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The stable carbon isotope fractionation for reactions of selected hydrocarbons with OH-radicals and its relevance for atmospheric chemistry

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Abstract. Measurements of the kinetic isotope effect (KIE) for the reactions of light n-alkanes as well as for several unsaturated hydrocarbons, including alkenes, dienes, benzene, and ethyne with OH-radicals are presented. All measured KIEs are positive; that is, molecules containing only C-12 react faster than the C-13 labeled molecules. However, the KIEs for n-alkanes are quite small; between one and four permil. They can be explained mainly by the mass dependence of the collision frequency between the n-alkanes and OH-radicals. KIEs for the reaction of alkenes with OH-radicals are considerably higher. They can be explained by a fractionation of 24.5 ± 1.1‰ for the addition of an OH-radical to a double bond. Inverse dependence on number of carbon atoms and mass dependence of the collision frequencies explain our observations. For benzene the KIE is slightly higher; for ethyne it is somewhat lower than expected from this simple model. For the reaction of many light nonmethane hydrocarbons (NMHC), especially of unsaturated hydrocarbons, with OH-radicals the KIEs are sufficiently large to have significant impact on the isotopic composition of atmospheric NMHC. A small series of stable carbon isotope ratio measurements of atmospheric NMHC were made in the greater Toronto area. Traffic related NMHC emissions were also studied for their stable carbon isotope ratios. From these data it is possible to quantitatively determine the extent of photochemical processing due to OH-radical reactions that the individual NMHC has experienced. Thus such measurements allow quantitative evaluation of the extent of chemical processing the different NMHC have gone through. This also includes the possibility to differentiate between the impact of local sources and regional or large scale transport. It is shown that in combination with concentration measurements isotope ratio measurements are extremely valuable to study the complex interaction between chemical removal mechanisms, mixing, and dilution processes.

1. Introduction

During the last years the number of studies of nonmethane hydrocarbons (NMHC) in the troposphere has increased rapidly. These studies range from polluted, urban to pristine, remote areas [cf. *Rudolph and Koppmann*, 1998; *Rudolph and Khedim*, 1985; *Rudolph and Johnen*, 1990; *Rudolph et al.*, 1992a, 1992b; *Jobson et al.*, 1994a, 1994b; *Koppmann et al.*, 1998; *Goldan et al.*, 1995; *Greenberg and Zimmerman*, 1984; *Hov et al.*, 1989; *Bonsang et al.*, 1990; *Koppmann et al.*, 1992; *Blake et al.*, 1997; *Gong and Demerjian*, 1997; *Young et al.*, 1997; *Blake et al.*, 1999]. They include such diverse regions as tropical rain forests, polar regions, open oceans, and boreal wetlands [cf. *Jobson et al.*, 1994b; *Koppmann et al.*, 1998; *Greenberg and Zimmerman*, 1984; *Greenberg et al.*, 1985; *Bonsang et al.*, 1987; *Greenberg et al.*, 1990, 1992; *Bonsang et al.*, 1990; *Rudolph and Johnen*, 1990; *Bonsang et al.*, 1991; *Rudolph et al.*, 1992a; *Rudolph et al.*, 1992b;; *Rudolph*, 1995; *Rudolph et al.*, 1995; *Koppmann et al.*, 1997] as well as areas that are strongly affected by civilization-related emissions [cf. *Goldan et al., 1995; Rudolph and Khedim*, 1985; *Elliott et al.*, 1997; *Kramp and Volz-Thomas*, 1997]. The studies of the atmospheric sources, sinks, and temporal and spatial distributions of NMHC are motivated by two different, although not necessarily separate, questions. First, such investigations are needed to better understand the role of NMHC for the chemistry of the atmosphere [cf. *Chameides and Cicerone*, 1978; *Singh et al.*, 1981; *Ehhalt and Rudolph*, 1984; *Singh and Kasting*, 1986; *Chatfield et al.*, 1987; *Chameides et al.*, 1988; *Volz-Thomas and Kolahgar, 2000*]. NMHC are important precursors for atmospheric oxidants, including ozone, and peroxides, as well as other secondary pollutants such as aldehydes and organic nitrates. Furthermore, they influence the concentrations of HO_x - radicals (OH and HO_2) and thus impact on oxidizing capacity of the atmosphere. Second, measurements of NMHC have successfully been used to study important atmospheric mechanisms [*McKeen and Liu*, 1993; *Rudolph and Koppmann*, 1998; *Roberts et al.*, 1984; *Parrish et al.*, 1992; *Volz-Thomas and Kolahgar*, 2000; *Penkett et al.*, 1993; *Kramp et al.*, 1994; *Ehhalt*, 1994; *Jobson et al.*, 1994b; *Lindskog and Moldanova*, 1994; *Mckenna et al.*, 1995; *McKeen et al.*, 1996; *Rudolph et al.*, 1996; *Ehhalt et al.*, 1997; *Ramacher et al.*, 1997; *Rudolph et al.*, 1997a; *Jobson et al.*, 1998; *Ehhalt et al.*, 1998; *Ramacher et*

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al., 1999; *Kramp and Volz-Thomas*, 1997]. For example, they were used to estimate OH-radical concentrations, identify and quantify other oxidizing constituents in the troposphere such as Cl- and Br- atoms, and characterize transport and mixing processes.

A new promising tool to further improve the usefulness of NMHC measurements and advance our understanding of atmospheric chemistry is the analysis of the isotope composition of NMHC. Stable isotope ratio measurements have been extremely valuable to improve the understanding of a variety of important atmospheric trace gases, for example, ozone, carbon monoxide and dioxide, nitrous oxide, methane, and hydrogen [*Lowe et al.*, 1994; *Conny and Currie*, 1996; *Conny et al.*, 1997; *Manning et al.*, 1997; *Brenninkmeijer and Röckmann*, 1997; *Manning*, 1999; *Lowe et al.*, 1999]. In the past, however, stable isotope ratio measurements in the atmosphere have been limited to more abundant trace gases with mixing ratios of at least several 10 ppb. Only very recently have suitable techniques to study the stable carbon isotope composition of atmospheric NMHC been developed [*Rudolph et al.*, 1997b] and applied to ambient studies [*Rudolph et al.*, 1997b; *Tsunogai et al.*, 1999]. Although presently the number of measurements is still extremely limited, it is already evident that such measurements are very promising to obtain deeper insight into the sources and sinks as well as transport and mixing processes relevant for atmospheric NMHC. Comparable to the need of knowing rate constants and source strength for the interpretation and modeling of hydrocarbon mixing ratios, equivalent information is needed to interpret stable isotope ratio measurements of atmospheric NMHC. Specifically, the isotopic compositions of the sources as well as the isotopic fractionation occurring during atmospheric removal reactions have to be determined.

In this paper we will present results from measurements of the kinetic isotope effect (KIE) associated with the reaction of several hydrocarbons with OH-radicals, by far the most important removal process for NMHC in the atmosphere. Results from a small series of ambient measurements of NMHC concentrations and stable carbon isotope ratios in the greater Toronto area also will be presented. These include some limited studies of the isotopic composition of traffic-related emissions. On the basis of these results and the few published observations of stable carbon isotope ratios in atmospheric NMHC, we will explore the usefulness of the technique and identify missing knowledge needed to use the full potential of stable isotope ratio measurements for atmospheric NMHC.

2. Experiment

The kinetic studies were conducted in a PTFE reaction chamber (0.5 mm wall thickness) of approximately 30 L in volume. The reactions of 11 different NMHC with OH radicals were studied in synthetic air at ambient pressure. OH-radicals were generated by photolysis of isopropyl nitrite (1000 ppm) in the presence of ppm levels of NO. Generally, three hydrocarbons of comparable reactivity were studied in each experiment, of which 10 experiments in total were conducted. The studied hydrocarbons and their initial concentrations for the different experiments are listed in Table 1. The change of hydrocarbon concentration and stable carbon isotope ratio as a function of time was measured by isotope ratio mass spectrometry in

Table 1. Measurements of the Kinetic Isotope Fractionation Effect for the Reaction of Selected NMHC With OH-Radicals.

Hydrocarbon	Initial Concentration, ppm	KIE, ‰	Error, ‰	Relative. Error, %	*R*
Propane	331	3.39	0.19	5.6	0.9887
Propane	255	4.04	0.38	9.4	0.9833
Propane	285	3.38	0.17	5.0	0.9904
Propane	90	2.96	0.27	9.1	0.9729
n-Butane	254	3.14	0.11	3.5	0.9960
n-Butane	299	3.00	0.21	7.0	0.9903
n-Butane	63	2.46	0.22	8.9	0.9698
n-Butane	171	2.76	0.20	7.2	0.9820
n-Hexane	8.5	2.32	0.13	5.6	0.8872
n-Hexane	48	1.43	0.60	42.0	0.6696
n-Hexane	85	0.48	0.34	70.8	0.5790
n-Hexane	54	7.14	11.00	154.1	0.2404
Propene	101	11.80	0.28	2.4	0.9984
Propene	107	11.40	0.32	2.8	0.9981
Propene	267	11.90	0.31	2.6	0.9983
1-Butene	82	7.46	0.49	6.6	0.9874
1-Butene	210	6.93	0.28	4.0	0.9960
1-Butene	233	7.82	0.32	4.1	0.9960
1-Hexene	87	5.08	0.14	2.8	0.9978
1-Hexene	65	4.72	0.19	4.0	0.9961
1-Hexene	67	5.86	0.47	8.0	0.9845
(z)-2-Butene	99	9.34	1.98	21.2	0.9054
1,3-Butadiene	62	7.55	0.88	11.7	0.9681
Isoprene	24	8.23	0.97	11.8	0.9552
Isoprene	36	6.18	0.22	3.6	0.9955
Isoprene	320	6.40	0.24	3.8	0.9973
Ethyne	181	15.80	0.61	3.9	0.9957
Benzene	37	9.08	0.56	6.2	0.9874
Benzene	33	9.43	0.58	6.2	0.9928
Benzene	56	7.59	0.20	2.6	0.9973
Benzene	40	6.43	0.37	5.8	0.9889

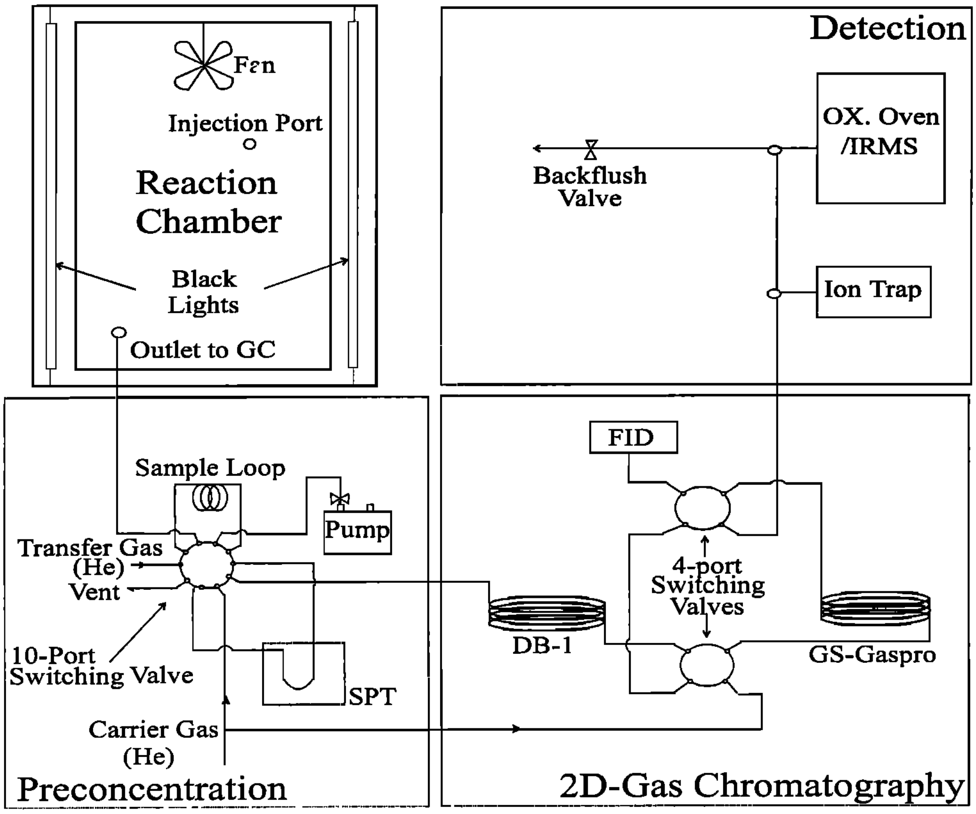

Figure 1. Schematic drawing of the experimental setup for measurements of kinetic isotope effects of reactions of NMHC with OH-radicals.

combination with a gas chromatographic separation and a combustion interface (GCC-IRMS). A schematic set up of the experiment is shown in Figure 1.

The reaction chamber was housed in a rectangular box with an approximate dimension of 1.3 m x0.5 m x0.3 m. The box contained four fluorescent lamps ("black lights") emitting in the wavelength range from 320 to 400 nm. The number of lights and the period of time during which they were turned on between measurements depended on the desired OH-radical concentration and reaction time. The temperature in the box was measured, but not controlled. Owing to the heat generated by the fluorescent lights inside the box, the temperature of the reaction chamber was for some experiments between 10 K and 15 K above ambient. An electric fan of 10 cm diameter was placed inside the reaction chamber to ensure complete mixing during the experiments.

Prior to each experiment the reaction chamber was flushed with synthetic air for at least 24 hours at a flow rate of 100 mL/min with the lights in the box turned on. After turning off the lights, the reaction chamber was filled with synthetic air, and appropriate amounts of pure hydrocarbons were injected into the reaction chamber through a septum (injection port, Figure 1) to produce hydrocarbon mixtures with the desired concentrations. The hydrocarbons were obtained from Sigma Aldrich Canada Ltd.

NO was added in the form of a commercial mixture containing 1% NO in nitrogen. Isopropyl nitrite was synthesized by the procedure described by *Levin and Hartung* [1995] and injected as a pure liquid through the injection port. For all experiments the initial isopropyl nitrite concentration was approximately 1000 ppm.

At least one sample was taken from the reaction chamber and analyzed by GCC-IRMS before starting the reaction by turning on the lights in the reaction box. During the course of an experiment, samples were taken and analyzed at intervals of about 1 hour. Air from the reaction chamber was transferred via a 3 mm PTFE transfer line to a 0.5 mL sample loop using a small pump downstream of the sample loop (see Figure 1). The transfer line and sample loop were flushed with 50-100 cm^3 of reaction chamber air before each measurement. The samples were then transferred by a helium flow of 15 mL/min from the sample loop to a Varian Sample Preconcentrator Trap (SPT) for cryogenic focussing at 113 K. After rotating the 10 port switching valve (Figure 1), the samples were injected onto the separation columns by rapidly (about 40 K/s) heating the SPT to 473 K.

The gas chromatograph (Varian 3600) was equipped with a DB-1 wall coated capillary column (60 m, 0.32 mm ID, 1μm film thickness) and a GS-GasPro porous layer open tubular column (60 m, 0.32 mm ID) in a configuration that allowed selective transfer between the columns and two-dimensional separation for the analysis of complex mixtures. For the few components in the samples analyzed in the kinetic studies, optimized temperature programs without selective sample transfer were used. This allowed efficient separation of all relevant compounds. Carrier gas flow rate was 3.9 mL/min (He). Flow rate was kept constant by varying the column head pressure as a function of column temperature using a commercial electronic pressure control unit.

About 0.3 mL/min of the column effluent were transferred via a deactivated fused silica capillary to an Ion Trap mass spectrometer for peak identification and verification of peak purity. The remainder of the carrier gas flow entered a commercial (Finnigan MAT) combustion interface that converts hydrocarbons to carbon dioxide and water. The design of the interface is very similar to that described by *Matthews and Hayes* [1978]. After removal of water by a Nafion ® permeation dryer, about 0.5 mL/min of the carrier gas is transferred via an open split and a fused silica restriction capillary to the ion source of the isotope ratio mass spectrometer (Finnigan MAT 252). For calibration of the isotope ratio measurements a reference gas containing carbon dioxide with a known $^{13}C/^{12}C$ ratio was added via an open split for 20 s at the beginning and end of each analysis. Masses 44 ($^{12}C^{16}O_2$), 45 ($^{13}C^{16}O_2$ and $^{12}C^{17}O^{16}O$), and 46 ($^{12}C^{18}O^{16}O$) were monitored and stored in digitized form for subsequent evaluation of the chromatograms.

The areas of the chromatographic peaks for masses 44, 45, and 46 were determined using a commercial software package (ISODAT). Peak boundaries and baselines were defined manually. The $^{13}C/^{12}C$ ratio was calculated from the mass 45/44 ratio after applying a small correction for the ^{17}O contribution to mass 45 following the procedure suggested by *Craig* [1957]. The concentrations of the hydrocarbons were determined from the areas of the mass 44 peak. They were calculated relative to the first measurement of the experiment. The reproducibility of the isotope ratio measurements is estimated to about 0.3‰. The relative uncertainty of the mass 44 concentration measurements is about 2-3%.

In addition to the laboratory studies, 15 measurements of stable carbon isotope ratios and concentrations of atmospheric NMHC were made at York University on June 21 and 22, 1999. York University is located about 20 km northwest of downtown Toronto in a suburban, mixed industrial/residential area. Details about the sampling location and its characterization are described by *McLaren et al.* [1996]. The air samples were pressurized (about 3 bar) into stainless steel canisters of 3 L volume and then transferred to the laboratory for analysis. The setup for ambient stable carbon isotope ratio measurements was very similar to the procedure described above. The main difference was the use of a two-step preconcentration procedure very similar to that described by *Rudolph et al.* [1997b] to allow analysis of larger sample volumes, typically between 2000 and 5000 cm^3. The samples were also analyzed for NMHC mixing ratios by established GC-FID methods, closely following the procedure described by *McLaren et al.* [1996] and *Rudolph* [1999].

Furthermore, 15 samples were collected at different sites heavily impacted by traffic related emissions. These sites included a downtown Toronto tunnel, a gas station, and an underground parking garage. These samples were analyzed by the same procedure used for the York University samples, with smaller sample volumes used for analysis, generally a few hundred cubic centimeters. The reproducibility of the ambient isotope ratio measurements is in the range of 0.3-1‰, while the reproducibility of the mixing ratio analysis is about 5%, its accuracy 10-15%. The carbon dioxide used for calibration of the isotope ratio measurements is traceable to Peedee belemnite, the internationally accepted reference point for $^{13}C/^{12}C$ ratio measurements with an estimated accuracy better than 0.1‰. All isotope ratio measurements presented here are relative to this internationally established Peedee belemnite scale.

Stable isotope ratios are generally measured and calculated in the form of relative differences between the sample and a reference standard (δ notation). Since changes in isotopic composition are generally small, they usually are given in permil

$$\delta\ (‰) = (c_{13}/c_{12} - {}^{ref}c_{13}/{}^{ref}c_{12})/({}^{ref}c_{13}/{}^{ref}c_{12}) \mathrm{x} 1000. \qquad (1)$$

Here c_{13} and c_{12} denote the abundance of different isotopes in the studied compound, and ${}^{ref}c$ is the reference standard. As mentioned above, we use a standard that is traceable to Peedee belemnite, but it should be noted that the actual reference point is of little importance for the KIE determinations since the method we use only requires exact determination of the changes in δ^{13C} values.

Our measurements of the KIEs for reaction of hydrocarbons with OH-radicals are essentially relative rate constant measurements. Only relative isotopic compositions can be determined with sufficient accuracy to observe the small changes associated with KIEs. Consequently, the procedure has to be adapted to the specific problem. A plot of the following form

$$\ln\ ({}^{12}c_t/{}^{12}c_0) = k_{12}/k_{13}\ /(1 - k_{12}/k_{13})\ \ln\ [({}^{13}c_t/{}^{12}c_t)\ /\ ({}^{13}c_0/{}^{12}c_0)] \qquad (2)$$

results in a straight line with a slope of $k_{12}/k_{13}\ /(1 - k_{12}/k_{13})$. This allows the calculation of the fractionation factor α, the ratio of the rate constants of only ^{12}C containing molecules (k_{12}) over that of molecules containing a ^{13}C atom (k_{13}) from the slope of a plot according to equation (2). The concentrations c_0 and c_t refer to time zero and t, respectively.

Strictly speaking, a plot according to equation (2) might result in a slightly curved line. The use of equation (2) assumes that the measured δ^{13C} value represents the isotopic composition of the reacting carbon atom. However, very often the reaction of NMHC with OH-radicals primarily occurs at specific carbon atoms. For example, the reaction of propane with OH-radicals preferentially occurs via abstraction of a hydrogen atom from the secondary carbon atom, and the addition of OH radicals to propene preferentially happens at the 1-carbon atom. Since our isotope ratio measurements only determine the average composition of the molecule, we do not know the actual ^{12}C depletion for the reactive site. We can estimate an upper limit for this if we assume that the OH reactions only occur at one specific carbon atom. In this case for a molecule with n carbon atoms the depletion of ^{12}C (δ_{pref}) for the preferred C-atom can be calculated according to

$$\delta_{pref} = (\delta_t - \delta_0)\ n. \qquad (3)$$

Consequently, our measurements might systematically underestimate the actual depletion in ^{12}C atoms for all hydrocarbons with n>1. However, in our experiments the overall change in the stable carbon isotope ratio was always below 20‰, and in most cases below 10‰. Consequently, we can expect that the relative change in the $^{13}C/^{12}C$ ratio of the reacting carbon atom, and thus of the experimentally derived KIE, will at most be in the range of 1% to 7%. Furthermore, this represents an upper limit since very seldom do the reactions of OH-radicals with NMHC occur only at one specific C-atom. Thus, generally, this change is well below the uncertainty of our measurements. Still, such an effect might be visible in the case of compounds with large KIEs, high reactivity, and high accuracy of the measurements. Indeed, if we calculate the KIE for the reaction of propene with OH-radicals from our measurements for different ranges of δ_t, we find a small but statistically significant difference. For the range of δ^{13C} from 0‰ to 6‰ we find a KIE of 12.44 ± 0.17‰; for the range from 10-19‰ it is of 11.53 ± 0.11‰. Although the difference is statistically significant, both values are sufficiently close to the average KIE of 11.7 ± 0.19‰ to justify the use of an average KIE. For the other hydrocarbons studied these effects are even smaller, generally lower than the statistical uncertainties of the KIEs. Consequently, we decided to use average KIEs without correcting for fractionation effects occurring at specific carbon atoms of the studied molecules.

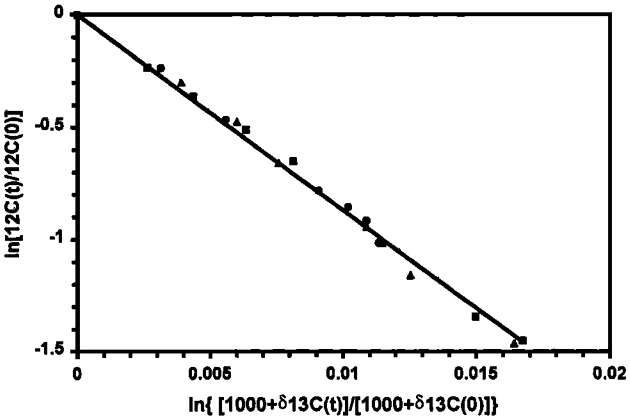

Figure 2. Plot of ln (12ct/12c0) versus ln {[1000+δ13Ct]/1000+ δ13C0]}, which is equivalent to ln [(13ct/12ct) / (13c0/12c0)], for propene. The different symbols (squares, circles, and triangles), represent the results from three different experiments. Also shown is a linear least squares fit to the data.

KIEs are generally very small, and thus the fractionation factors will be close to one and similar to the isotopic composition they can be conveniently expressed as a relative difference (${}^{OH}\delta_{KIE}$) in permil. In this paper the KIEs will be presented in the following form as delta values in permil:

$$ {}^{OH}\delta_{KIE}\ (\text{‰}) = ({}^{OH}k_{12}/{}^{OH}k_{13} - 1) \times 1000. \qquad (4) $$

3. Results of KIE Measurements

An example of a linear plot of the dependence between concentration and stable carbon isotope ratio according to equation (2) is shown in Figure 2. The results of the KIE measurements are listed in Table 1. Also given are their uncertainties and the regression coefficients for linear least square fits to equation (2). With the exception of n-hexane and (Z)-2-butene the regression coefficients are higher than 0.989 (R^2>0.978), and the error of the KIE measurements is below 1‰. The average error is around 0.5‰. The relative uncertainties are lower than 12%, on average 6%. Only the uncertainties for hexane and (Z)-2-butene are higher. For hexane the high uncertainty is due to the small KIE; a change in concentration of an order of magnitude is only associated with a change in isotope composition of approximately 3‰. The somewhat high error of the (Z)-2-butene KIE is the consequence of only a small change in concentration during the experiment. The maximum change in concentration was less than 60%; the corresponding change in isotopic composition was less than 4‰.

In Table 2 the average KIEs, their standard deviations, and the 95% confidence intervals are summarized. The KIEs for n-hexane and (Z)-2-butene have substantial uncertainties. For all other compounds the error of the mean is less than 1‰, and the relative uncertainty is below 12%. The 95% confidence intervals cover a range from less than 1‰ to around 2.5‰. In view of the range of the measured KIEs from roughly 1‰ to nearly 16‰ it is evident that by far the largest part of the observed variations are well above the uncertainty of the measurements.

All observed KIEs are normal isotope effects; that is, molecules containing only ^{12}C react faster than those containing a ^{13}C atom. For statistical reasons (see below), within a homologous series such as the n-alkanes or the 1-alkenes the isotope fractionation effect is expected to decrease with increasing carbon number. For n-alkanes the KIEs are only a few permil or less. For all n-alkanes studied the KIE is significantly below that of methane (5.4 ± 0.9‰ [*Cantrell et al.*, 1990]. The KIEs for the studied unsaturated substances are substantially higher than for saturated NMHC. On average, the different unsaturated hydrocarbons have KIEs about a factor of 3 higher than that of the saturated NMHC with the same carbon number, although there are also indications for a dependence of the KIE on details of the chemical structure of the unsaturated hydrocarbon (see below).

To our knowledge, there are no other studies of the KIE for reaction of NMHC with OH-radicals. However, there is one indirect estimate of the KIE for the reaction of ethane with OH-radicals based on atmospheric measurements of the stable carbon isotope composition of ethane [*Tsunogai et al.*, 1999]. On the basis of the assumption that the dependence between concentration and isotopic composition of atmospheric ethane can be described by a Rayleigh fractionation, they estimate that the fractionation factor for the reaction of ethane with OH-radicals is 1.003 ± 0.001 corresponding to a δ_{KIE} value of 3 ± 1‰. This is about half the KIE reported for the reaction of methane and OH-radicals [*Cantrell et al.*, 1990]. *Tsunogai et al.* [1999] argue that this is in agreement with the expectation that the KIE for a

Table 2. Statistics of the Kinetic Isotope Effect Measurements for the Reaction of NMHC With OH-radicals

Compound	Average KIE, ‰	Error of Mean, ‰	Relative Error, %	95% Confidence Interval, ‰	k_{OH}, 10^{-12} cm^3 Molecule^{-1} s^{-1} [a]
Propane	3.44	0.26	7.5	3.00-3.88	1.12
n-Butane	2.84	0.17	6.1	2.55-3.13	2.44
Hexane[b]	1.41	0.92	65.2	0.49-2.33	5.45
Propene	11.70	0.19	1.6	11.39-12.01	26.3
1-Butene	7.40	0.32	4.3	6.89-7.91	31.4
1-Hexene	5.22	0.41	7.9	4.56-5.88	37
(z)-2-Butene[c]	9.34	1.98	21.2		56.4
1,3-Butadiene[c]	7.55	0.88	11.7		66.6
Isoprene	6.94	0.80	11.5	5.67-8.21	101
Ethyne[c]	15.80	0.61	3.9		0.9
Benzene	8.13	0.80	9.8	6.77-9.49	1.2

[a] From *Atkinson* [1997, 1994].

[b] Results of last measurement in Table 1 not included due to extreme uncertainty.

[c] Confidence interval can not be calculated since results are only available for a single experiment.

compound containing two carbon atoms is, due to statistical reasons, half of the effect for a hydrocarbon with only one carbon atom. We did not measure the KIE for ethane, but we can compare the estimate of *Tsunogai et al.* [1999] with our measurements for other n-alkanes. Our measurements of the KIEs for propane and butane give values of 3.4 ± 0.4‰ and 2.8 ± 0.3‰, respectively. Considering the expected decrease of the KIE with increasing carbon number, this suggests that the estimate of *Tsunogai et al.* [1999] is somewhat low. One of the reasons for the underestimation may be that the use of the Rayleigh equation to describe the dependence between concentration and isotopic composition in the atmosphere is a simplification that might result in an underestimation of the KIE (J. Rudolph and E. Czuba, On the use of isotopic composition measurements of volatile organic compounds to determine the "photochemical age" of an air mass, submitted to *Geophysical Research Letters*, 2000, hereinafter referred to as Rudolph and Czuba, submitted manuscript, 2000). As shown below, a purely statistical dependence of the KIE on carbon number is not sufficient to reconcile our measured KIEs for n-alkanes with the KIE for methane published by *Cantrell et al.* [1990].

4. Chemical Structure and KIE

We studied 11 different hydrocarbons. Measurements of hydrocarbons in urban and semiurban areas have shown that the number of hydrocarbons present at significant levels is very high [*Chameides and Cicerone*, 1978; *Chameides et al.*, 1988; *Elliott et al.*, 1997]. Even in rural and remote areas some 30-50 different hydrocarbons are frequently observed [*Greenberg and Zimmerman*, 1984; *Rudolph and Khedim*, 1985; *Rudolph et al.*, 1986; *Bonsang et al.*, 1987; *Greenberg et al.*, 1990, 1992; *Koppmann et al.*, 1992; *Young et al.*, 1997; *Blake et al.*, 1999].

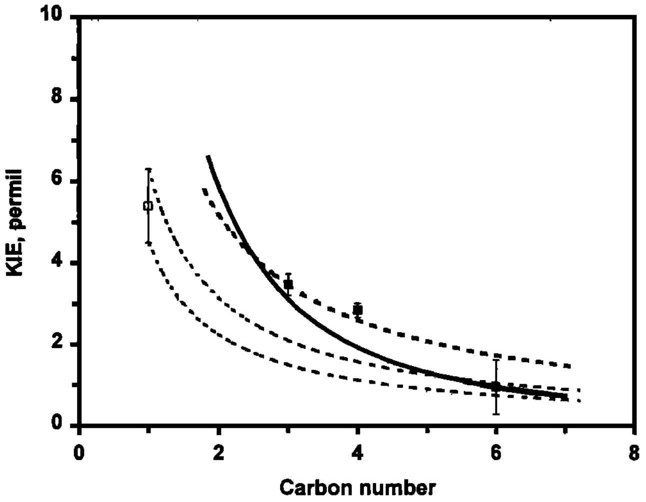

Figure 3. Kinetic isotope effect (KIE) for the reaction of alkanes with OH-radicals as function of carbon number. Solid squares: n-alkanes (this work), open square: methane [*Cantrell et al.*, 1990]. The solid line gives the theoretical dependence based on the assumption that the KIE is determined by the mass dependence of the collision frequency alone. The two thin dashed lines indicate the range that would be expected if the KIE for the abstraction of a hydrogen atom from n-alkanes is identical to the KIE reported for the reaction of methane with OH-radicals. The thick dashed line is calculated for an KIE of 10‰ for the abstraction of an H-atom from a carbon atom by OH-radicals and an inverse dependence of the KIE on carbon number.

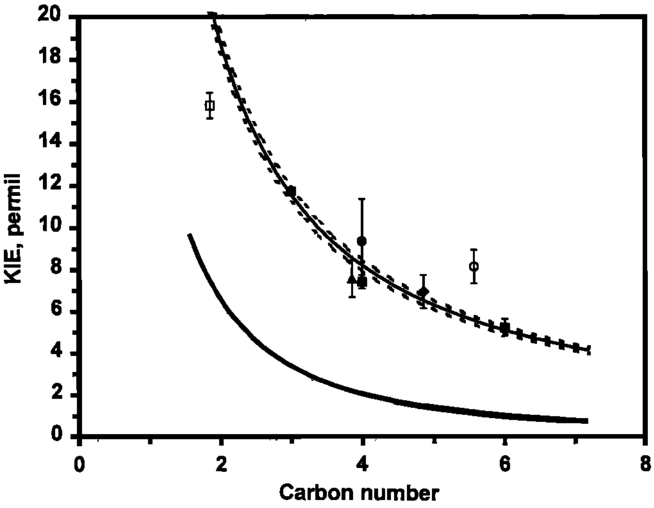

Figure 4. Kinetic isotope effect (KIE) for the reaction of alkenes with OH-radicals as function of carbon number. Solid squares: 1-Alkenes, solid circle: (z)-2-Butene, triangle: 1,3-Butadiene, diamond: isoprene, open square: ethyne, open circle: benzene. Also shown is the KIE due to the mass dependence of the collision frequency only (thick line) and the total KIE including a fractionation of 24.5 ± 1.1‰ for the addition of an OH-radical to a double bond (thin solid line). The dashed thin lines show the ± 1σ uncertainty range of this fit. In order to allow the correct representation of the mass-dependent collision frequency, the plot uses a modified carbon number that is calculated by dividing the molecular weight by 14.

The available KIE measurements for the reactions of hydrocarbons with OH-radicals presently cover only a small fraction of these various NMHC. However, there are systematic dependencies between chemical structure and KIE that can be very useful to estimate KIEs for reactions that have not been studied. Owing to the still very limited number of available data, such estimates will have considerable uncertainties. Nevertheless, they will be extremely valuable for the interpretation of ambient observations, planning of atmospheric studies, and model calculations of stable carbon isotope ratios in NMHC.

As mentioned above, within a homologous series of hydrocarbons KIEs for reaction with OH-radicals show significant decrease with increasing carbon number (Table 2 and Figures 3 and 4). Such a decrease is expected due to statistical reasons. Only about 1% of all carbon atoms has an atomic mass of 13. The probability that more than one carbon atom in a small molecule is a 13-C atom is therefore negligible. Thus the probability that the carbon atom that is attacked by the OH-radical is a carbon 13 atom instead of carbon 12 is inversely proportional to the number of carbon atoms of the studied molecule. This theoretical dependence is shown in Figure 3 for n-alkanes based on the assumption that the KIE for each carbon atom in the n-alkanes is identical to that reported by *Cantrell et al.* [1990] for the reaction of methane with OH-radicals. Our measured KIEs for propane and n-butane are roughly a factor of two higher than expected from such a prediction. This is outside of the uncertainty of the measurements. Obviously, the results for propane and n-butane do not agree with the concept that the KIE for the reaction of alkanes with OH-radicals can be calculated from the KIE for methane based on statistical considerations only. For n-hexane the difference is not significant, but this is the consequence of the large uncertainty of the measured KIE.

One possible explanation for the disagreement is a dependence of the KIE on the degree of substitution of the carbon atoms. We can describe our observations by the assumption of a fractionation of 10.0‰ ± 2.2‰ for the abstraction of a hydrogen atom from a secondary carbon atom and the expected inverse dependence on number of carbon atoms (Figure 3). However, our data also fully agree with the idea that KIEs for reaction of n-alkanes with OH-radicals are predominantly due to the mass dependence of the collision frequency between n-alkanes and OH-radicals (Figure 3). Although our data still leave some room for fractionation effects that are not due to the mass dependence of the collision frequency, such effects most likely are quite small. For example, the difference between measured and calculated KIE for n-butane is compatible with an additional fractionation effect of around 0.8–1.2‰. The values for propane and n-hexane suggest that such an effect might even be lower. These small fractionation effects suggest that in the transition state the strength of the C-H bond of the abstracted hydrogen atom is only slightly decreased relative to the educt. This is compatible with apparent activation energies close to zero or below zero for hydrogen abstraction by OH for the alkanes we studied [*Atkinson*, 1997]. Furthermore, the reaction of alkanes with OH radicals occurs via OH attack at the hydrogen atom, that is a C-H-OH transition state. Strictly speaking, the influence of the atomic mass of the carbon atom on this reaction rate is a secondary isotope effect. Secondary isotope effects are generally small and are fully consistent with our observations.

For the studied alkanes, hydrogen atom abstraction occurs primarily from the secondary carbon atoms. Because of the limited amount of data, we presently cannot decide whether the KIEs for other alkanes will exhibit a similar carbon number dependence. Extrapolation of our results suggests that the KIE for reaction of ethane with OH-radicals is around 6‰. However, the activation energy, that is substantial is about half the activation energy for the reaction of methane with OH-radicals. Furthermore, ethane has only primary carbon atoms. An extrapolation of our results to all alkanes based on the assumption that the KIE is dominated by the mass dependence of the collision frequency therefore is highly uncertain. If the KIE for hydrogen abstraction by OH-radicals from a primary carbon atom is between those for secondary carbon atoms and isolated carbon atoms (methane), we would expect the KIE for ethane plus OH to be somewhat lower than 6‰, probably in the range of 4-5‰.

The higher KIEs for the reaction of unsaturated compounds with OH-radicals cannot be explained by predominantly collision frequency dependent KIEs (Figure 4). The measured KIEs are between 4‰ and 9‰ higher than calculated from the mass dependence of the collision frequencies alone. These differences can be described by assuming a fractionation of 24.5 ± 1.1‰ for the addition of a hydroxyl radical to a C-C double bond and an inverse dependence of this KIE on the number of carbon atoms. It can be seen from Figure 4 that the combined effects describe the observations very well. Both for alkenes and dienes the calculated values agree with the experimental data within the uncertainty of the measurements. The KIE for addition of OH to a double bond can qualitatively be explained by the lower frequency of the ^{13}C-O vibration frequency compared to that for ^{12}C-O in the transition state of the OH addition reaction. This results in a lower zero point energy of the ^{13}C containing transition state and consequently lower activation energies for the formation of the transition state. Since the activation energies for the addition of OH-radicals to a double bond are negative [cf. *Atkinson*, 1997], lower activation energies will result in less efficient formation of the transition state.

The assumptions of an inverse carbon number dependence of the KIEs neglects the possible influence of secondary isotope fractionation effects. Depending on chemical structure, secondary isotope effects may involve more than one carbon atom and consequently this effect would decrease less rapidly with increasing carbon number. For the addition of an OH-radical to a C-C double bond we expect that in the transition state the strength of the double bond is diminished, corresponding to a change in vibration frequencies. This will result in an isotope effect if any of the two C-atoms forming the double bond is a 13-C atom. Similarly, for conjugated double bonds or aromatic systems addition of an OH-radical most likely will affect the bond strength between several carbon atoms. Obviously, such secondary isotope effects cannot be described by the inverse carbon number dependence. However, as mentioned above, secondary isotope effects generally are small. Nevertheless, they may be one of the reasons for the deviations between experimental observations and the inverse carbon number dependence shown in Figure 4. Especially for ethyne and benzene the KIEs are somewhat different from those expected for alkenes with identical mass and carbon number. However, a different strength of the C-O bond in the transition state or the high symmetry of the ethyne and benzene molecules can also influence the KIEs. The lack of any other studies of KIEs for reactions of aromatic substances or alkynes with OH-radicals prevents the conclusion as to these differences can be generalized for the homologues of ethyne and benzene.

The stable carbon isotope ratios in the atmosphere are determined by a variety of processes, for example, removal reactions associated with isotope fractionation, transport, and mixing of air masses, or sources with different δ^{13C} values. These factors are essentially equivalent to those that determine the atmospheric mixing ratios of hydrocarbons. The change in stable isotope ratios is a function of the average extent of photochemical processing of the studied compound and the KIE associated with the removal process, but independent of the mixing processes that resulted in a given average photochemical age (Rudolph and Czuba, submitted manuscript, 2000). This is based on the assumption of an isotopic composition of the sources that does not vary or is sufficiently well averaged to justify treatment as constant. This simplifies the interpretation of atmospheric observations of stable carbon isotope ratios in NMHC, but still requires knowledge of a representative value for the isotopic source compositions.

Unfortunately, the number of published measurements of δ^{13C} in atmospheric NMHC is extremely small. *Rudolph et al.* [1997b] published the first compound specific measurements of the 13C/12C ratio in atmospheric NMHC. They determined δ^{13C} values for light NMHC in a small set of samples from the Southern Hemisphere. More recently, *Tsunogai et al.* [1999] reported several measurements of δ^{13C} values for selected C_2-C_5 hydrocarbons in an urban, coastal, and marine atmosphere of the Northern Hemisphere. Owing to the lack of measured KIEs for reaction of NMHC with OH, they estimated KIEs based on the published literature value for methane and the assumption of an inverse carbon number dependence (see above). As pointed out, this results in a potential underestimation of the KIE.

There are two published studies of isotopic composition of NMHC sources: one study of biomass burning emissions and one tunnel study [*Rudolph et al.*, 1997b]. Thus we have to rely on ambient measurements in areas strongly impacted by local sources to obtain some estimate of isotopic compositions of NMHC emissions. Table 3 summarizes the range of isotopic compositions observed in urban air masses by *Tsunogai et al.* [1999], the tunnel measurements of *Rudolph et al.* [1997b]. For comparison, isotopic composition measurements of NMHC emitted from burning C-3 plant material [*Rudolph et al.*, 1997b] are also included. Some information is available on the isotopic composition of natural and petroleum gas. Although these are

Table 3. Overview of Published Isotopic Composition Studies of NMHC Strongly Impacted by Local NMHC Emissions

Compound	Range Urban Air [*Tsunugai et al.*, 1999], ‰	Tunnel Study[*Rudolph et al.*, 1997], ‰	Biomass Burning [*Rudolph et al.* 1997], ‰
Ethane	- 25 to - 28	- 31.3	- 28.7
Propane	- 27 to - 30	- 24.4	- 27.7
n-Butane	- 26 to - 30	- 25.7	- 25.4
i-Butane	- 24 to - 33	-27.6	- 30.3
n-Pentane	- 24 to - 25		- 28.0
i-Pentane	- 25 to - 26		- 26.6
Ethene	- 12 to - 22	-25.9	- 24.4
Propene	- 19 to - 25	-23.1	- 25.2
Acetylene	- 5 to - 12		- 13.0

not direct emission studies, they allow some tentative estimate of the composition of natural gas losses. For ethane in natural gas the data cover quite a substantial range; *Fuex* [1977] reports a range from - 37‰ to - 32‰; *Jenden and Kaplan* [1986] report a range of - 34.5‰ to - 26.6‰. The range for C_3 and C_4 alkanes is considerably smaller, - 30‰ to - 28‰ [*Fuex*, 1977]. These values are very similar to the urban values and source compositions listed in Table 3.

For alkanes the δ^{13C} measurements in urban areas generally give values that fall into the range of the isotopic composition of fossil fuels, compatible with the concept that usage and incomplete combustion of fossil fuels is the dominant source for NMHC in urban air. Moreover, they fall into quite a narrow range, with only a few values slightly outside a ± 1.5‰ range. This is compatible with the relatively low isotope fractionation for the reactions of alkanes with OH-radicals, their low reactivity and observations close to the emission sites.

For a hydrocarbon that primarily is removed from the atmosphere by reaction with OH-radicals the change in isotopic composition relative to the source composition can be calculated according to the following equation (Rudolph and Czuba, submitted manuscript, 2000):

$$\delta_z = (t_{av}\,{}^{OH}k_z\,[OH])\,{}^{OH}\delta_{KIE} + {}^{0}\delta_z \qquad (5)$$

where

δ_z	observed delta ^{13}C value for compound z;
t_{av}	average age of compound z;
[OH]	average OH-radical concentration;
$^{OH}k_z$	rate constant for the reaction of compound z with OH-radicals;
$^{OH}\delta_{KIE}$	kinetic isotope effect for the reaction of com pound z with OH-radicals;
$^{0}\delta_z$	delta ^{13}C value of the emissions of compound z.

The rate constants for C_2-C_4 alkanes with OH-radicals are in the range of 0.25-2.4 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} [cf. *Atkinson*, 1997]. Using our measured KIEs, we can estimate that for typical tropospheric OH-radical concentrations in the range of some 10^6 cm^{-3} [cf. *Prinn et al.*, 1995] it will take at least several hours to cause a change of isotopic composition in n-alkanes that exceed one permil.

The situation is different for ethene and propene. Because of their high reactivity toward OH-radicals [cf. *Atkinson*, 1997] and the large KIEs (see Figure 4), we can expect considerably larger changes in isotopic composition than for light alkanes. For a daytime OH-radical concentration of 4 x 10^6 cm^{-3} we calculate that the change in isotopic composition within 1 hour will be about 2.5‰ for ethene and nearly 6‰ for propene. This can explain both the variability of the ethene and propene $\delta^{13\text{-}C}$ values in urban air and the observation of occasionally significantly enriched $\delta^{13\text{-}C}$ values for the light alkenes [*Tsunogai et al.*, 1999].

The $\delta^{13\text{-}C}$ values for ethyne do not allow such a straightforward explanation. Although the KIE of 15.8‰ for reaction of ethyne with OH-radicals is the largest effect we measured, the reactivity of ethyne toward OH is quite low. Thus either very high OH-radical concentrations or long reaction times are needed to cause significant changes in the δ^{13C} values of ethyne. Nevertheless, the observed urban δ^{13C} values for ethyne are significantly higher than those of the other NMHC and indicate the occurrence of substantial fractionation [*Tsunogai et al.*, 1999]. There are two possible reasons for these high fractionation effects. The measurements of biomass burning emissions indicate that most studied NMHC have a δ^{13C} value in the range of – 25‰ to – 29‰, very similar to the material burnt [*Rudolph et al.*, 1997b]. An exception is ethyne, with - 13‰ its δ^{13C} value is about 12–15‰ heavier than that of the burnt fuel. Although biomass burning is in many ways different from most combustion processes that use fossil fuels, it is conceivable that incomplete combustion in general results in formation of substantially enriched ethyne. Since incomplete combustion is the dominant urban source of ethyne, the relatively high values and the substantial variability observed for the δ^{13C} values of ethyne in urban air might simply reflect the source composition and its variability.

It also has to be considered that, due to the low reactivity of ethyne, its continental background can be in the range of a fraction of a ppb or more. Depending on the magnitude of local emissions, such background levels will contribute a highly variable fraction to urban ethyne levels. Moreover, due to the large KIE for the reaction of ethyne with OH-radicals, we can expect that background ethyne will be substantially enriched in 13-C. Thus variable extent of mixing between recent emissions and aged background ethyne would also result in substantial variations of the δ^{13C} values of ethyne in urban air. Unfortunately, no isotopic composition measurements of ethyne outside urban areas are presently available to quantify the possible impact of the ethyne background.

For the less reactive substances, especially those with high KIEs, we would expect to find changes in isotopic composition primarily at remote locations. Indeed, the δ^{13C} values of –22‰

for ethane and –6.7‰ for propane, reported by *Rudolph et al.* [1997b] for a clean air site (Baring Head, New Zealand) in March 1996, indicate significant enrichment in ^{13}C. These values are about 6‰ and 20‰, respectively, higher than their urban δ^{13C} values (Table 3). For propane the difference is several times the KIE for the reaction with OH-radicals, the main removal process for atmospheric propane. This suggests that the studied air mass has been subject to photochemical processing equivalent to several lifetimes of propane (equation (5)). This is in very good agreement with the conclusion by *Clarkson et al.* [1997] derived from measurements of ethane and propane mixing ratios at Baring Head. They estimated that the transport times from the source regions to Baring Head range around 4-6 weeks. On the basis of equation (5) we can use this estimated transport time, the change in δ^{13C}, the rate constant published by *Atkinson* [1997], and our KIE for the reaction of propane with OH radicals to calculate an average OH radical concentration. With about 1.4 10^6 cm^{-3} the result is reasonable for midlatitude OH-radical concentrations in late summer [cf. *Spivakovsky et al.*, 1990; *Prinn et al.*, 1995]. Thus the low propane mixing ratios and the observed stable carbon isotope ratio of propane at Baring Head are consistent with the idea that chemical removal during transport plays a major role in determining the mixing ratios at remote locations in the Southern Hemisphere.

We did not measure the KIE for the reaction of ethane with OH-radicals. However, if we use a value of 4-5‰ (see above) for the same type of calculation for ethane, we obtain an OH-radical concentration fully consistent with the value derived for propane. *Rudolph et al.* [1997b] also reported one δ^{13C} measurement for ethane in the remote Southern Hemisphere in early winter (July). With - 29.7‰ this value is considerably lighter than the measurement reported for March. Qualitatively, this can be explained by lower OH-radical concentrations in winter than in late summer. However, the observed value is still in the range observed in urban areas (Table 3). This indicates that the amount of photochemical processing in this case is quite small. In other words, transport from the source regions must have been fast compared to the atmospheric residence time of ethane.

It has to be remembered that the dependence between isotopic composition and concentration of atmospheric NMHC is not as simple as the dependence between average photochemical age of a hydrocarbon and change in stable carbon isotope ratio (Rudolph and Czuba, submitted manuscript, 2000). The Rayleigh equation may be written in the following form to describe the dependence between concentration and isotopic composition for an isolated air mass:

$$^{t}\delta_z = \ln(^{0}c_z/^{t}c_z)\ ^{OH}\delta_{KIE} + {}^{0}\delta_z \qquad (6)$$

where

$^{t}\delta_z$	observed delta ^{13}C value of compound z at time t;
$^{0}c_z$	concentration of compound z at t=0;
$^{t}c_z$	concentration of z at time t;
$^{OH}\delta_{KIE}$	kinetic isotope effect for the reaction of compound z with OH-radicals;
$^{0}\delta_z$	delta ^{13}C value of z at time t=0.

As already mentioned, the assumption of an isolated air mass is not necessarily a suitable description of the real atmosphere. Mixing and dilution processes play a major role in determining hydrocarbon concentrations [cf. *McKeen and Liu*, 1993] and equation (6) therefore cannot be used as a general description of atmospheric observations.

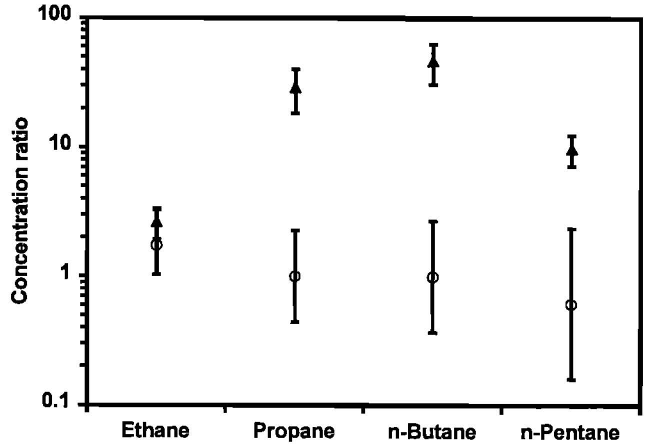

Figure 5. Comparison of the impact of chemical removal processes (circles) with observed changes (triangles) for different n-alkanes. The ratios are calculated from the measurements reported by *Tsunogai et al.* [1999] for coastal areas in Japan and the marine boundary over the Pacific. It should be noted that the δ13C values reported by *Tsunogai et al.* [1999] for coastal areas are within their variability identical to the available source composition data (Table 3). The change due to chemical removal is calculated according to equation (7). The KIEs for the atmospheric removal of ethane and n-pentane were interpolated according to Figure 3 (for details, see text).

However, we can combine isotopic information and concentration data to obtain some constraints on the processes that caused the changes in air mass composition. To characterize the impact of mixing and dilution, we can compare the idealized effect of photochemical removal with the observed change in concentration. Rearrangement of equation (6) results in

$$^{t}c_z\,/\,^{0}c_z = \exp\left(-\{^{t}\delta_z - {}^{0}\delta_z\}\,/\,^{OH}\delta_{KIE}\right). \qquad (7)$$

In Figure 5 the thus calculated impact of chemical removal is compared with the observed changes in concentration for the available limited data sets of δ^{13C} values and concentrations of n-alkanes [*Tsunogai et al.*, 1999]. At first sight the results are surprising. Direct photochemical processing has only a marginal impact on the more reactive C_3-C_5 alkanes, whereas it seems that there is a visible impact for the least reactive of the n-alkanes, although this difference is significant only at the 1 σ level. The need to use an interpolated KIE for the reaction of ethane with OH-radicals is one of the major sources for the uncertainty of the impact of chemical removal on the change of ethane mixing ratios.

Having a more detailed look at the available data helps to understand the processes determining the changes in concentration and δ^{13C}. The reported δ^{13C} values for C_3-C_5 alkanes in the marine atmosphere (5°N–30°N) are very similar to values found in urban areas (Table 3). Consequently, the concentration change due to chemical processing can be only small, and the ratio of $^{t}c_z\,/\,^{0}c_z$ according to equation (7) is close to one (Figure 5). However, the concentrations of C_3-C_5 alkanes reported by *Tsunogai et al.* [1999] differ between urban or coastal air and the marine atmosphere by a factor of 10-30. If this change were due to direct photochemical removal of the alkanes in the studied air mass, it would be equivalent to 2 or 3 atmospheric residence times. On the basis of our measured KIEs the corresponding δ^{13C} change for propane would be around 7‰ to 10‰, and for n-butane it would be around 5 ‰ to 8 ‰ (equation (5)).

If we use an estimate for the KIE of n-pentane based of the interpolation between measured n-alkane KIEs (Figure 3), the change should be around 3‰ -7‰. The reported $\delta^{13\text{-}C}$ values [*Tsunogai et al.* 1999] are only compatible with a change that amounts to a fraction of these values (see also Figure 5). We therefore conclude that the observed decrease in mixing ratio is not directly due to photochemical removal of these alkanes. The most likely explanation is dilution with air masses that have been effectively depleted in alkanes. Although it cannot be completely ruled out that sources with δ^{13C} values different from the urban observations contribute to the C_2-C_5 alkanes in the marine atmosphere, it seems very unlikely that such an impact would exactly balance the changes expected due to chemical reactions.

The ethane δ^{13C} values reported by *Tsunogai et al.* [1999] indicate a systematic decrease with decreasing mixing ratios. They interpret this dependence on the basis of a Rayleigh dependence between isotopic composition and concentration. However, as mentioned above, this treatment does not consider the impact of dilution and mixing processes. The observed decrease in ethane mixing ratios is systematic with latitude; the mixing ratios in the marine samples decrease from nearly 2 ppb at 30°N to around 0.5 ppb at 6°N. The changes in the δ^{13C} values are also systematic; they increase from around -27.5‰ at 30°N to - 22‰ at 6°N. A KIE of 4-5‰ (see above) for the reaction of ethane with OH-radicals would allow reconciliation with the concentration gradient and the $\delta^{13\text{-}C}$ gradient for ethane. This suggests that these ethane concentrations are predominantly due to the background levels of this compound. Indeed, the ethane mixing ratios reported by *Tsunogai et al.* [1999] for the Pacific are compatible with the average tropospheric background mixing ratios derived by *Rudolph* [1995] for the same latitude and season. In contrast to this the propane, n-butane and n-pentane levels reported by *Tsunogai et al.* [1999] are somewhat higher than other observations of these compounds in the remote marine boundary layer at low latitudes [*Rudolph and Johnen*, 1990; *Koppmann et al.*, 1992; *Donahue and Prinn*, 1993]. This supports our conclusion that for these compounds the observations of *Tsunugai et al.* [1999] are impacted by diluted, but nevertheless rather recent emissions. However, due to the limited number of available isotope composition measurements we cannot decide whether this is specific for the studied situation or typical for this region of the Pacific and this season.

5. Stable Carbon Isotope Ratio Measurements in the Greater Toronto Area

The results of our study of a diurnal cycle of stable carbon isotope ratios and mixing ratios of NMHC at York University are summarized in Figures 6a-6e. Average and standard deviation of the source studies conducted in the greater Toronto area are also given. These source studies concentrated on automotive related emissions for the greater Toronto area the by far dominant sources of the light NMHC studied here [*McLaren et al.*, 1996]. Wind direction and velocity during the study period are shown in Figure 6f; temperature and pressure are shown in Figure 6g.

On the morning of June 21, wind was from ENE at a very low speed of about 1.5 m s^{-1}. Toward noon the wind direction changed to ESE and SE with wind speed varying between 1.5 and 5 m s^{-1}. This prevailed until early evening. Under these conditions the air sampled at York University passed over downtown Toronto or its near vicinity about 1-2 hours before collection. During this period the atmospheric pressure dropped by about 3 hPa, and the temperature increased from around 19°C in the morning to 27°C in the afternoon. Later in the evening, around 2300 LT., wind direction changed to more northerly directions, and wind velocity stabilized at 1-2 m s^{-1}. Atmospheric pressure remained at 1023 hPa and temperature dropped from 26°C at 1900 LT to 15°C at 0300 LT the following morning. After 0500 LT the temperature increased again. The sky was clear until around noon. Very early afternoon conditions were partly cloudy, but still sunny.

There is a clear difference in atmospheric mixing ratios between daytime and nighttime or very early morning. Although there is considerable variability, between midnight and 0700 LT, the mixing ratios of the different NMHC are on average between a factor of 2.5 and 16 higher than during the day. This is the result of the formation of a strong and shallow nighttime inversion layer. In such an inversion layer, emitted trace gases accumulate and even in the vicinity of only moderate sources high mixing ratios can be observed. The formation of a strong nighttime inversion is fully compatible with the low wind speed and clear sky during the night, as well as the substantial drop in temperature between 1900 and 0500 LT. On the basis of our observations we conclude that for the given situation, the impact of the nighttime inversion far outweighs the influence of downtown Toronto emissions during the daytime. The low daytime mixing ratios may be the result of both fast atmospheric dispersion and photochemical removal of the trace gases. In this context, information on isotopic composition is extremely valuable since it allows differentiating between dilution and chemical removal. We will therefore have a closer look at the diurnal variation of stable carbon isotope ratios.

Three generalized conclusions can be drawn from the results in Figures 6a-6e. First, there is no obvious correlation between mixing ratios and stable carbon isotope ratios. The highest correlation coefficient we found is around 0.3. Second, the lower range of ambient isotope ratios is identical to the known isotopic composition of the transport related sources. Only one of the ambient stable carbon isotope ratios is significantly (1 σ level) lower than the average of the studied sources. However, a substantial number of the stable carbon isotope ratios are significantly heavier than the average source composition. Finally, as predicted by equation (5), the differences between the average isotopic composition of the sources and ambient observations are higher for compounds with a larger KIE or higher reactivity toward OH-radicals. For example, propane and benzene have a very similar reactivity toward OH-radicals, whereas the KIEs for the reaction with OH-radicals differ substantially. Here the effect of different KIEs is reflected by the observation that the difference between source composition and ambient isotope ratio is on average a factor of 2.3 ± 0.4 higher for benzene than propane, comparable to the ratio of the corresponding KIEs of 2.2. For propane and n-butane where the OH k differs, we find an average ratio of 0.69 ± 0.17, whereas the ratio of the KIEs is 1.2. However, as predicted by equation (5), the ratio of the products of rate constants and KIEs for reaction with OH is 0.56, which is in good agreement with the observations. Also, the high fractionation effects seen for propene are fully compatible with the high KIE and rate constant for the reaction of propene with OH-radicals.

On the basis of these observations we conclude that our measurements of the stable carbon isotope ratios of NMHC sources give a realistic estimate of the average source composition for the greater Toronto area. Furthermore, the results indicate that the differences between source composition and atmospheric observation are primarily the result of atmospheric removal processes, specifically the reaction with OH-radicals.

Under these conditions we can use equation (5) to estimate the extent of photochemical aging for the individual hydro-

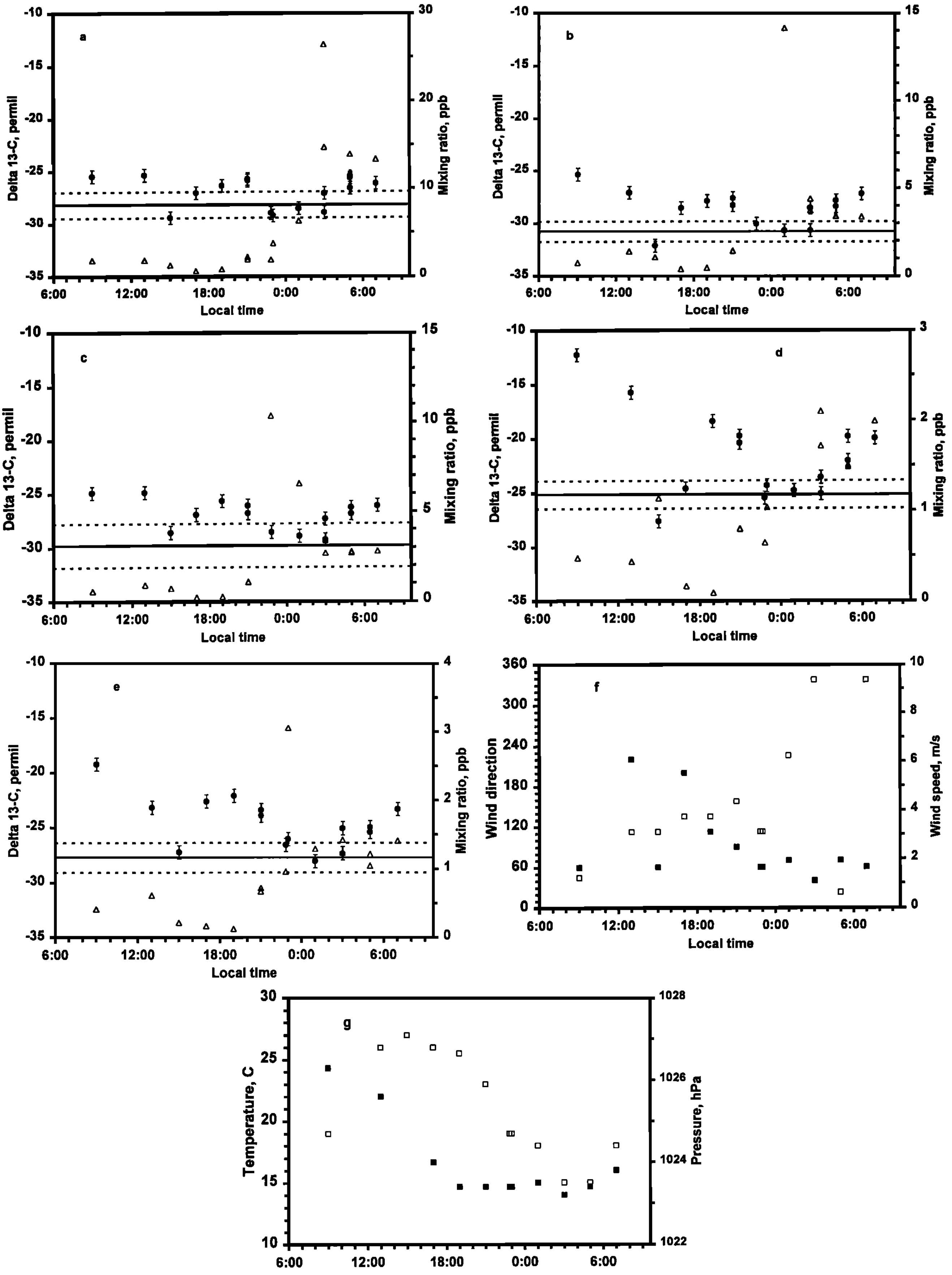

Figure 6. Stable carbon isotope ratios (solid circles) and mixing ratios of NMHC (open triangles) measured at York University between June 21, 0900 LT. and June 22, 1999, 0700 LT. The horizontal lines indicate the average (solid line) the one σ uncertainty (dashed lines) of the source studies in the greater Toronto area. (a) Propane, (b) n-butane, (c) n-pentane, (d) propene, (e) benzene. (f) wind direction (open squares) and wind speed (solid squares), and (g) atmospheric temperature (open squares) and pressure (solid squares).

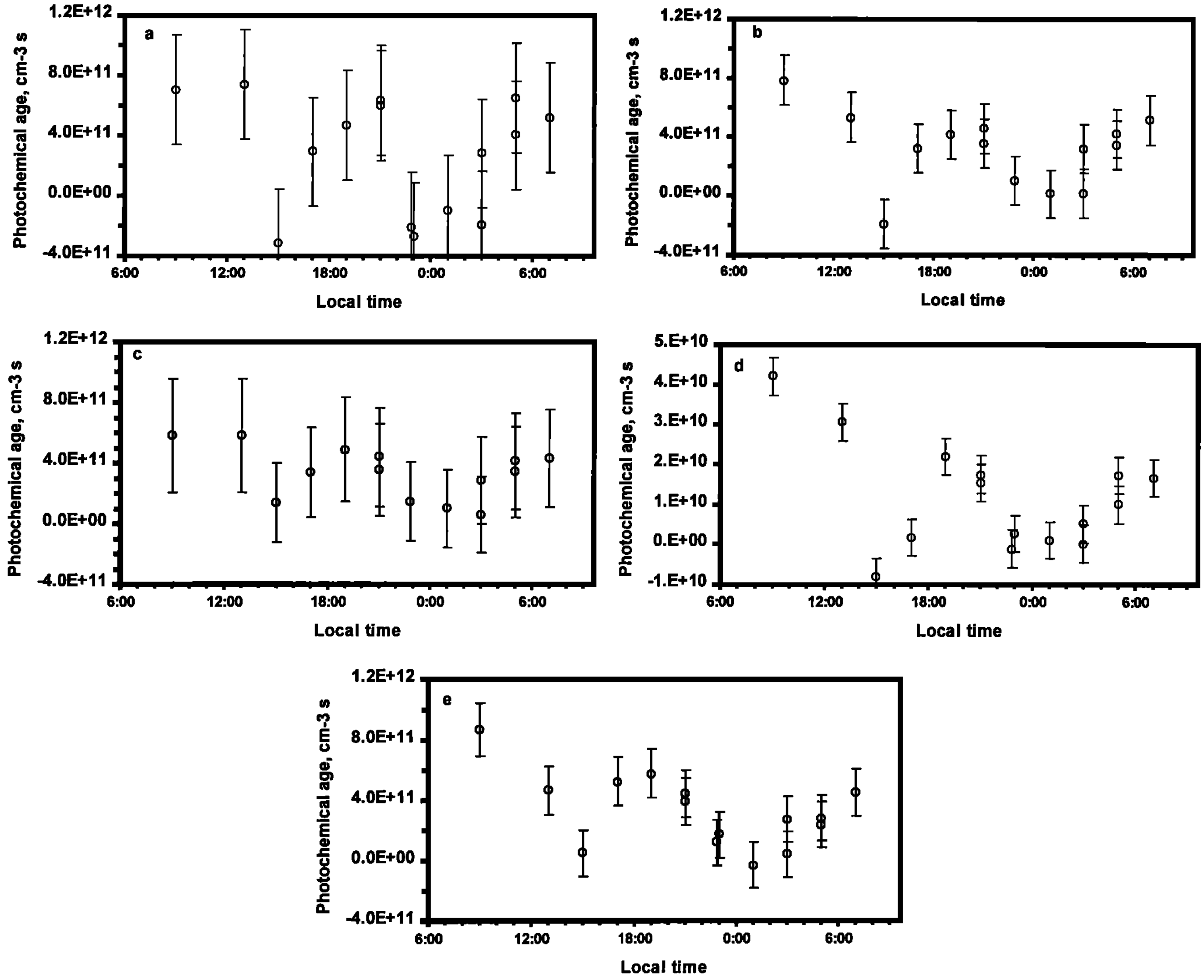

Figure 7. Photochemical age of hydrocarbons derived from the stable carbon isotope ratios in Figure 6. (a) Propane, (b) n-butane, (c) n-pentane, (d) propene, and (e) benzene. The calculations are based on measured KIEs for the reactions with OH-radicals and the source composition given in Figure 6. For n-pentane, no measured KIE is available. On the basis of the dependence between KIE and carbon number in Figure 3, a value of 2.1 ± 1‰ was used. The reaction rate constants for reaction with OH-radicals were taken from *Atkinson* [1994, 1997]. The error bars indicate the uncertainties due to uncertainties of the KIEs and isotopic source signature.

carbons. The time-integrated OH-radical concentration that can be obtained by rearranging equation (5) is a useful measure for photochemical processing. Obviously, the extent of photochemical aging may depend on the atmospheric lifetime of the studied NMHC. In other words, a compound with a low reactivity will on average remain for a longer period in the atmosphere than a more reactive substance and thus most likely be exposed to a higher time-integrated OH-radical concentration. Only if the studied NMHC are predominantly due to emissions that occurred within periods that are short relative to the lifetimes of the NMHC we can expect an identical photochemical age for substances with different reactivity.

Indeed, the photochemical ages derived from our stable carbon isotope measurements (Figure 7) are completely different for the highly reactive propene and the less reactive alkanes and benzene. The uncertainties for the photochemical ages of the n-alkanes are quite substantial. This is the consequence of their small KIEs and the uncertainty of the source composition. Nevertheless, it is evident that the time-integrated OH-radical concentration derived for propene is generally more than an order of magnitude lower than for the less reactive NMHC. On the basis of the OH-rate constants (Table 2) and a diurnal average OH-radical concentration of about 2 x 10^6 cm^{-3} for 40°N in June [*Spivakovsky et al.*, 1990] we calculate average lifetimes in the range of several days for the light n-alkanes and benzene and a few hours for propene. Consequently, the values derived from propene will represent local conditions, whereas those from the alkanes and benzene give more regional information. We also have to consider that the derived photochemical age is an average value that may be due to the mixing of air masses with NMHC of different photochemical age.

The average photochemical ages derived for propene range from zero to about 4 x 10^{10} cm^{-3} s. Most of the low photochemical ages occur during night, consistent with the strong impact of local emissions as a consequence of the shallow nighttime inversion layer (see above) and the absence of significant photochemistry during darkness. There are also two very low values in the afternoon, but all other daytime values range be-

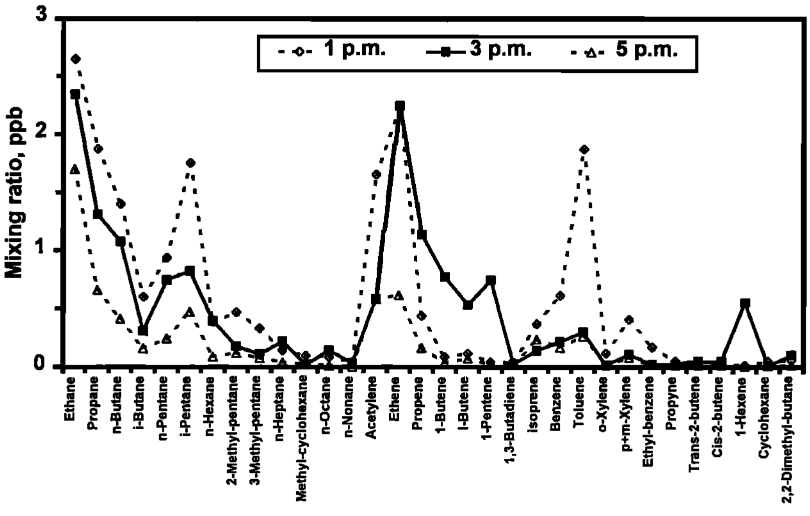

Figure 8. Profile of hydrocarbon mixing ratios for samples collected in the early afternoon of June 21, 1999.

tween 1 x 10^{10} cm^{-3} s and 4 x 10^{10} cm^{-3} s. Assuming that the daytime average OH-radical concentration is about twice the diurnal average value of 2 x 10^6 cm^{-3}, we obtain an actual age of roughly 1-3 hours. On the basis of the wind speeds during the measurement period this corresponds to distances in the range of 10 to 40 km. Thus, in this example, the isotopic composition measurements of propene allow us to study photochemical processing of the sampled air mass which occurs on timescales of a few hours and less.

The situation is different for other NMHC. Here the photochemical age is sometimes as high as 8 x 10^{11} cm^{-3} s and often around 2-4 x 10^{11} cm^{-3} s. On the basis of 24-hour average OH-radical concentrations of 2 x 10^6 cm^{-3} this corresponds to an average age of a few days. This indicates that the benzene and the light alkane mixing ratios during a considerable part of the study period are not so much of local origin, but predominantly dominated by transport from regional sources. On the basis of the wind velocities observed during our study, the estimated time allows for transport over distances in the range of a few hundred kilometers. However, there are also several samples where the isotopic signature clearly indicates predominance of local sources. For the nighttime measurements this is not surprising. The effect of a shallow inversion results in a high impact of local emissions on the atmospheric trace gas levels (see above) and consequently an isotopic signature essentially identical to the sources. However, there is one measurement in the afternoon with an isotopic signature that is very similar to the source composition. This sample was collected during a period of substantial drop of atmospheric pressure and low wind speed. Meteorological conditions do not otherwise indicate a significant difference between this sample and the samples collected at noon or later in the afternoon. Alkene mixing ratios are elevated, but the mixing ratios of all other NMHC are in the range expected from comparison with the samples collected immediately before and after this sample (Figure 8). However, the isotopic signature clearly shows that also the light alkanes and benzene are of very recent origin, very different from the other afternoon samples.

6. Comparison With 2-D Model Calculations

Presently, there are no published model predictions of the stable carbon isotope ratio of atmospheric NMHC. Therefore we set up a simple two-dimensional model using prescribed transport, OH-radical, and temperature fields. For ethane source strength we used the latitudinal dependence of the emission rates derived by *Rudolph* [1995] from atmospheric observations of ethane mixing ratios. The total source strength in this scenario is 15.5 Tg/yr. For consistency, we also use the OH-radical, transport, and temperature fields used by *Rudolph* [1995]. We assume that the ethane source strength is independent of season. On the basis of the available results of emission studies (see Table 3) we used a stable carbon isotope ratio of – 30‰ for the ethane emissions, independent of season and latitude. The results of *Rudolph* [1995] indicate that there might be a systematic seasonal variation of emission rates; however, on a global scale this variability is relatively small and essentially absent in the Southern Hemisphere. Furthermore, information that would allow for construction of a detailed seasonal and latitudinal dependence of the stable carbon isotope composition for ethane sources is essentially absent. The model has only a coarse resolution with a latitude band size of 10° and 13 vertical layers with a thickness of 1 km each. Propane emissions are scaled to the ethane sources using a molar propane to ethane emission ratio of 0.6, compatible with average relative source compositions [cf. *Hough*, 1991]. Stable carbon isotope ratio for propane emission is -28 ± 1.5‰, compatible with the limited available data (Table 3 and Figure 6a). The rate constants and their temperature dependence for reaction with OH-radicals are taken from *Atkinson* [1997]. For reaction of ethane with OH-radicals we use a KIE of 5‰ with an uncertainty of ± 2‰ (see discussion above). For the fractionation of propane due to reaction with OH-radicals we use our measured KIE and its experimental uncertainty.

For 40-50°N (the latitude band where Toronto is situated) we calculate a stable carbon isotope ratio of –25.7 ± 1.6‰ for propane. This is at the heavy end of the observed average of -27.1 ± 1.5‰ (error of mean is 0.4‰). Still, the average of the highest 5 measured stable carbon isotope ratios is -25.6 ± 0.2‰, which is compatible with our model predictions. However, the model-predicted mixing ratios are with 0.4 ppb well below all our observations.

The comparison of model and observations for coastal areas of Japan (Table 4) gives a similar picture. Within the uncertainties the model-predicted stable carbon isotope ratios of ethane and propane agree with observations, although the model results are somewhat at the heavy end of the range of observations. Similar to the greater Toronto area, model-predicted

Table 4. Comparison of Observed Stable Carbon Isotope Ratios and Mixing Ratios With Results From 2-D Model Calculations

Compound	Pacific, 5°-15°N[a]		Pacific, 25°-35°N[a]		Japanese Coast, 35°N[a]	
	Mixing Ratio, ppb	δ ^{13C}, ‰	Mixing Ratio, ppb	δ ^{13C}, ‰	Mixing Ratio, ppb	δ ^{13C}, ‰
Ethane						
Observed	0.6 to 1.0	-23 to -25	1 to 1.8	-25.5 to -27.5	3.0-3.5	-26.5 to –28
2-D model[b]	1.3	-25.5 ± 2.2	1.9	-26.8 ± 2.0	1.9	-27± 1.9
Propane						
Observed	0.07 to 0.1	-26 to -29	0.1 to 1	-26 to -29	1 to 1.2	--26 to -29
2-D model[c]	0.25	-25.1 ± 1.6	0.5	-25.5 ± 1.5	0.54	-25.7 ± 1.5

[a] *Tsunugai et al*, [1999].

[b] δ ^{13C} calculated for a KIE of 5±2‰ and –30.0 ± 1.5‰ as average source composition.

[c] δ ^{13C} calculated for our measured KIE of 3.44 ± 0.26 and –28.0 ± 1.5‰ as average source composition.

mixing ratios are well below the observations. For the marine atmosphere over the tropical and subtropical Pacific the model predicts the stable carbon isotope ratios correctly within the uncertainties of observations and model. However, in contrast to continental and coastal areas, the model predicts somewhat higher mixing ratios than actually observed (Table 4).

The few stable carbon isotope data available for the Southern Hemisphere present a completely different picture. The seasonal cycles of the ethane and propane mixing ratios calculated for 40°S agree very well with the published observations by *Clarkson et al.* [1997] (Figure 9). However, a comparison of model predictions of stable carbon isotope ratios (Figure 10) with observations shows major differences. For ethane, model and observations still show an acceptable agreement, although the model calculations fail to describe the substantial variability of the measurements. For propane this is extremely obvious. Although one observation at a moderately polluted coastal site shows good agreement between model and measurement, for the other data point there is a difference of nearly 20‰ between prediction and observation. This difference is far beyond the estimated uncertainties of the model or measurement errors.

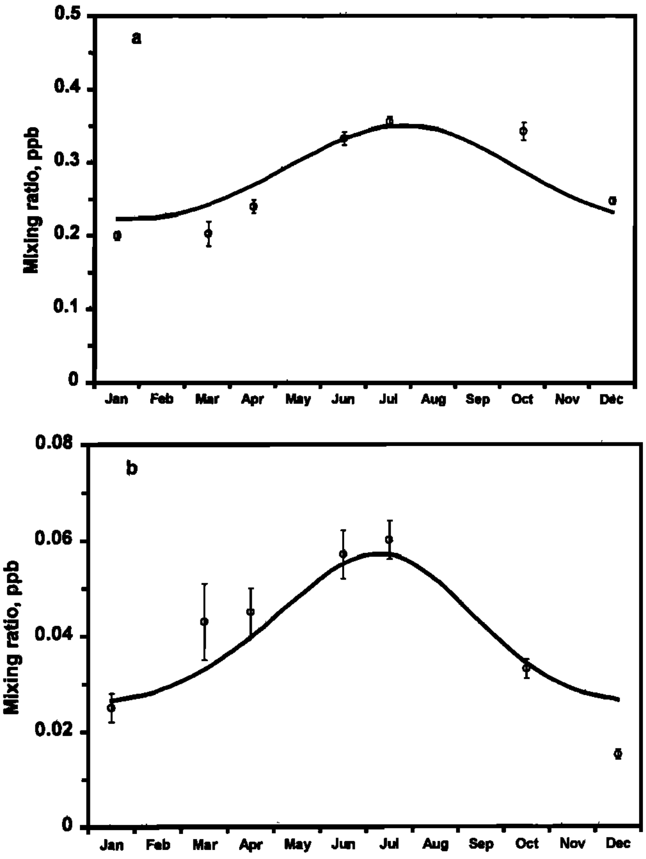

Figure 9. Comparison of (a) ethane and (b) propane mixing ratios predicted by two-dimensional model calculations for 40°S with the observations of *Clarkson et al.* [1997].

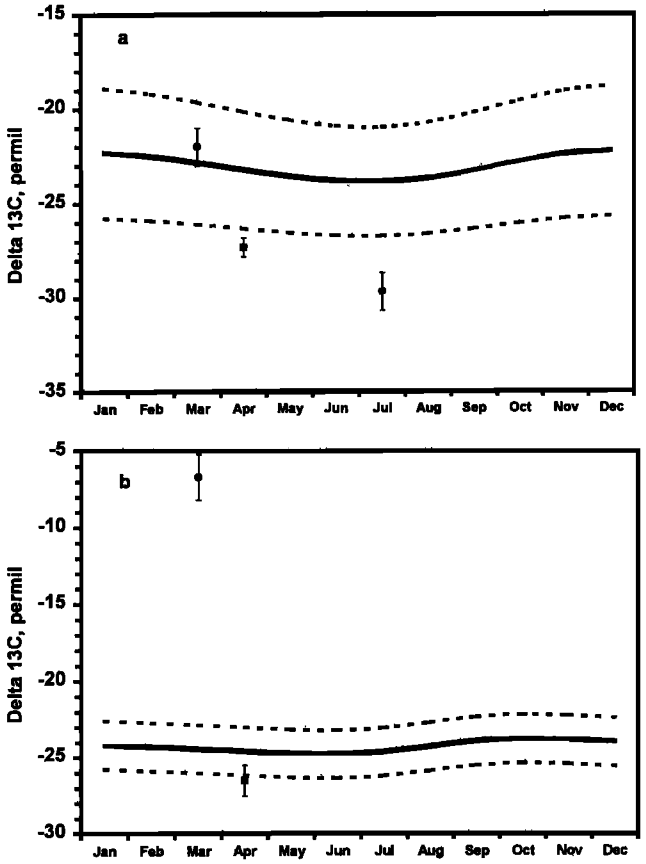

Figure 10. Comparison of stable carbon isotope ratios for (a) ethane and (b) propane predicted by two-dimensional model calculations for 40°S with the observations of *Rudolph et al.* [1997b] at Greta point (squares) and Baring Head (circles). Baring Head is a clean air site at the southern end of the New Zealand North Island, and Greta Point a coastal site in the area of Wellington (New Zealand).

The available carbon isotope ratio measurements are few in numbers and do not necessarily agree with representative averages. Since our model describes average situations, we cannot decide whether observed discrepancies are the consequence of general model deficits or simply the result of seemingly random variations in the real atmosphere. Thus conclusions drawn from such a limited data set may only be valid for the studied situation.

Atmospheric stable carbon isotope ratios of NMHC are predominantly determined by source composition and extent of photochemical processing (equation (5)), whereas for the mixing ratios source strengths also have a very significant impact. Thus comparison of isotope ratio measurements between model and observations will allow conclusions about atmospheric transport, mixing, and photochemical removal mechanisms without additional uncertainties induced by possible errors in absolute source strength.

On the basis of stable carbon isotope ratios we calculated the average photochemical age for the model results using equation (5). For the Pacific the average photochemical age of ethane changes from 0.9 atmospheric lifetimes near the equator to about 0.6 lifetimes at 35 °N. The corresponding model-derived average ages for propane are somewhat larger, 1.5 and 1.2 lifetimes. Uncertainties in photochemical age are primarily due to uncertainties of the source signature. They amount to an uncertainty of 0.3 atmospheric lifetimes for ethane and 0.5 atmospheric lifetimes for propane. Within these errors our model correctly estimates the photochemical age of ethane and propane for this area of the Pacific. The uncertainty in photochemical age translates into a possible error in mixing ratio of about 35% for ethane and 65% for propane. The differences between model-predicted and observed mixing ratios discussed above (see also Table 4) often exceed this uncertainty. For the marine atmosphere the model values are at the high side of the observations; for coastal and continental sites the model underestimates the mixing ratios. This is not surprising since the model calculates zonal mean mixing ratios. Thus for all latitude bands containing significant fractions of both land and ocean we expect that the modeled mixing ratios are somewhere between observations in continental and marine air. The isotope ratio measurements show that the difference in NMHC mixing ratio between continental or coastal air masses and the marine boundary layer is primarily the consequence of dilution processes and only to a lesser extent directly due to photochemical removal. This explains why a zonal averaged model correctly predicts the stable carbon isotope ratio in individual measurements, but not the mixing ratios.

The situation is reversed for the observations in the Southern Hemisphere at 40°S. As pointed out above, model predictions and measured mixing ratios agree very well. However, the stable carbon isotope ratios indicate that the model-derived photochemical age does not always agree with the observations. The number of data points is too small to generalize this finding. However, independent of the lack of sufficiently representative data sets, isotopic evidence points toward a discrepancy that would not have been evident from mixing ratio measurements alone.

7. Conclusions

Our measurements show that the KIEs for reactions of NMHC with OH-radicals strongly depend on the structure of the molecules. For n-alkanes with more than two carbon atoms they are substantially higher than might be expected from an extrapolation of published values for the reaction of methane with OH-radicals. Still, the isotope fractionation occurring during reaction of n-alkanes with OH-radicals is small and in magnitude comparable to the mass dependence of the frequencies for the collision of n-alkanes with OH-radicals. Consequently, the impact of atmospheric removal on isotopic composition of alkanes, especially the heavier alkanes, is relatively small. This is fully compatible with our measurements in the greater Toronto area and the few published values for remote and urban regions. For these compounds, source composition has a substantial impact on ambient stable carbon isotope ratios. Potentially, such measurements will be useful for source-receptor modeling, or source reconciliation techniques. However, presently our knowledge of isotopic composition of NMHC emissions is extremely limited, and thus we are not yet able to derive any details on the importance of different types of sources from ambient stable carbon isotope ratio. In spite of these uncertainties, the observed stable carbon isotope ratios for light n-alkanes are generally very close to our estimated average source composition. The differences between source composition and ambient observations rarely exceed 5‰. Owing to the relatively small impact of removal processes on the stable carbon isotope ratios of n-alkanes, the photochemical age derived from n-alkanes has substantial uncertainties.

The situation is completely different for light, unsaturated NMHC (alkenes, dienes, ethyne, and benzene). Their KIEs are substantial, in some cases exceeding 10‰. Consequently, we find a substantial impact of atmospheric removal processes on the stable carbon isotope ratios. Our measurements in the greater Toronto area demonstrate that the impact of photochemical removal is sometimes as high as 10‰, more than a factor of 5 higher than the estimated uncertainty of the average source composition. Consequently, photochemical ages derived from measurements of isotopic composition for such compounds allow differentiating between local and regional or large-scale contributions. Specifically, such measurements are very useful to differentiate between the impact of dilution or mixing processes, and atmospheric removal mechanisms. In this context, it is very important that the NMHC with substantial KIEs for reaction with OH-radicals include compounds with a wide range of atmospheric residence times. Benzene and ethyne have tropospheric lifetimes of several weeks; reactive alkenes or dienes such as isoprene, butadiene, or butene have lifetimes of a few hours or less. This allows studies of atmospheric processes on different temporal and thus spatial scales.

The discrepancy between measurements and model prediction of stable carbon isotope ratios points toward the existence of model deficiencies in spite of the good agreement between model and observations for the mixing ratios. For our simple two-dimensional model this is not too surprising. Nevertheless, this demonstrates that isotope ratio measurements can be used to test model performance beyond the quality of mixing ratio predictions. Qualitatively, the observed KIEs can be explained by conventional isotope effects resulting from the mass dependence of collision frequencies and, for unsaturated hydrocarbons, of the mass dependence of vibration frequencies in the transitions state for addition of an OH-radical to a double bond. The KIEs show the expected decrease with increasing number of carbon atoms of the reacting molecules. Although presently the number of measurements of KIEs for reaction of NMHC with OH-radicals is limited, the observed carbon number and structure dependencies already allow first-order estimates of KIEs for other NMHC.

For NMHC only the KIEs of reactions with OH-radicals have been studied. Although this is the most important, and sometimes the only relevant atmospheric loss mechanism for NMHC, there are a number of potentially important other removal reactions for NMHC. Alkenes and dienes react with ozone and NO_3.

Under specific conditions, for example, at night, these reactions may well be the dominant loss processes for NMHC. Depending on the magnitude of isotope fractionation effects associated with these reactions, stable isotope ratio measurements might be extremely useful to study these processes in the atmosphere, for example, the nighttime loss processes of biogenic NMHC. Similarly, several NMHC reaction with Cl or Br atoms can be relevant under specific conditions, for example, in the polar troposphere [cf. *Jobson et al.*, 1994a, 1994b; *Ramacher et al.*, 1999]. Again, studies of isotope fractionation reactions associated with these processes might be very useful to further improve our understanding of the role of halogen chemistry for the troposphere.

The presently available data are extremely limited. Nevertheless, the few examples discussed in this paper demonstrate that measurements of stable carbon isotope ratios of atmospheric NMHC combined with concentration measurements allow us to study chemical removal mechanisms as well as dilution and mixing effects. Presently, the extent and accuracy of quantitative information that can be extracted from stable carbon isotope ratio measurements in NMHC is still limited due to the lack of data on source composition, KIEs for the main removal mechanisms of NMHC, and the extreme scarcity of ambient isotope ratio measurements.

The use of stable isotope ratio measurements most likely will be of equal value to study other volatile organic trace gases, for example, halocarbons, including CFC substitutes, and oxygenated hydrocarbons as well as the oxidation products of NMHC. Presently, isotope ratio measurements for NMHC and other VOC are limited to carbon. However, nearly all VOC contain hydrogen atoms; many VOC contain chlorine, bromine, sulphur, oxygen, or nitrogen atoms. For all these elements there is more than one stable isotope. We expect that measurements of other stable isotope ratios will add further possibilities to gain insight into the mechanisms determining ambient VOC concentrations and distributions once suitable measurement methods are available.

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