Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 73 (2009) 7076–7086

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Equilibrium $^{2}H/^{1}H$ fractionations in organic molecules. II: Linear alkanes, alkenes, ketones, carboxylic acids, esters, alcohols and ethers

Ying Wang[a,*], Alex L. Sessions[a], Robert J. Nielsen[b], William A. Goddard III[b]

[a] *Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA*
[b] *Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA, USA*

Received 9 March 2009; accepted in revised form 20 August 2009; available online 23 August 2009

Abstract

Equilibrium $^{2}H/^{1}H$ fractionation factors (α_{eq}) for various H positions in alkanes, alkenes, ketones, carboxylic acids, esters, alcohols, and ethers were calculated between 0 and 100 °C using vibrational frequencies from ab initio QM calculations (B3LYP/6-311G**). Results were then corrected using a temperature-dependent linear calibration curve based on experimental data for H_{α} in ketones (Wang et al., 2009). The total uncertainty in reported α_{eq} values is estimated at 10–20‰. The effects of functional groups were found to increase the value of α_{eq} for H next to electron-donating groups, e.g. —OR, —OH or —O(C=O)R, and to decrease the value of α_{eq} for H next to electron-withdrawing groups, e.g. —(C=O)R or —(C=O)OR. Smaller but significant functional group effects are also observed for H_{β} and sometimes H_{γ}. By summing over individual H positions, we estimate the equilibrium fractionation relative to water to be −90‰ to −70‰ for *n*-alkanes and around −100‰ for pristane and phytane. The temperature dependence of these fractionations is very weak between 0 and 100 °C. Our estimates of α_{eq} agree well with field data for thermally mature hydrocarbons ($\delta^{2}H$ values between −80‰ and −110‰ relative to water). Therefore the observed $\delta^{2}H$ increase of individual hydrocarbons and the disappearance of the biosynthetic $\delta^{2}H$ offset between *n*-alkyl and linear isoprenoid lipids during maturation of organic matter can be confidently attributed to H exchange towards an equilibrium state. Our results also indicate that many *n*-alkyl lipids are biosynthesized with $\delta^{2}H$ values that are close to equilibrium with water. In these cases, constant down-core $\delta^{2}H$ values for *n*-alkyl lipids cannot be reliably used to infer a lack of isotopic exchange.

1. INTRODUCTION

Compound-specific hydrogen isotope analysis has become widespread over the past decade and has led to a variety of studies using the H isotopic composition ($\delta^{2}H$ value) of sedimentary organic matter (SOM) and oils as paleoenvironmental proxies (Xie et al., 2000; Huang et al., 2002; Dawson et al., 2004; Sachse et al., 2006). However, such applications implicitly assume the preservation of biosynthetic isotopic compositions over geological timescales, and therefore must address the exchangeability of C-bound H (Sessions et al., 2004). A recent review of field data (Schimmelmann et al., 2006) shows that, as thermal maturity increases, $\delta^{2}H$ values of individual hydrocarbons steadily increase while the typical 100‰ biosynthetic offsets between linear and isoprenoid structures (Sessions et al., 1999) steadily disappear. Furthermore, this systematic change in $\delta^{2}H$ values is negligible where the hydrocarbons are ^{2}H-depleted relative to water by 80–110‰ (typically associated with very high maturity) and is more apparent where the depletion is smaller or larger (dos Santos Neto and Hayes, 1999; Lis et al., 2006). These observations can

---

[*] Corresponding author. Present address: Division of Geological and Planetary Sciences, California Institute of Technology, Mail Code 100-23, 1200 East California Blvd., Pasadena, CA 91125, USA. Tel.: +1 626 200 5850.
E-mail address: ywjojo@gps.caltech.edu (Y. Wang).

0016-7037/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.gca.2009.08.018

potentially be explained by H exchange between hydrocarbons and sediment porewater and imply that the endpoint of exchange results in fractionations between hydrocarbons and water in the range of $-80‰$ to $-110‰$ (Schimmelmann et al., 2006). Testing this hypothesis requires quantitative knowledge of the equilibrium $^2H/^1H$ fractionation factors (α_{eq}).

Currently, accurate values of α_{eq} are not known for fractionations involving organic molecules larger than methane. This primarily reflects the difficulties involved in measuring equilibrium fractionations in organic materials: experimental studies suffer from very slow exchange rates of C-bound H (Koepp, 1978; Sessions et al., 2004), while theoretical calculations incorporate potential systematic errors that are particularly limiting for the H-isotope system (Richet et al., 1977). Knyazev et al. (1992) systematically calculated β factors for various H positions in major organic compounds. The results were later modified by Sessions et al. (2004) who incorporated the vapor pressure isotope effect to give α_{eq} values in aqueous phase at 27 °C, but the estimated systematic errors amount to ±100‰, far too large to be useful for studies of natural-abundance isotopic variations.

To address these issues, we developed a calibration based on α_{eq} values measured via isotope exchange experiments to correct theoretical estimates using frequencies calculated by the B3LYP/6-311G** method. Details of that calibration are provided in a companion paper (Wang et al., 2009), where we show that α_{eq} values for H_α in various linear ketone molecules can be calculated with uncertainties <8‰ for temperatures between 0 and 100 °C. Here we apply the same computational methods and calibration to systematically estimate α_{eq} values for H positions in other common organic compounds, including alkanes, alkenes, carboxylic acids, esters, alcohols, and ethers. In doing so, our goal is to provide a modular dataset for equilibrium $^2H/^1H$ fractionations in organic moieties common to sedimentary organic matter, in a form that can be used to piece together estimated fractionation factors for any complete molecule without resorting to further molecular modeling. As a demonstration of this approach, we calculate α_{eq} values for *n*-alkane and linear isoprenoid molecules and discuss the implications of those values to paleoenvironment and petroleum studies.

2. METHODS AND NOMENCLATURE

Methods for ab initio calculations are described fully in the companion paper (Wang et al., 2009) and only briefly here. Complete vibrational frequencies for selected organic molecules were calculated for the optimized geometries using the hybrid Hartree–Fock and Density Functional Theory (DFT), B3LYP/6-311G** method, with solvation effect treated by the Polarizable Continuum Model (PCM). Values of the reduced partition function ratio (β factor) for ^2H-substitution at individual organic H positions were then calculated from vibrational frequencies based on the theoretical method of Urey (1947) and Bigeleisen and Mayer (1947). The β factor for liquid water was obtained by first calculating the β factor for gaseous molecules using the same method, which was then multiplied by the experimental liquid–gas fractionation factor measured by Horita and Wesolowski (1994). The complete dataset of calculated β factor values are provided as the online Electronic Annex.

Equilibrium $^2H/^1H$ fractionation factors (α_{eq}) were then calculated as the ratio of β factors between the organic molecule in aqueous phase and liquid water:

$$\alpha_{eq} = \frac{\beta(\mathrm{CH})_{\mathrm{aqueous}}}{\beta(\mathrm{H_2O})_{\mathrm{liquid}}}$$

The value of α_{eq} was then corrected using a linear calibration curve based on experimental data for ketones (Wang et al., 2009) with slope = $1.081 - 0.00376T$ and intercept = $8.404 - 0.387T$, where T is the temperature in degrees Celsius. Application of the ketone-derived calibration curve assumes the same calculation error for other organic compounds as that for ketones. We have shown that the dominant error in the calculation of β factors is the omission of anharmonicity, which is of similar size for C-bound H in most other linear compounds as in ketones (Wang et al., 2009). Therefore errors resulting from the application of ketone-derived calibration are generally expected to be small (4–8‰).

Fractionation factors were calculated over the temperature range 0–100 °C for molecules in several major classes, including alkanes, alkenes, acids, esters, alcohols and ethers. In each compound class, the value of α_{eq} was calculated for every H position in 4–10 different molecules with carbon numbers between C_5 and C_{11}. In order to compactly summarize data for a large number of compounds, we average data for analogous positions (i.e. methyl group, methylene group, etc.) in different molecules to report a single α_{eq} value. Reported uncertainties for that value then combine the uncertainty of the calibration curve with true variations in α_{eq} for analogous H positions in different molecules (typically 1–7‰). This approach gives a total uncertainty in the estimated α_{eq} values in the range of 10–20‰.

It is important to realize that the calculated values of β and thus α_{eq} presented here are specific to individual atomic positions within a molecule, rather than to the whole molecule. When equilibrium has been established with respect to non-equivalent groups in the same molecule, the molecular β factor can be estimated based on the individual β factors for each group, using the method derived by Galimov (1971). It takes on the form of the arithmetic mean of individual β factors weighted by the number of equivalent atoms in each group. In the text and figures, fractionation factors are often presented in terms of the isotopic enrichment factor ε_{eq}:

$$\varepsilon_{eq} = (\alpha_{eq} - 1)$$

which is reported in permil (‰) units for easier comparison with the standard δ^2H (‰) notation.

Finally, we remind the reader that we have followed the convention (Wang et al., 2009) of using Greek letters in subscripts to denote molecular positions of specific H atoms, i.e. H_α is the H atom on the first carbon (C_α) that attaches to a functional group, H_β is on the second carbon (C_β), etc. In addition, a saturated C atom is classified as pri-