Stable carbon isotopic compositions of light hydrocarbons over the western North Pacific and implication for their photochemical ages

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[1] Light hydrocarbons collected over the western North Pacific in canisters during an oceanographic cruise in May 1999 were analyzed for the mixing ratios and the stable carbon isotopic compositions (δ13C). Their mixing ratios decreased during the passage of a warm front. By contrast, they increased after the passage of a cold front. The δ13C values of ethane were found to be in a range of −26 to −19‰ and to be systematically heavier when the mixing ratios (range of 1.7–0.6 ppbv) became lower. The δ13C values of ethane over the open ocean generally showed heavier values than those previously reported in the source regions, suggesting an isotopic fractionation during a long-range atmospheric transport. In contrast, δ13C values of i- and n-butanes varied in a wide range (−37 to −16‰ and −37 to −21‰, respectively); however, their averaged values are comparative to the isotopic source compositions. Likewise, no systematic relationships were found between the mixing ratios and the δ13C values of the butane isomers. For n-butane the observed relationship was substantially different from that predicted by kinetic isotope effect by the reaction with OH radicals probably due to the contribution of effective mixing process. From the changes in the δ13C values for ethane and n-butane the averaged photochemical ages were calculated to be 49 ± 26 days and 2 ± 6 days, respectively. The difference in the estimated ages is attributed to the different reactivity of hydrocarbons. The average ages for n-butane were found to be consistent with numbers of days, which the air mass took for the transport from the continent to the sampling site over the ocean, on the basis of backward trajectory analysis. This study suggests that the photochemical ages are useful for assessing the importance of recent emission in the marine atmosphere.

INDEX TERMS: 0365 Atmospheric Composition and Structure: Troposphere-composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere-constituent transport and chemistry; 4820 Oceanography: Biological and Chemical: Gases; 9320 Information Related to Geographic Region: Asia; 9355 Information Related to Geographic Region: Pacific Ocean; KEYWORDS: light hydrocarbons, carbon isotopic compositions, marine boundary layer, photochemical age, kinetic isotope effect, western North Pacific

1. Introduction

[2] Light hydrocarbons are ubiquitous in the troposphere at concentrations ranging from a few parts per billion by volume (ppbv) to a few parts per trillion by volume (pptv). They play an important role in the troposphere as a sink of OH radicals and as a source of photochemical oxidants (e.g., ozone) and polar organic compounds (e.g., acetaldehyde, peroxyacetyl nitrate, and acetic acid). Further, light hydrocarbons of anthropogenic origin have been used as valuable atmospheric tracers to better understand the source strength and transport processes of air masses. A difference in the reaction rate constants among individual hydrocarbons has also been used, coupled with the measured concentrations of light hydrocarbons, to estimate the OH-radical concentrations in the atmosphere [e.g., McKeen et al., 1990] and/or to understand the evolution of air masses [e.g., Blake et al., 1996a]. However, many uncertainties still remain concerning the source strength, distributions, and sinks of light hydrocarbons in the atmosphere, especially over the open ocean.

[3] Recently, the on-line gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) method has been applied to measure the carbon isotopic ratios for individual volatile organic compounds (VOCs) at pptv and ppbv levels in the atmosphere [Rudolph et al., 1997]. They reported a wide range of δ13C values for the VOCs, indicating that their stable carbon isotopic compositions can be used as a tool to complement their concentration measurements and to better our understanding of the processes governing the distribution of VOCs in the atmosphere. Tsunogai et al. [1999] measured δ13C values for C2-C3 hydrocarbons and methyl chloride in urban, coastal, and marine atmosphere and reported that δ13C values of ethane are inversely correlated to its concentrations in the coastal and remote marine atmosphere. They reported that there is a significant isotope fractionation during the reaction of ethane with OH radicals. Very recently, Rudolph et al. [2000] reported laboratory studies on the kinetic isotope effects (KIE) for the reactions of selected hydrocarbons with OH radicals. Furthermore, Rudolph and Czuba...
were transported to the laboratory for the analysis. Contamination prior to use. Canister samples (45 total samples) were measured using a cryogenic vacuum extraction line and a stainless steel canister. The standard deviation of the mean was estimated to be better than 0.3% for injections >100 pmol C and <4% for 20 pmol C. All of the measurements of δ13C of ethane, i-butane, and n-butane were performed for 27 samples out of 45 canister samples.

[4] In this study, we report the stable carbon isotopic compositions of light hydrocarbons (including ethane, i-butane, and n-butane) over the western North Pacific, where continental outflow from Asia and Eurasia is an important factor in controlling the trace atmospheric composition and photochemical processes. The purposes of this study were (1) to observe the temporal variations of the mixing ratios and δ13C values for light hydrocarbons over the western North Pacific, (2) to assess the influence of sources, sinks, and mixing processes on the mixing ratios and δ13C during long-range transport over the western North Pacific, and (3) to assess the consistency of the averaged ages of individual hydrocarbons with the ages of air masses estimated from the backward trajectory analysis.

2. Experiments

2.1. Air Sampling

Fresh air was taken in a 6-L fused silica-lined stainless steel canister (SilicoCan, Restek Co., Ltd.) during a cruise of R/V Mirai (Japan Marine Science and Technology Center), 8–31 May 1999. The ship track is illustrated in Figure 1. Air samples were collected on a compass deck of the ship at an elevation of ~30 m above sea level. Air was taken in the canister when winds were coming from the ship bow in order to avoid possible contamination from the ship itself. The canisters were carefully prepared in the laboratory by rinsing with the humidified, ultrapure-grade nitrogen and by evacuating at elevated temperatures of ~100°C to eliminate the contamination prior to use. Canister samples (45 total samples) were transported to the laboratory for the analysis.

Ozone mixing ratios were measured on board using an ozone meter (model 1150, Dyleck). The air was sucked into the ozone meter through a Teflon tubing (10 m long, 1/4 in ID), which is connected to the inlet located on the compass deck.

2.2. Analysis

Stable carbon isotopic compositions of light hydrocarbons were measured using a cryogenic vacuum extraction line and GC/C/IRMS based on the work by Rudolph et al. [1997]. A complete description of the system design, operation, and performance of the combustion and IRMS interface was described by Tsunogai et al. [1999]. Light hydrocarbons in the canister samples were preconcentrated using a three-stage cryofocusing system. The sample air was passed through the first trap, which is composed of a 1/4-in stainless steel tube packed with porous glass beads immersed in liquid nitrogen. In order to introduce most of the sample air to the first trap, the canister was flushed three times by using ultrapure helium. The first loop was then heated by using hot water, and the sample was flushed with ultrapure helium and was passed through a glass tube filled with a magnesium perchlorate [Mg(ClO4)2] and Ascarite II to remove a moisture and carbon dioxide. In the second trap, consisting of a 1/16-in stainless steel tube cooled with liquid nitrogen, light hydrocarbons were condensed again. The second trap was then heated in order to inject the samples onto a short length (~20 cm) capillary column, while the column was immersed in a liquid nitrogen bath. The column was then flash-heated by using hot water, and the thermally desorbed light hydrocarbons were transferred to the separation column of Pora PLOT Q-HT (25 m long, 0.32 mm ID; Chrompack) in the GC oven (Hewlett-Packard 6890). The stable carbon isotopic ratios of the individual light hydrocarbons were measured on an IRMS (Finnigan MAT 252) following the on-line oxidation of light hydrocarbons to CO2. The δ13C measurements for ethane, i-butyne, and n-butane were performed for 27 samples out of 45 canister samples.

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[8] Precision of the isotopic measurements, which is calculated from the standard deviation of the mean value by measuring a working standard in a various volume, depended mainly on the carbon size of the sample analyzed. The working standard mixture, containing 1–10 ppmv hydrocarbons, was made from the ambient air in our laboratory and was contained in a stainless steel canister. The standard deviation of the mean was better than 0.7‰ for injections >100 pmol C and <4‰ for 20 pmol C. All of the measurements of δ13C of ethane were conducted with the analytical precision less than ± 0.7‰. For i-butyne and n-butyne most of the samples were measured with analytical precision less than ± 4‰. The accuracy of the isotopic measurements was estimated to be better than 0.3‰ versus Pee Dee belemnite (PDB) by measuring an isotopic standard made from the National Institute of Standards and Technology (NIST) RM 8560 (International Atomic Energy Agency (IAEA) NGS2) standard. We do not report propane data here because of
3. Results and Discussion

3.1. Variation of Light Hydrocarbons and Ozone

[10] Figure 2a presents the ship location as latitude (in degrees north) and longitude (in degrees east). Figures 2b–2d give variations in the mixing ratios of ethane, i-butane, n-butane, as well as their carbon isotopic compositions as a function of sampling dates. Relatively high mixing ratios were obtained for ethane throughout the cruise (1.42 ± 0.30 ppbv). They were relatively constant from 8 to 19 May. However, a significant change of the mixing ratios was found from 20 to 23 May. Especially, a drastic decrease in the ethane mixing ratios was detected around 140°N and 165°E on 21 May. This decrease seems to coincide with the passage of a surface weather front, which is shown in the weather map (see Figure 3). On 20 May a warm front was located on the east of the sampling site (Figure 3a). When the front passed through the sampling site (Figure 3b), the surface temperature and dew point increased drastically (Figure 4), and the field site came under the influence of a subsaturnal air mass in which ethane mixing ratios are generally lower [Donahue and Prinn, 1993]. On the contrary, after the passage of a cold front (Figure 3c), both temperature and dew point showed a sharp drop, whereas the ethane mixing ratios increased from 22 May.

[11] The temporal variations of the mixing ratios of i-butane and n-butane (Figures 2c and 2d) are somewhat similar to that for ethane, but the change in the mixing ratios of butane isomers are more pronounced than that of ethane, similar to the previously published results [Singh et al., 1988; Rudolph and Johnen, 1990; Kopppmann et al., 1992; Saito et al., 2000]. Average mixing ratios of i-butane and n-butane are 0.04 and 0.06 ppbv, respectively, which are comparable with the previously reported results in the similar latitudes and season from the North Atlantic Ocean [Rudolph and Johnen, 1990].

[12] Ozone mixing ratios are shown in Figure 2c. Relatively high ozone mixing ratios were observed throughout the cruise. Averaged mixing ratio of ozone was 50.4 ± 1.1 ppbv. Figure 2c shows that the frontal passage also affected the ozone concentrations. Drastic changes in the mixing ratios of trace gases associated with the frontal passages have been observed in the atmosphere [Singh et al., 1988; Koppmann et al., 1998]. Singh et al. [1988] pointed out that the frontal system and upper level trough are associated with downward transport of stratospheric ozone, which could account for the high ambient ozone concentrations after the cold frontal passage. However, the mixing ratios of ethane, a continually derived compound, increased after the cold front passage on 22 May. Further, the mixing ratios of the short-lived compounds (butane isomers) also increased during this period. Thus we argue that after the frontal passage the ozone and light hydrocarbons over the sampling site were influenced by a long-range transport of continental air mass.

3.2. Relationship Between Mixing Ratios and Carbon Isotopic Compositions

[13] Isotopic compositions of ethane ranged from −19 to −26‰ (see Figure 2c). When a drastic decrease of mixing ratios from 1.4 to 0.6 ppbv was found on 20 May before the passage of a cold front, in the warm and wet sector the δ13C values show an increase from −23 to −19‰. Conversely, when the mixing ratios increased from 0.6 to 1.8 ppbv on 22 May in the cold sector immediately after the frontal passage, the δ13C values decreased from −19 to −25‰. These δ13C values are heavier than those previously reported in the urban, coastal, fossil fuel combustion, and biomass-burning sources [Rudolph et al., 1997; Tsunogai et al., 1999]. The isotopic variations of i-butane and n-butane are from −37 to −16‰ and −37 to −21‰, respectively. These isotopic compositions were found to be similar to or heavier than those in the sources (−24 to −33‰ for i-butane and −25 to −30‰ for n-butane) [Rudolph et al., 1997; Tsunogai et al., 1999], except for very light δ13C for two samples collected on 23 May (−37‰ for i-butane) and 20 May (−37‰ for n-butane).

[14] The change in the δ13C values of the light hydrocarbons should be explained by the KIE during the degradation of the hydrocarbons in the atmosphere as well as by the mixing of air masses with different isotope compositions. Figure 5 illustrates the relations between mixing ratios and δ13C of ethane, n-butane, and i-butane. A good relationship was found between the mixing ratios of ethane and its δ13C values, indicating that the δ13C systematically becomes heavier as the mixing ratio decreases.

[15] A similar relationship has been reported in the coastal atmosphere and maritime atmosphere over the western North Pacific in winter [Tsunogai et al., 1999]. Rudolph et al. [2000] reported the KIEs for the reactions of the various hydrocarbons (including n-alkanes, alkenes, dienes, benzene, and acetylene) with OH radicals. They reported that δ13C values of the hydrocarbons increase as a result of preferential attack of OH radicals on hydrogen atoms in molecules consisting of 12C only. However, there is no KIE value reported for the reaction of ethane with OH, even though the value was estimated to be <6‰ (−4−5‰) on the basis of mass dependence of the collision frequency found in the measured KIEs for the other higher homologues (propane, n-butane, and hexane) and the difference of the activation energy in the hydrogen abstraction by OH radicals from n-alkanes [Rudolph et al., 2000]. Assuming the Rayleigh dependence between mixing ratios and δ13C values, the estimated KIE is presented in Figure 5a. The relationship observed between the mixing ratios, and δ13C values for ethane are similar to the trend predicted by the estimated KIE. However, most of the data points are located in the upper right side of the estimated KIE lines (Figure 5a). As already pointed by Rudolph et al. [2000], the estimated KIE for ethane may have significant uncertainties. The difference is probably explained by the variability of the isotopic source compositions as well as by the uncertainties of the estimated KIE, although we cannot rule out the possible contribution of other oxidative species (e.g., chlorine atoms) with different KIE from that of OH radicals.

[16] In contrast to ethane, no correlation is found between the mixing ratios and δ13C values of i-butane (Figure 5b) (the correlation coefficient is 0.28 for i-butane). The averaged δ13C value for i-butane of −27‰ is lighter than that for ethane (−23‰) in the marine atmosphere (Figure 5c). To our knowledge, there are no reported studies of the KIE for the reaction of i-butane with OH radicals. Rudolph et al. [2000] discussed the relationship between the chemical structures of n-alkanes and their isotopic effects in detail. Furthermore, the relationship of n-alkanes with OH radicals are connected with the C-H bond strength, which relies on whether the hydrogen is primary, secondary, or tertiary.
Figure 2. Temporal variations of (a) ship location presented by latitude and longitude and measured mixing ratios (solid circles) of (b) ethane, (c) i-butane, (d) n-butane, and (e) ozone, with their carbon isotopic compositions (open circles). The shaded areas indicate the range of the averaged $^{13}$C with 1-sigma uncertainty for the light hydrocarbons from the urban, car exhaust, and biomass burning [Rudolph et al., 1997; Tsunogai et al., 1999]. PDB, Peedee belemnite.
Note that i-butane has one tertiary hydrogen atom in addition to nine primary hydrogen atoms, and the reaction of i-butane with OH radicals proceeds primarily by the abstraction of tertiary hydrogen atom [e.g., Warneck, 1988]; hence it is expected that the KIE for the reaction of i-butane with OH radicals differs from that for n-butane. Laboratory studies for isotopic fractionation in the degradation of branched alkanes are clearly required to characterize the isotopic variations of i-butane in the atmosphere.

[17] For n-butane the relationship between the mixing ratios and its $\delta^{13}C$ values in urban and marine atmosphere is quite different from that predicted for the KIE of $2.8 \pm 0.3\%_o$ in the reaction of n-butane with OH radicals [Rudolph et al., 2000]. Furthermore, the $\delta^{13}C$ values ($-26.6 \pm 3.3$) are comparable with those in the urban atmosphere, being similar to the case of i-butane. At a glance it seems that the removal process for n-butane does not affect the mixing ratios and the $\delta^{13}C$ values. However, it should be noted that the Rayleigh dependence neglects the effect of mixing process on the relationship between mixing ratios and the $\delta^{13}C$ values. As pointed out by Rudolph et al. [2000], an impact of mixing and dilution processes can be inferred by the rearranged Rayleigh equation, which is described as:

$$C_i/C_t = \exp \left[ \left( \frac{\delta^{13}C_i - \delta^{13}C_t}{\delta^{13}C_{KIE}} \right) \right], \quad (1)$$

where $C_i$ and $C_t$ are the initial and temporal mixing ratios, respectively. Likewise, $\delta^{13}C_i$ and $\delta^{13}C_t$ are the initial and temporal carbon isotopic compositions, respectively, and $\delta^{13}C_{KIE}$ is the kinetic isotope effect for the reaction of light hydrocarbons with OH radicals.

[18] Assuming that $\delta^{13}C$ values do not vary due to the mixing and dilution processes but vary by the removal process driven by the OH radicals, we can calculate the idealized change of the concentration ratios ($C_i/C_t$) solely by the removal process from the difference between the observed $\delta^{13}C$ values over the ocean and those in the urban atmosphere. The calculated and observed concentration ratios for ethane agree on an average basis (Figure 6). In contrast, the calculated ratio for n-butane is lower than the observed one. However, the mixing of the studied air mass with the background air containing meaningful amounts of hydrocarbons must result in changing the $\delta^{13}C$ values. The mixing effect on the $\delta^{13}C$ values for ethane ought to be superior to that for n-butane because the lower reactivity of ethane to OH radicals leads to an enhanced accumulation of ethane in the atmosphere for a long period of time. Therefore the agreement found in the concentration ratios for ethane seems due not only the result of removal process, but also to the result of the effective mixing process. For n-butane the difference between the calculated and the observed values is likely to be the result of mixing of the studied air mass with near-zero background air. Consequently, we conclude that the difference in the observed and predicted relationship between the mixing ratios and $\delta^{13}C$
values for \(n\)-butane is mainly caused by the mixing process, as already pointed out by Rudolph et al. [2000].

### 3.3. Average Ages of Light Hydrocarbons and Air Mass Ages

As proposed by Rudolph and Czuba [2000], a method to estimate the averaged photochemical age of ambient hydrocarbons from the change of the \(\delta^{13}C\) is a unique feature, where the estimated age is a weighted average and is independent of the mixing of air masses with different photochemical ages. They applied the method to the data set obtained in the urban atmosphere in Canada [Rudolph et al., 2000]. Here we apply the method to the isotopic measurements performed in the marine boundary layer (MBL) and then compare the estimated age of light hydrocarbons with different reactivity with the air mass age inferred from the results of backward trajectory analysis.

The change in the \(\delta^{13}C\) of light hydrocarbons accompanied with the reaction by OH radicals can be rearranged [Rudolph and Czuba, 2000]

\[
\tau_{av} = \frac{(\delta^{13}C_i - \delta^{13}C_t)}{[\delta^{13}C_{KIE} k (OH)]},
\]

where \(\tau_{av}\) is the average age of hydrocarbon, \(\delta^{13}C_t\) is temporal isotopic composition in the atmosphere, \(\delta^{13}C_i\) is the averaged initial isotopic composition in sources, \(\delta^{13}C_{KIE}\) is the kinetic isotopic effect for the reaction of hydrocarbon with OH radicals, \(k\) is the rate constant for the reaction between hydrocarbon and OH radicals, and \((OH)\) is the average OH radical concentration.

The uncertainty of calculated average age depends on the accuracy of the KIEs [Rudolph and Czuba, 2000]. Because temperature dependences of KIEs are unknown for \(n\)-butane as well as for other hydrocarbons, KIE at around ambient temperature is used in this calculation [Rudolph et al., 2000]. For ethane we use the estimated KIE of 4–5\%, although the uncertainty might be substantial [Rudolph et al., 2000]. In addition to the error of KIE, the uncertainties of the isotopic measurements and the variability of the initial isotopic compositions can cause the uncertainties of derived averaged age. The uncertainties of the measurements are estimated to be 0.7\% for ethane and 1.5–4.0\% for \(n\)-butane, as

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**Figure 5.** Mixing ratios versus \(^{13}C\) plots for (a) ethane, (b) \(i\)-butane, and (c) \(n\)-butane in the marine atmosphere (open circles) and the urban atmosphere (solid circles) reported by Tsunogai et al. [1999]. The open squares indicate the averaged mixing ratios and isotopic compositions in the urban atmosphere. The dashed lines in Figure 5a indicate the estimated upper and lower limits of kinetic isotope effects (KIE) in the reaction with OH radicals [Rudolph et al., 2000]. The solid and dashed lines in Figure 5c indicate an average and 1 d of the KIE in the reaction with OH radicals, respectively [Rudolph et al., 2000].

**Figure 6.** Comparison of (a) ethane and (b) \(n\)-butane concentration ratios for observations (solid circles) and Rayleigh model results (open circles). The error bars indicate lower and upper concentration ratios.
described in section 2.2. The basic assumption of the method is that the isotopic compositions of hydrocarbon in sources do not vary significantly. We use the average and the standard deviation of the previously published $\delta^{13}C$ values in urban, car exhaust, and biomass-burning sources [Rudolph et al., 1997; Tsunogai et al., 1999]. The rate constants and their temperature dependence for the reaction with OH radicals are taken from Atkinson [1997]. The OH radical concentration is assumed to be $10^6$ cm$^{-3}$ for 40–50$^\circ$C, [e.g., Spivakovsky et al., 2000].

In order to compare the derived age with the actual age of air mass, we need to assume that local sources of ethane and $n$-butane, i.e., oceanic emissions, do not contribute significantly to the observed $\delta^{13}C$ values during long-range transport from their source regions over the continents to the ocean. The emissions of light hydrocarbons from the oceans have been studied [Bonsang et al., 1988; Plass et al., 1992; Plass-Dülmer et al., 1993; Donahue and Prinn, 1993], and the ethane emissions from the open oceans were estimated to be $\sim0.2$ Tg/yr, which correspond to 1% of the global emissions of ethane [Rudolph, 1995]. The oceanic emissions were estimated to contribute <1 pptv for ethane [Wingenter et al., 1996] or <10 pptv for ethane and $n$-butane in the atmosphere [Rudolph and Johnen, 1990], which correspond to <1% and 20% of the average mixing ratios of ethane and $n$-butane observed in this study, respectively.

Figure 7 shows the average ages calculated from the changes in $\delta^{13}C$ values for ethane and $n$-butane. The mean ages (49 days) for ethane are significantly longer than those for $n$-butane (2 days). The ethane ages varied between 9 and 96 days, with standard deviations ranging from 12 to 16 days. Qualitatively, the difference in the calculated ages for ethane and $n$-butane can be explained by the difference of their reactivity to OH radicals (see section 3.2). The results of the backward trajectory analysis in several cases are shown in Figure 8. We conducted a 10-day backward trajectory analysis at 500, 1500, and 3000 m. As shown in Figure 8a, the trajectory analysis at 44$^\circ$N, 155$^\circ$E on 13 May, 2200 LT, indicates that the air came to the sampling location from east Asia within 1–2 days. During the period of 13–14 and 28–30 May the trajectories for eight samples were similar to each other, which are consistent with the very short ages derived from the change of $\delta^{13}C$ values for $n$-butane in this period ($\sim2 \pm 2$ days, one standard deviation of the mean), while ethane shows a long and variable age of $25 \pm 12$ days.

Figure 7. Average ages of (a) ethane and (b) $n$-butane estimated from the $^{13}C$ values in Figure 2. The error bars indicate the overall uncertainties calculated from the uncertainties of the KIEs and isotopic source compositions using the propagation of error technique.

Figure 8. Ten-day backward trajectories arriving over the sampling locations at heights of 500, 1500, and 3000 m on (a) 13 May, 2200 LT, (b) 15 May, 2100 LT, (c) 17 May, 1000 LT, (d) 21 May, 2000 LT, and (e) 22 May, 0800 LT. The open symbols (triangles for 500 m, squares for 1500 m, and circles for 3000 m) on each trajectory indicate locations at daily intervals. The lower plots show the altitude changes of the air masses during 10 days for the individual trajectories. The trajectories were calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT 4) model. (Data available at http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, Maryland.) Sampling locations are marked with solid stars.
In contrast, for the dates between 15 and 20 May, most trajectories indicate that the air has reached over the eastern part of Siberia and/or Kamchatka Peninsula 2–4 days before (Figure 8b). Again, the averaged ages for n-butane (5 ± 4 days), which were calculated for the air samples collected during the period except for one sample whose δ13C is obviously less than those for the source, are consistent to the results of the backward trajectory analysis. On the other hand, the trajectories on 17 May indicate that air was circulating over the northern North Pacific and the Bering Sea for at least the preceding 10 days (Figure 8c). The derived ages for n-butane (6 ± 2 days) are shorter than those from the trajectories. In both cases, between 15 and 20 May, ethane shows the long ages of 46 ± 6 days. These results suggest that the calculated ages for ethane reflect the weighted average age during the long-range transport in continental or hemispheric scale, but the ages for n-butane reflect the recent input sensitively.

During the passage of front on 21 May, hydrocarbon-depleted air that was characterized by high surface temperature, and high dew point was observed as described above (see Figures 2 and 4). The trajectories at 500 m demonstrate that the air masses originate from the southeast (Figure 8d). During this event the ages for ethane are extremely long (94 ± 2 days), longer than the estimated global average atmospheric lifetime of ethane (78 days) [Blake et al., 1996b]. However, the long ages may be overestimated because of the higher concentrations of OH radicals in the tropical or subtropical regions than the assumed OH concentrations [e.g., Spivakovsky et al., 2000]. The ages of n-butane range from 0 to 10 days, suggesting that n-butane was occasionally influenced by the emission followed by the advection in the subtropical to western North Pacific region. After the passage of the front the wind direction shifted to the west, and the continental air masses were advected from the east Asian region to the sampling location instantaneously (Figure 8e). Such short ages (14 days for ethane and <0 days for n-butane) may suggest an important emission source of hydrocarbons in east Asia. This also suggests that the averaged age of n-butane is a good indication of the actual age of air masses with an influence of continental outflow.

For the calculation we used the initial δ13C values reported in urban atmosphere [Tsunogai et al., 1999] as well as in individual emission sources [Rudolph et al., 1997]. Since the light hydrocarbons deplete even in urban atmosphere with time emitted from the sources [Rudolph et al., 2000], the δ13C values reported in the urban atmosphere should have already been affected by the reaction with OH radicals. The effect of this factor on the estimation of the ages can be seen for several samples, where the estimated ages for n-butane are <0. Nevertheless, the estimated ages based on the changes in δ13C are somewhat consistent to the results of backward trajectory analysis, demonstrating a significant impact of light hydrocarbon emission in east Asia on the budget of hydrocarbons in the marine atmosphere of the western North Pacific. Further investigations of emission sources as well as KIEs in the reaction with OH radicals are clearly required to improve the accuracy and precision of this method for the estimation of the photochemical ages of light hydrocarbons.

4. Summary and Conclusions

Light hydrocarbons in air samples collected over the western North Pacific show a wide variation of mixing ratios and δ13C of light hydrocarbons. The δ13C values of ethane become systematically heavier from −26 to −19‰, inversely proportional to the logarithm of the mixing ratios (1.7–0.6 ppbv). Most of the δ13C values are heavier than those previously reported in the urban and coastal air in Japan, suggesting that ethane over the western North Pacific is transported long distances from such anthropogenic source regions in the continents (e.g., east Asia). Also, i-butane
and n-butane displayed a wide variation in $^{13}$C ($-37$ to $-1\%$ for i-butane and $-37$ to $-21\%$ for n-butane), which does not correlate with the variation in the mixing ratios. By comparing the observed and calculated concentration ratios of light hydrocarbons, a mixing process is suggested to be important for observed concentration ratios of n-butane. The changes in the $^{13}$C values of ethane and n-butane are used to estimate the mean photochemical ages. The $^{13}$C-based ages for ethane are always longer than those for n-butane. The differences in the estimated ages may be attributed to the difference of the reactivity of hydrocarbons to OH radicals. The average ages for n-butane are consistent to the results of the backward trajectory analysis, suggesting that the ages are useful for assessing the importance of recent emission in the marine atmosphere.

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