Stable carbon kinetic isotope effects for the production of methacrolein and methyl vinyl ketone from the gas-phase reactions of isoprene with ozone and hydroxyl radicals

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ABSTRACT

The stable-carbon kinetic isotope effects (KIEs) associated with the production of methacrolein (MACR) and methyl vinyl ketone (MVK) from the reactions of isoprene with ozone and OH radicals were studied in a 25 L reaction chamber at (298 ± 2) K and ambient pressure. The time dependence of both the stable-carbon isotope ratios and the concentrations was determined using a gas chromatography combustion isotope ratio mass spectrometry (GCC-IRMS) system. The average yields of ^{13}C-containing MACR and MVK generated from the ozone reaction of ^{13}C-containing isoprene differed by $-3.6‰$ and $-4.5‰$, respectively, from the yields for MACR and MVK containing only ^{12}C. For MACR and MVK generated from the OH-radical oxidation of isoprene the corresponding values were $-3.8‰$ and $-2.2‰$, respectively. These values indicate a significant depletion in the ^{13}C abundance of MACR and MVK upon their formation relative to isoprene's pre-reaction $^{13}C/^{12}C$ ratio, which is supported by theoretical interpretations of the oxidation mechanism of isoprene and its ^{13}C-substituted isotopomers. Numerical model calculations of the isoprene + O_3 reaction predicted a similar depletion in ^{13}C for both reaction products upon production. Furthermore, the model predicts mixing ratios and stable carbon delta values for isoprene, MACR, and MVK that were in agreement with the experimental results. The combined knowledge of isotope enrichment values with KIEs will reduce uncertainties in determinations of the photochemical histories of isoprene, MACR, and MVK in the troposphere. The studies presented here were conducted with using isoprene without any artificial isotope enrichment or depletion and it is therefore very likely that these results are directly applicable to the interpretation of studies of isoprene oxidation using stable carbon isotope ratio measurements.

1. Introduction

It is now widely recognized that isoprene, a biogenic hydrocarbon with estimated annual emissions of $410-600$ Tg yr^{-1} (Guenther et al., 1995, 2006; Wang and Shallcross, 2000; Lathière et al., 2006; Müller et al., 2008) contributes toward aerosol formation (Limbeck et al., 2003; Claeys et al., 2004; Kroll et al., 2005, 2006; Kleindienst et al., 2007; Zhang et al., 2007) and the generation of ozone in the presence of VOCs/NO$_x$ (Chameides et al., 1997; Starn et al., 1998; Ryerson et al., 2001; Dreyfus et al., 2002; Xie et al., 2008). Methacrolein (MACR) and methyl vinyl ketone (MVK) are important first generation products of isoprene

oxidation that have been routinely quantified alongside isoprene in kinetics studies (Atkinson et al., 1982a; Edney et al., 1986; Tuazon and Atkinson, 1989, 1990; Greene and Atkinson, 1992; Treacy et al., 1992; Carter, 1996; Chuong and Stevens, 2002, 2003, 2004; Avzianova and Ariya, 2002; Klawatsch-Carrasco et al., 2004) and in field studies (Pierotti et al., 1990; Martin et al., 1991; Montzka et al., 1993, 1995; Biesenthal et al., 1997; Warneke et al., 2001; Stroud et al., 2001; Apel et al., 2002; Hakola et al., 2003). Laboratory and mechanistic studies have shown that MACR and MVK are the dominant products of both the isoprene oxidation via OH and O_3 (Paulson et al., 1992; Miyoshi et al., 1994; Lei et al., 2000).

Over the past decade, measurements of $^{13}C/^{12}C$ and D/H kinetic isotope effects (KIEs) have been performed for a series of gas-phase reactions between atmospherically relevant VOCs (including alkanes, alkenes, and simple aromatic compounds) and hydroxyl radicals (Rudolph et al., 2000; Iannone et al., 2004; Anderson et al., 2004a,b),

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ozone (Iannone et al., 2003), and chorine atoms (Iannone et al., 2005; Anderson et al., 2004a,b). These KIEs are required to derive additional constraints on the processes determining atmospheric VOC concentrations using isotope ratio measurements (Rudolph et al., 2000; Goldstein and Shaw, 2003; Rudolph and Czuba, 2000; Saito et al., 2002). More recently, measurements of KIE values for the reactions of isoprene, MACR, and MVK with OH (Iannone et al., 2009) and O_3 (Iannone et al., 2008) were carried out in order to aid in the quantitative analysis of ambient $^{13}C/^{12}C$ isotope ratio measurements for said VOCs. The KIEs, and indeed all KIEs for VOC reactions of atmospheric relevance measured thus far, studied the loss of the VOC. Further to this, the measurable changes in $^{13}C/^{12}C$ ratios have been largely attributed to primary KIEs, where fractionation is the result of a reaction occurring directly at a ^{13}C atom site, rather than secondary KIEs, where usually only little fractionation occurs for a ^{13}C-containing compound if the reaction does not occur at the ^{13}C atom site. Rudolph et al. (2003) describes the potential use of $^{13}C/^{12}C$ isotope ratio measurements of isoprene for studying the photochemical processing of isoprene in the troposphere. Other recent studies have utilized KIEs of precursor reactions toward the understanding of the $^{13}C/^{12}C$ composition in secondary organic aerosol (Irei et al., 2006; Fisseha et al., 2009).

Since one of the carbon atoms of isoprene is lost in the formation reactions of MACR and MVK, the carbon isotope ratios of MVK and MACR cannot be determined from the KIE for reaction of isoprene and mass balance considerations alone. Therefore the KIE values associated with MVK and MACR formation may be distinct from the KIEs for isoprene oxidation reactions (Schmidt et al., 2004). To our knowledge, there are no published measurements of the KIEs for the formation of MVK and MACR through the OH- and O_3-initiated oxidations of isoprene.

Several experiments were conducted to examine $^{13}C/^{12}C$ isotope ratios of isoprene, MACR, and MVK during the $ISO + O_3$ and $ISO + OH$ reactions. The KIEs associated with the production of MACR and MVK are presented and discussed. A chemical box model which incorporates site-specific KIEs for the isoprene $+ O_3$ system is compared with experimental observations.

2. Experimental

The gas-chromatography combustion isotope-ratio mass spectrometry (GCC-IRMS) system used here was also used in two recent studies by Iannone et al. (2008, 2009) and the laboratory technique for measuring carbon kinetic isotope effects of gas-phase reactions is given in detail by Anderson et al. (2003). Furthermore, the methods for producing ozone and OH radicals and suppressing interfering reactions are identical to those found in Iannone et al. (2008, 2009). Synthetic air (99.999%, Praxair) was used to produce ozone and CO (5×10^4 ppmV; 99.997%, Messer) was used as an OH scavenger as OH, which is produced at significant yields from $O_3 +$ alkene reactions (Paulson et al., 1999; Atkinson and Aschmann, 1993; Atkinson et al., 1992, 1995, 2006).

Three experiments were conducted to observe mixing ratios and $\delta^{13}C$ values of isoprene, MACR and MVK in the presence of O_3. In the first experiment, a large mixing ratio of isoprene was introduced into the chamber to rapidly procure concentrations of MACR and MVK well above the lower detection limit of the GCC-IRMS system. First, a mixture containing $\sim 1 \times 10^{15}$ molecules cm^{-3} of isoprene in synthetic air was prepared in a reaction chamber made of 0.005 mm thick FEP fluorocarbon film (DuPont Polymer Products) and measured twice for concentration and $\delta^{13}C$ values. Then more isoprene was added to the reaction chamber, increasing its mixing ratio to $\sim 3 \times 10^{15}$ molecules cm^{-3}, which is above the linear range of the IRMS but a suitable concentration for the fast generation of MACR and MVK levels above the detection limit of the GCC-IRMS.

The mixture of isoprene and CO was given 10 min to undergo mixing before the addition of O_3 and starting measurements on the GCC-IRMS system. Ozone was admitted into the reaction chamber as a mixture in synthetic air at flow rates between 3.0–6.0 mL min^{-1}. The air/O_3 stream was admitted to the chamber for defined periods depending upon the desired rate of reactant depletion. On average, O_3 mixing ratios in the chamber were ~ 1 ppmV. Sample measurements were performed at regular intervals of ~ 0.5 h and continued until the isoprene was depleted to <25% of the initial concentrations. The second and third experiments followed a similar procedure, but without the additional injection of isoprene into the reaction chamber after the first measurement. Thus, the initial concentration of isoprene in these two experiments was approximately 4×10^{14} molecules cm^{-3}.

One experiment was performed to study the $ISO + OH$ reaction. The experimental procedure was very similar to that described previously in detail by Iannone et al. (2004, 2005, 2009). In this experiment a large quantity of isoprene ($\sim 1 \times 10^{15}$ molecules cm^{-3} well above the upper limit of the linear range of the m/z-44 signal) was injected into the chamber in one step, to allow for the formation of MACR and MVK concentrations in the early phase of the experiment which are sufficient for accurate isotope ratio measurements (in the range of $(0.3-1.3) \times 10^{14}$ molecules cm^{-3}). Because of the large initial amount of isoprene present, the $\delta^{13}C$ of isoprene for the first three measurements could not be determined.

Evaluation of the IRMS data followed the procedure described by Iannone et al. (2008, 2009). All isotope ratios presented here are given relative to the internationally accepted Vienna Pee Dee Belemnite (V-PDB) scale.

3. Results and discussion

3.1. Carbon kinetic isotope effects (KIEs) for the $ISO + OH$ and $ISO + O_3$ reactions

The KIEs for the isoprene loss reactions via OH radicals and ozone were determined using procedures given in Iannone et al. (2008, 2009), thus no detailed discussion is presented here. KIE values are often represented in the literature as per mille ε values where $\varepsilon = (KIE - 1)1000‰$. The ε values determined for the $ISO + O_3$ reaction were $(8.05 \pm 0.17)‰$ and $(8.46 \pm 0.22)‰$. The sole ε value determined for the $ISO + OH$ reaction was $(7.30 \pm 0.78)‰$. These values are in agreement with the average ε values of $(8.40 \pm 0.11)‰$ ($ISO + O_3$) and $(6.56 \pm 0.12)‰$ ($ISO + OH$) reported in two recent studies by Iannone et al. (2008, 2009).

3.2. Isotopic fractionation for MACR and MVK produced from the $ISO + O_3$ and $ISO + OH$ reactions

The effect of secondary reactions of MACR and MVK with OH or O_3 has to be considered before any yield determinations can be made. This was done by calculating and applying correction factors which are based on the following simple reaction scheme for the oxidation of isoprene, using only three reactions and combining products other than MACR and MVK into a generic products category (PROD):

$$ISO + oxidant \rightarrow MACR + MVK + PROD \quad (R1)$$

$$MACR + oxidant \rightarrow PROD \quad (R2)$$

$$MVK + oxidant \rightarrow PROD \quad (R3)$$

The methodology for this correction was first described by Atkinson et al. (1982b) and it allows for the determination of yields, y, for first-generation oxidation products (MACR and MVK in this case) using published rate constants for Reactions (R1)–(R3). Rate constants for specific reactions are provided in Table 1. It should be noted that for the ozone reactions with ISO, MACR, and MVK, concentration values at every time interval t were corrected for additional losses from any unscavenged OH radicals. The procedures used to determine corrected MACR and MVK concentrations from ISO + O$_3$ and ISO + OH oxidations were described in detail in two recent publications by Iannone et al. (2008, 2009) and the reader is referred to these studies for details on corrections, thus, no further explanations are given here. Yields for MACR and MVK thus determined were independent of simultaneous MACR and MVK losses due to reaction with the oxidant present in the reaction system (Table 2).

To determine the extent to which each of the MACR and MVK products was enriched or depleted in ^{13}C during their formation, isotopologue specific (i.e., for ^{13}C-containing and solely ^{12}C-containing molecules) yields of MACR and MVK were determined. Thus, corrections for MACR and MVK isotopologue losses via either OH or O$_3$ were performed using isotope-specific formulations where ^{12}F and ^{13}F correction factors for MACR and MVK were calculated in terms of isoprene containing only ^{12}C (^{12}ISO) and isoprene containing one ^{13}C atom (^{13}ISO). The correction factors were calculated using the following equations:

Table 2
Formation yields of MACR and MVK experimentally obtained from the gas-phase reactions of O$_3$ and OH with isoprene.

Product	Reaction	
	ISO + O$_3$	ISO + OH
MACR	0.334 ± 0.042[a]	0.304 ± 0.014[a]
	0.67 ± 0.09 (lit.)[b]	0.22 ± 0.05 (lit.)[e]
	0.44 (lit.)[c]	0.25 ± 0.03 (lit.)[b]
	0.387 ± 0.030 (lit.)[d]	0.28 (lit.)[f]
MVK	0.152 ± 0.003[a]	0.273 ± 0.013[a]
	0.26 ± 0.06 (lit.)[b]	0.32 ± 0.07 (lit.)[e]
	0.17 (lit.)[c]	0.36 ± 0.04 (lit.)[b]
	0.159 ± 0.013 (lit.)[d]	0.44 (lit.)[f]

[a] Average yield obtained from isoprene oxidation experiments using GCC-IRMS in this study; error given is the standard error.
[b] Taken from Paulson et al. (1992).
[c] Taken from Grosjean et al. (1993).
[d] Taken from Aschmann and Atkinson (1994).
[e] Taken from Tuazon and Atkinson (1990).
[f] Taken from Sprengnether et al. (2002).

constants given in Table 1 are used. The ^{13}k rate constants were derived from ^{12}k rate constants and KIE ε values using the relationship: $^{13}k = {}^{12}k(1 + \varepsilon/1000‰)$. Epsilon values and the derived ^{13}k rate constants are also summarized in Table 1. Using integrated IRMS peak areas of m/z-44 signals and δ^{13}C values, the following

$$^{12}F_{C_4H_8O} = \left(\frac{^{12}k_{ISO} - {}^{12}k_{C_4H_8O}}{^{12}k_{ISO}} \right) \left[\frac{1 - ([^{12}ISO]_t/[^{12}ISO]_0)}{([^{12}ISO]_t/[^{12}ISO]_0)^{^{12}k_{C_4H_8O}/^{12}k_{ISO}} - ([^{12}ISO]_t/[^{12}ISO]_0)} \right] \quad (1)$$

and

$$^{13}F_{C_4H_8O} = \left(\frac{^{13}k_{ISO} - {}^{13}k_{C_4H_8O}}{^{13}k_{ISO}} \right) \left[\frac{1 - ([^{13}ISO]_t/[^{13}ISO]_0)}{([^{13}ISO]_t/[^{13}ISO]_0)^{^{13}k_{C_4H_8O}/^{13}k_{ISO}} - ([^{13}ISO]_t/[^{13}ISO]_0)} \right] \quad (2)$$

Here, C$_4$H$_6$O represents either MACR or MVK and thus four separate, isotope-specific correction factors were calculated: $^{12}F_{MACR}$, $^{13}F_{MACR}$, $^{12}F_{MVK}$, and $^{13}F_{MVK}$. As ^{12}k rate constants the literature rate

two equations can be used to calculate values for [^{12}VOC] and [^{13}VOC] (where VOC can be either ISO, MACR, or MVK) on a molecular basis:

Table 1
Summary of reactions, rate constants, and KIE ε values for ^{12}C- and ^{13}508 C-containing 509 isotopomers of isoprene, MACR, and MVK.

Reaction No.	Reactants	Products	Rate constants		ε, ‰
			Name	Value, cm^3 molecule^{-1} s^{-1}	
(R4)	^{12}ISO + O$_3$	^{12}MACR + ^{12}MVK + PROD	$^{12}k_{ISO+O_3}$	12.8×10^{-17} [a]	8.40 ± 0.11[b]
(R5)	^{12}MACR + O$_3$	PROD	$^{12}k_{MACR+O_3}$	1.08×10^{-18} [c]	8.38 ± 0.42[b]
(R6)	^{12}MVK + O$_3$	PROD	$^{12}k_{MVK+O_3}$	5.84×10^{-18} [c]	8.01 ± 0.07[b]
(R7)	^{12}ISO + OH	^{12}MACR + ^{12}MVK + PROD	$^{12}k_{ISO+OH}$	1.01×10^{-10} [a]	6.56 ± 0.12[d]
(R8)	^{12}MACR + OH	PROD	$^{12}k_{MACR+OH}$	3.35×10^{-11} [a]	6.47 ± 0.27[d]
(R9)	^{12}MVK + OH	PROD	$^{12}k_{MVK+OH}$	1.88×10^{-11} [a]	7.58 ± 0.47[d]
(R10)	^{13}ISO + O$_3$	MACR + MVK + PROD	$^{13}k_{ISO+O_3}$	1.259×10^{-17}	–
(R11)	^{13}MACR + O$_3$	PROD	$^{13}k_{MACR+O_3}$	1.071×10^{-18}	–
(R12)	^{13}MVK + O$_3$	PROD	$^{13}k_{MVK+O_3}$	5.794×10^{-18}	–
(R13)	^{13}ISO + OH	MACR + MVK + PROD	$^{13}k_{ISO+OH}$	1.003×10^{-10}	–
(R14)	^{13}MACR + OH	PROD	$^{13}k_{MACR+OH}$	3.328×10^{-11}	–
(R15)	^{13}MVK + OH	PROD	$^{13}k_{MVK+OH}$	1.866×10^{-11}	–

[a] Taken from Atkinson et al. (2006).
[b] Taken from Iannone et al. (2008).
[c] Taken from Grosjean and Grosjean (1998).
[d] Taken from Iannone et al. (2009).

$$[^{12}VOC] = \frac{1}{N_C}[^{12}C]_{VOC} - \left(\frac{N_C - 1}{N_C}\right)$$
$$\times \left[([^{12}C]_{VOC}R_{V-PDB})\left(\frac{\delta^{13}C_{VOC}}{1000‰} + 1\right)\right] \qquad (3)$$

and

$$[^{13}VOC] = [^{12}C]_{VOC}R_{V-PDB}\left(\frac{\delta^{13}C_{VOC}}{1000‰} + 1\right) \qquad (4)$$

where $[^{12}C]_{VOC}$ represents the VOC m/z-44 peak area, $\delta^{13}C_{VOC}$ represents the stable carbon delta value of the VOC, N_C represents the number of carbon atoms present in the VOC, and R_{V-PDB} is the absolute $^{13}C/^{12}C$ ratio of the V-PDB standard which is equal to 0.0112372 (Brand, 1996). The first term in Equation (3) represents $[^{12}C]$ from VOCs containing no ^{13}C atoms and the second term subtracts the small contribution toward the $[^{12}C]$ signal from the ^{13}C-containing VOC.

Upon obtaining $[^{12}VOC]$, $[^{13}VOC]$, and F values for every time interval t, corrected concentration values were obtained through multiplication with the appropriate F correction factor,

$$[^{12}MACR]_{t,corr} = {}^{12}F_{MACR}[^{12}MACR]_t \qquad (5)$$

$$[^{12}MVK]_{t,corr} = {}^{12}F_{MVK}[^{12}MVK]_t \qquad (6)$$

$$[^{13}MACR]_{t,corr} = {}^{13}F_{MACR}[^{13}MACR]_t \qquad (7)$$

$$[^{13}MVK]_{t,corr} = {}^{13}F_{MVK}[^{13}MVK]_t \qquad (8)$$

The corrected concentrations for MACR and MVK isotopomers were plotted against the change in either ^{12}ISO or ^{13}ISO ($-\Delta[^{12}ISO]$ or $-\Delta[^{13}ISO]$, respectively) for every measurement interval. Linear regression analyses provided slopes that represented the yields of each product isotopologue (Fig. 1 provides an example). The yields could then be used to determine the isotope enrichment factors $\varepsilon_{ISO \to MACR}$ and $\varepsilon_{ISO \to MVK}$ using the following equations:

$$\varepsilon_{ISO \to MACR} = \left(\frac{y_{12MACR}}{y_{13MACR}} - 1\right)1000‰, \qquad (9)$$

$$\varepsilon_{ISO \to MVK} = \left(\frac{y_{12MVK}}{y_{13MVK}} - 1\right)1000‰. \qquad (10)$$

An additional step is required to correctly determine the yields of MACR and MVK through the reaction of ISO with O_3 since unscavenged OH radicals will cause interference. Estimates for the yields of MACR ($^{O_3}y_{MACR}$) and MVK ($^{O_3}y_{MVK}$) solely by the reaction of $ISO + O_3$ were determined using the following general equation:

$$^{O_3}y_{C_4H_6O} = \frac{^{eff}y_{C_4H_6O}{}^{eff}k_{ISO}}{\left(^{OH}y_{C_4H_6O}/^{O_3}y_{C_4H_6O}\right)_{lit}{}^{OH}k_{ISO}\frac{[OH]}{[O_3]} + {}^{O_3}k_{ISO}} \qquad (11)$$

where $^{OH}y_{C_4H_6O,lit}$ and $^{O_3}y_{C_4H_6O,lit}$ are literature values for yields of MACR and MVK from the $ISO + OH$ and $ISO + O_3$ reactions, respectively. Yield values reported by Tuazon and Atkinson (1990) (OH experiments) and Aschmann and Atkinson (1994) (O_3 experiments) were used. The effective rate constant $^{eff}k_{ISO}$ was determined as the apparent rate of ISO loss through both O_3 and OH in the reaction system. The effective yields of MACR or MVK, $^{eff}y_{C_4H_6O}$, were determined for $^{12}C_4H_6O$ and $^{13}C_4H_6O$ species through a linear regression analysis of the corrected product concentrations against $-\Delta[ISO]$ for every interval of $t - t_0$. Values for $^{O_3}y_{12MACR}$, $^{O_3}y_{13MACR}$,
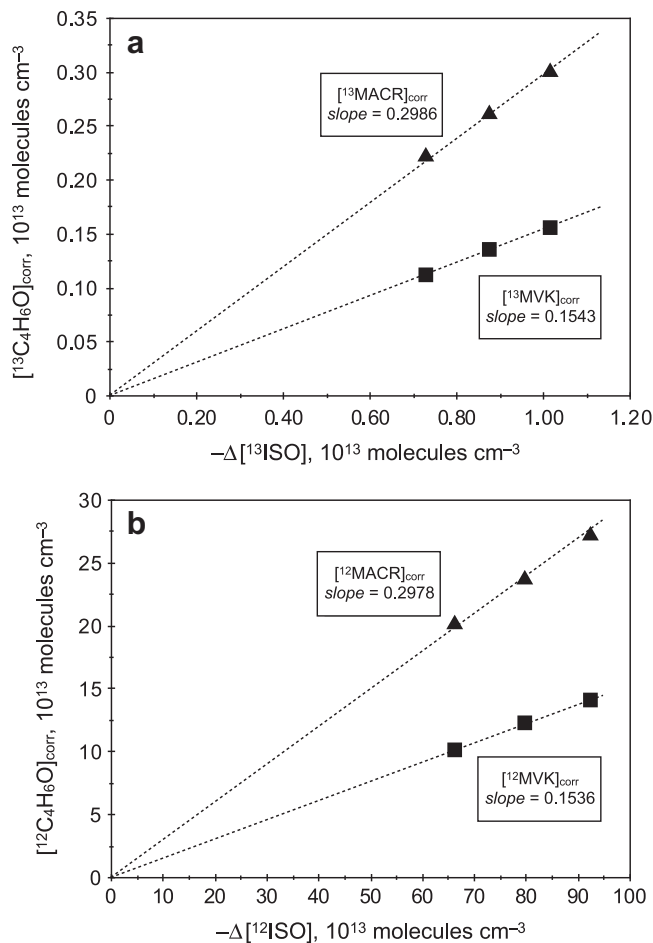

Fig. 1. Examples of plots used for the determination of corrected yields of $^{12}MACR$, ^{12}MVK (both graph a) and $^{13}MACR$, ^{13}MVK (both graph b) from the $ISO + O_3$ reaction. Fits from linear regression analyses were constrained through the origin since products are assumed to be directly associated with losses in isoprene.

$^{O_3}y_{12MVK}$, and $^{O_3}y_{13MVK}$ were averaged (standard error at the 2σ level was always $<0.1\%$) and the isotope enrichment factors $^{O_3}\varepsilon_{ISO \to MACR}$ and $^{O_3}\varepsilon_{ISO \to MVK}$ were then determined using Equations (9) and (10). ^{13}C enrichment values associated with the production of MACR and MVK from $ISO + OH$ and $ISO + O_3$ reactions are summarized in Table 3.

This enrichment is the result of a combination of different factors. For simplicity we will look at the formation of MVK, but the principle is the same for the formation of MACR. Due to the loss of a terminal carbon atom during the formation of MVK, the reaction of one of the ^{13}C-containing isoprene isotopomers will not result in the formation of ^{13}C-containing MVK, but in the formation of MVK containing no ^{13}C atoms. Of the remaining four isoprene isotopomers which form ^{13}C-containing MVK only the reaction of one of the isotopomers will result in the formation of MVK and at the same time be subject to a primary isotope effect. Therefore the isotope fractionation for the formation of MVK or MACR is lower than the KIE for the reaction of isoprene where only one of the possible five isotopomers is not subject to a primary isotope effect.

Another complication is the site-specific ^{13}C enrichment as the result of the reaction of isoprene. Due to the KIE for the reactions of isoprene with ozone or OH radicals, unreacted isoprene will become increasingly enriched in ^{13}C as the reaction progresses. However, the reactions of isoprene with ozone or OH nearly exclusively occur at the double bonds and, therefore, the enrichment of ^{13}C will occur

Table 3
Isotopomer yields and ^{13}C enrichment factors for MACR and MVK produced from the ISO + O$_3$ and ISO + OH reactions.

Experiment No.	Reaction	Product	y^{12}C$_4$H$_6$O	y^{13}C$_4$H$_6$O	(y^{12}C$_4$H$_6$O/y^{13}C$_4$H$_6$O)	^{13}C Enrichment, ‰
1	ISO + O$_3$	MACR	0.3173 ± 0.0008	0.3184 ± 0.0008	0.9967 ± 0.0016	3.3 ± 1.6
		MVK	0.1334 ± 0.0007	0.1339 ± 0.0007	0.9957 ± 0.0014	4.3 ± 1.4
2		MACR	0.2998 ± 0.0011	0.3008 ± 0.0011	0.9966 ± 0.0022	3.4 ± 2.2
		MVK	0.1688 ± 0.0014	0.1694 ± 0.0014	0.9965 ± 0.0028	3.5 ± 2.8
3		MACR	0.3427 ± 0.0012	0.3441 ± 0.0012	0.9959 ± 0.0024	4.1 ± 2.4
		MVK	0.1608 ± 0.0013	0.1617 ± 0.0013	0.9943 ± 0.0026	5.7 ± 2.6
1	ISO + OH	MACR	0.3043	0.3055	0.9962	3.8
		MVK	0.1766	0.1779	0.9930	7.0

predominantly at the double bond since the secondary isotope effects resulting from a ^{13}C atom at the methyl group are most likely too small to have a measurable impact. While it has been shown that typical naturally occurring site-specific isotope depletion or enrichment will only have a marginal impact on the KIEs for the loss reaction (Iannone et al., 2004), this is not necessarily correct for the impact of ^{13}C atoms at specific positions for the isotope ratios of reaction products. The analysis of the laboratory data presented above does not consider all of these details and is thus only a first-order approximation.

3.3. Isotope-specific kinetics model for isoprene ozonolysis

In order to evaluate the possible consequences of site-specific reactions and ^{13}C depletion or enrichment model simulations considering all isoprene isotopomers individually have been conducted. To examine the isotopic behavior of MACR and MVK during their production from the ISO + O$_3$ reaction, a set of coupled differential equations was developed to describe a simplified reaction system considering only the loss and production of the three VOCs, lumping all other products into one category (PROD). The resulting model accounts for total numbers of ^{12}C and ^{13}C atoms in isoprene, MACR, and MVK during reaction with O$_3$. The elaboration of the model is provided in the Supplementary Data section.

Measured concentration and δ^{13}C data are provided in Fig. 2 for two GCC-IRMS experiments. To present the data in a graph which is independent of the ozone concentration used in the model, the time axis was converted into an axis using the negative logarithm of the fraction of isoprene remaining.

There is generally close agreement between modeled and experimental results, but there are a few small deviations which deserve attention. The concentration data for MACR in the later part of the experiment are slightly, but consistently lower than the model results. This is the consequence of the presence of small, but not always negligible levels of OH radicals. The model does not include the impact of OH radicals and therefore the modeled concentrations for MACR, which has the highest value for the ratio of the OH rate constant over the O$_3$ rate constant, are somewhat overestimated by the model.

There are also noticeable deviations in δ^{13}C for MACR and MVK when their concentrations, and therefore also the corresponding peak areas, are very low. It is unlikely that this is due to errors in rate constants or yields used in the model since there is very good agreement for isotope ratios measured at higher concentrations. Most likely these differences are the result of the uncertainties in isotope ratio measurements for very small peaks.

Fig. 2 also includes a simplified model calculation predicting the MACR and MVK isotope ratios without differentiating between the various isotopomers, and using the yield data in Table 3 as averages representing the combined isotope enrichment from reactions of all isotopomers. The results of this calculation are similar, but not

completely identical to those using the complete model. Within the scatter of the experimental data, both approaches give a good description of the change of the MACR and MVK isotope ratios during the experiments.

The model results show nonlinearities in δ^{13}C for MACR and MVK that are especially pronounced during the period where isoprene experienced its greatest loss rate due to reaction with O$_3$. This is consistent with the overall change in δ^{13}C for MACR and MVK being the sum of three effects: (1) depletion of MACR and MVK in ^{13}C during their production due to the isoprene's likewise increase in ^{13}C abundance, (2) the change in the isotope ratio of
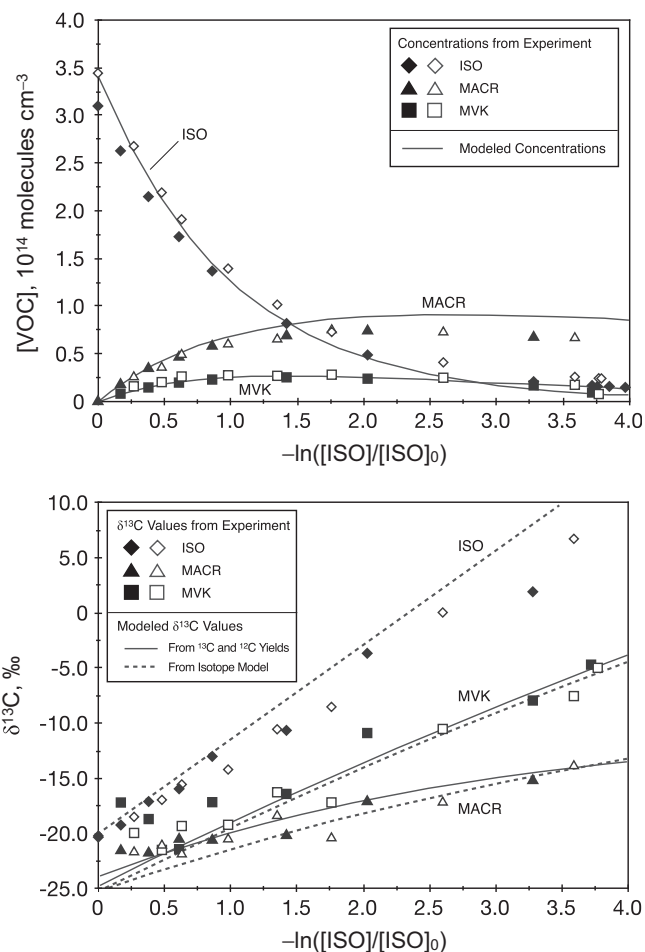

Fig. 2. Change in VOC concentration (top) stable carbon delta values (bottom) and during the O$_3$ oxidation of isoprene (diamonds), MACR (triangles), and MVK (squares) from two experiments (open and closed symbols). Solid lines represent expected concentrations and δ^{13}C values derived from the experimentally determined yields of ^{13}C and ^{12}C isotopomers of MACR and MVK. Dashed lines represent predictions of δ^{13}C values from the isotope-specific kinetics model.

MACR and MVK due to loss of a carbon atom during the formation of MACR and MVK from reaction of isoprene with ozone, and (3) isotopic fractionation due to the $MACR + O_3$ and $MVK + O_3$ reactions.

4. Conclusions

The carbon isotope ratios of MACR and MVK formed by the oxidation of isoprene by reaction with ozone or the OH radical are the result of several processes, which overall results in a potentially very complex behavior. The yield for ^{13}C-containing MACR and MVK from ^{13}C-containing isoprene is slightly higher than for the corresponding reactions of only ^{12}C containing isotopologues. This should not be confused with a faster formation. The ε values for reaction of isoprene with ozone and OH radicals are $(8.40 \pm 0.11)\%_0$ and $(6.56 \pm 0.12)\%_0$, respectively, as reported by Iannone et al. (2008, 2009). Combined, both effects result in a formation rate constant of heavy MACR and MVK which is a few per mille slower than that of light MACR or MVK.

The results of our laboratory experiments can be described by a basic model considering the reactions of all isotopomers. This gives confidence that the basic kinetic data derived and used in this work for describing carbon isotope enrichment or depletion provide the tools to use ambient measurements of the isotope ratio of MACR and MVK for the study of the oxidation of isoprene in the atmosphere. Moreover, a simplified, descriptive approach based on average experimentally determined yields for ^{13}C-containing MACR and MVK gives results which are very similar to the numerical simulation including all possible isoprene isotopomers containing a ^{13}C atom. This will allow incorporating prediction of isotope ratios as computationally efficient schemes in numerical modeling of isoprene and its oxidation products MACR and MVK.

Our model simulations do not take into account site-specific KIEs or site-specific ^{13}C enrichment or depletion, which may result in a potential bias for the interpretation of ambient measurements of the carbon isotope ratio of atmospheric MACR or MVK. Nevertheless, the good agreement between model calculations and experiments strongly suggests that any bias resulting from these simplifications is within the uncertainty of the currently known KIEs and the uncertainty of compound specific VOC isotope ratio measurements. The changes in isotope ratios resulting from reactions as well as the differences in isotope ratios between isoprene, MACR, and MVK are substantially larger than uncertainties form measurements and simplifications resulting from the necessity of using compound specific isotope ratios instead of isotopomer specific measurements.

Our model calculations and analysis of the laboratory data are based on a purely random distribution of ^{13}C atoms in isoprene at the beginning of the reaction. The good agreement between numerical simulations and experiments strongly suggests that this is a reasonable assumption for the batch of commercially available isoprene we used in the experiments. However, while there are several studies of the overall isotope ratio of isoprene emitted from vegetation, effectively nothing is known about the site-specific abundance of ^{13}C atoms in biogenic isoprene. In the absence of such information an evaluation of the resulting uncertainty for the isotope ratios of MVK or MACR formed from ambient isoprene would require laboratory studies using isoprene emitted from vegetation, which to our knowledge do not exist.

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Appendix. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2010.07.046.

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