removal processes, i.e. reaction with OH, which may be generated following photolysis of the CH_3OOH and H_2O_2

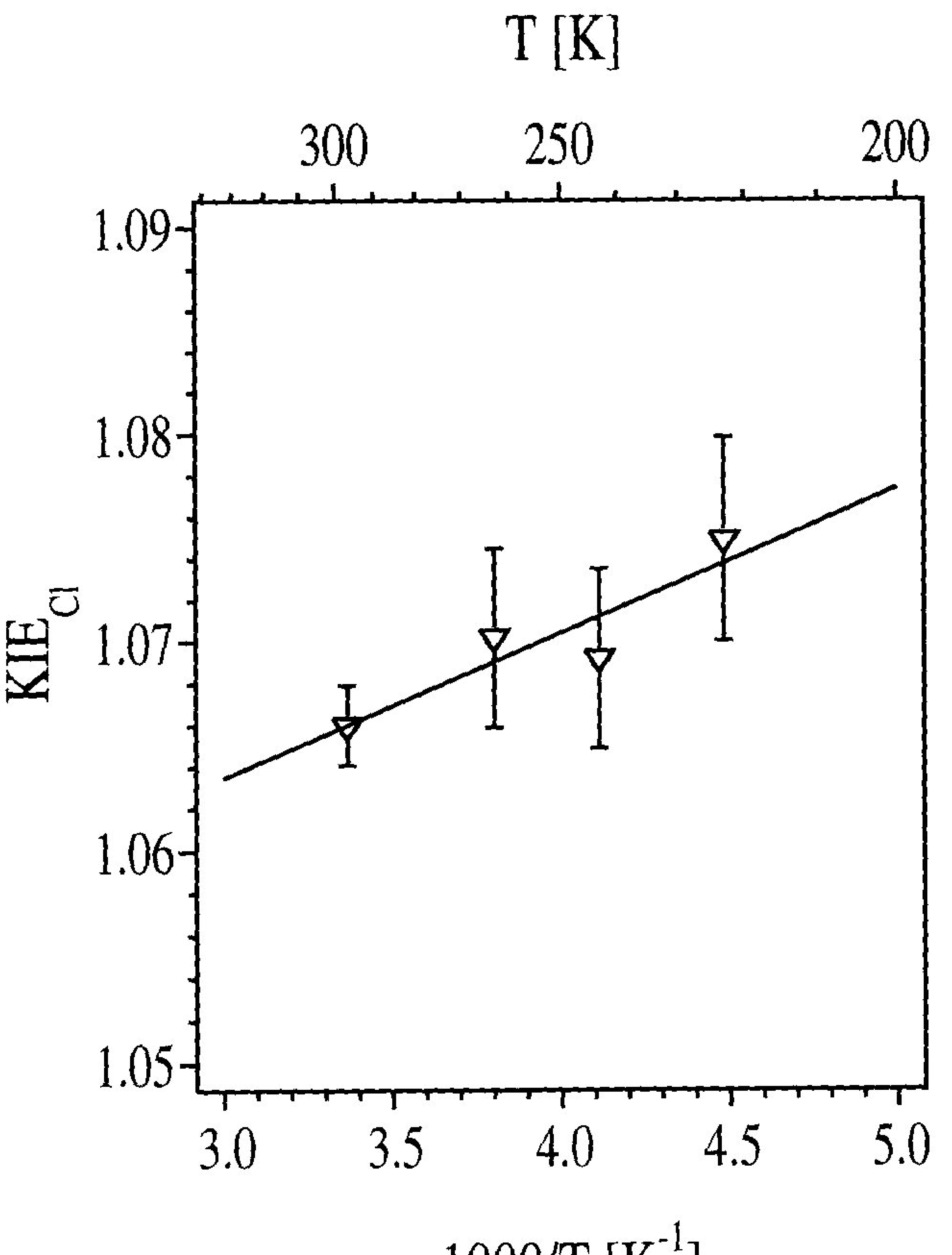

Figure 2. Temperature dependence of KIE_{Cl} between 223 and 297 K. $KIE_{Cl}(T) = 1.043 * \cdot exp(6.455/T)$.

secondary products of the CH_3O_2 radical reactions [*Lightfoot at al*, 1992], are unimportant. Numerical simulation [*Curtiss and Sweetenham*, 1987] of an assumed reaction mechanisms confirmed that less than 0.1% of the CH_4 was removed by OH.

Our results yield a temperature dependent KIE with a value of KIE_{Cl} of 1.066 ± 0.002 at 297 K, considerably larger than the KIE_{OH} = 1.0054 ± 0.0009 reported by *Cantrell et al.* (1990) for the reaction CH_4 + OH. Qualitatively, this trend is consistent with ab initio calculations which estimate a KIE_{Cl} of 1.034 for Cl + CH_4 [*Xiao et al.*, 1993] and a KIE_{OH} of 1.007 for OH + CH_4 [*Lasaga and Gibbs*, 1991].

To date a discrepancy exists between $^{13}CH_4/^{12}CH_4$ profiles measured in the lower stratosphere [*Wahlen et al.*, 1989; C.A.M. Brenninkmeijer, personal communication, 1995] and those expected from CH_4 destruction by the reaction with OH only using the KIE_{OH} = 1.0054 from the experiment of *Cantrell et al.* [1990]. In the lower stratosphere, CH_4 is destroyed predominantly by OH but reactions with $O(^1D)$ and Cl atoms are also important. Although methane oxidation through Cl reaction occurs predominantly in the middle and upper stratosphere, measurements in the lower stratosphere largely reflect high altitude destruction. The overall observable KIE for stratospheric CH_4 (KIE_{strat} = 1.013 as observed by Brenninkmeijer (personal communication, 1995) in the lower stratosphere (10-12 km) at mid to higher southern latitudes) reflects the mean fractionation of these three sinks, weighted with their relative contribution:

$$KIE_{strat} = KIE_{Cl}*f_{Cl} + KIE_{OH}*f_{OH} + KIE_{O(1D)}*f_{O(1D)} \quad \text{(III)}$$

where f_{Cl}, f_{OH} and $f_{O(1D)}$ are the relative contribution to CH_4 destruction by the reactions with Cl, OH and $O(^1D)$, respectively. Using literature values of KIE_{OH} = 1.0054 [*Cantrell et al.*, 1990)], $KIE_{O(1D)}$ = 1.001 [*Davidson et al.*, 1987], and KIE_{Cl} = 1.075 (from our measurement at T = 223 K) a relative contribution f_{Cl} = 11-13% of the Cl sink would be necessary to obtain a mean KIE_{strat} = 1.013. The new KIE_{Cl} measurements are presently being incorporated into a detailed modeling study of the influence of the three sinks on the isotope composition of stratospheric methane.

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P. Bergamaschi (correspondence), J. Crowley, H. Fischer and G. Saueressig, Max-Planck-Institut für Chemie, Division of Atmospheric Chemistry, Postfach 3060, 55020 Mainz, Germany.

G.W. Harris, Centre for Atmospheric Chemistry, York University, North York, 4700 Keele St., Ontario M3J1P3, Canada.

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