



Determination of position-specific carbon isotope ratios in propane from hydrocarbon gas mixtures



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ABSTRACT

Position-specific isotope ratios (PSIRs), also termed intramolecular isotope ratios, provide novel information to probe molecular structure, reaction mechanics, and molecular signatures for gas to source correlation. Successful application of this technique to natural gas may provide key insights into gas origin and formation mechanisms, which often cannot be satisfactorily addressed using bulk or compound-specific isotope analyses (CSIA) alone. In this study, we present a method to determine the PSIR of propane from hydrocarbon gas mixtures at natural abundance using a step-wise quantification and compound-specific isotope monitoring approach. First, we purify/enrich propane using a proprietary cryogenic gas processing unit, and then convert it to acetic acid (AA) by both enzyme-catalyzed and chemical reactions. Our method of PSIR analysis makes progress in several regards, including efficient propane separation from low-propane concentration gas mixtures (0.5% v/v) using relatively small sample quantities (below 8 mL propane). This advance in methodology enables more routine analysis and an optimized workflow for isotope analysis with strict quality control. Results obtained from oil-derived natural gas show that the center carbon in propane is more ¹³C-enriched than the terminal carbons by about 19.2%. Our results are discussed in the context of previous efforts in propane intramolecular analysis and potential future uses of this novel technique to improve understanding of the origin of gases, their formation, and the isotope reversal phenomenon.

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1. Introduction

Intramolecular or position-specific carbon isotope analysis (PSIA) of a single substrate (i.e., $\delta^{13}\text{C}$ values for different carbon positions within a single molecule) can provide valuable insights into molecular structure and formation mechanisms (e.g., Abelson and Hoering, 1961; Conrad et al., 2011; Gilbert et al., 2012; Monson and Hayes, 1982a, b), formation conditions (DeNiro and Epstein, 1977), isotope fractionation controls (Gleixner and Schmidt, 1997; Ivlev, 2005; Rossmann et al., 1991; Tcherkez et al., 2004), and source delineation of carbohydrates (e.g., Hattori et al., 2011; Hobbie and Werner, 2004; Lin et al., 2010). For example, intramolecular analysis of glucose reveals large carbon isotope fractionation during lipid synthesis, demonstrating large influences of formation environments on carbon isotope ratios of carbon atoms at different positions within acetyl coenzyme A and lipids (DeNiro and Epstein, 1977). PSIA can also serve as a unique method for probing the molecular formation pathways and origins (e.g., Hattori et al., 2011; Rossmann et al., 1991; Zhang et al., 1998) such as methane generation via either reduction of CO₂ or cleavage of acetate. Assessment of the relative contributions of these two pathways may be semi-quantitatively

achieved by knowing the stable carbon isotopic signatures of CO₂, total CH₄ and acetate methyl, and the isotopic fractionation factors for the conversion of both CO₂ and acetate methyl to CH₄ (Conrad, 2005; Conrad et al., 2011).

Application of the intramolecular isotope technique to natural gas analysis holds promise for the petroleum industry (Huang et al., 2002). There are several different mechanisms of hydrocarbon gas formation at subsurface conditions, including those associated with thermogenic, biogenic and abiogenic processes (e.g., Hosgormez et al., 2008; Schoell, 1988; Sherwood Lollar et al., 2002; Tissot and Welte, 1984; Whiticar et al., 1986). During gas formation, gas molecules are generated throughout a wide range of temperatures and under various environments, during which signature $\delta^{13}\text{C}$ values at specific carbon positions within hydrocarbon gas molecules can be preserved (DeNiro and Epstein, 1977; Hayes, 2004; Höld et al., 1999; Monson and Hayes, 1982a). In simple hydrocarbon gas mixtures with limited compositional information, compound-specific $\delta^{13}\text{C}$ values of low molecular-weight alkanes have been used to assess gas origin, maturity, and alteration, especially in conjunction with isotope compositions of hydrogen (δD), CO₂ concentration, and wetness data (e.g., Golding et al., 2013; Katz, 2002). In addition to bulk and compound-specific isotope ratios (CSIR), PSIA provides a new avenue to investigate some of the most fundamental questions in hydrocarbon exploration. Propane (C₃) is the

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simplest (and often the most abundant) species having intramolecular isotope ratio heterogeneity in a hydrocarbon gas mixture, therefore becoming the target of analysis.

Efforts to accurately and precisely analyze the position-specific isotopes of propane in a gas mixture have met limited success. In the analysis of glucose and other substrates, existing methods for measurements of intramolecular carbon isotope ratios make use of enzyme-catalyzed and chemical reactions (Huang et al., 2002; Rossmann et al., 1991), Nuclear magnetic resonance (NMR) analysis for small alcohol compounds (Zhang et al., 1998), and for chemically derivatized glucose (Gilbert et al., 2009, 2012), and computer modeling approaches (Ivlev, 2004; Schmidt et al., 1999). These methods, however, cannot be directly applied to the analysis of propane from natural or synthetic sources in a gas mixture, mainly due to the low concentration of propane in gas samples and/or the lack of efficient methods to cleave the carbon backbone of propane. Huang et al. (2002) re-determined the PSIR values of pure propane synthesized from precursors with known PSIR composition at each carbon position, to probe the kinetic isotope effects associated with conversion of propane to 2-propanol (2P) catalyzed by methane monooxygenases. These authors found that after multi-step reactions, the PSIR of synthesized C3 were largely consistent with expected values. However, CSIR monitoring did not take place at every step, including the acetic acid intermediate for example, and thus unintended deviations cannot be fully ruled out. In addition, since pure propane was used, it remained unclear whether the method would work on natural gas samples, and in particular how the enzyme used would behave in the presence of other hydrocarbons or potentially interfering impurities.

The objective of this study is to establish and optimize a method for routine evaluation of the $\delta^{13}\text{C}$ values for the middle carbon compared to the end carbons in C3 from hydrocarbon gas mixtures, that can be suitable for relatively small sample quantities and low C3 concentrations. We assembled a cold trap-based vacuum line apparatus capable of purifying C3 from gas mixtures with a C3 concentration as low as 0.5% v/v. C3 was converted to 2-propanol by a P450 enzyme and then to acetone and acetic acid. Compound-specific $\delta^{13}\text{C}$ values were closely monitored throughout the reaction series and used to solve for the position-specific $\delta^{13}\text{C}$ values. Direct aqueous injection was used for all analysis of non-gaseous samples via gas chromatography (GC) and gas chromatography–combustion–isotope ratio mass spectrometry (GC–C–IRMS), thus increasing convenience and efficiency. $\delta^{13}\text{C}$ values of 2-propanol, acetone, and acetic acid at concentrations below 100 ppm were measured with acceptable precision.

2. Samples and methods

2.1. Samples

We used the natural gas standard NG3 to establish our method (Dai et al., 2012). NG3 is an oil-related gas from the Tazhong gas field, Tarim Basin, China. This accumulation occurs in an Ordovician limestone reservoir and the source rocks were determined to be Cambrian–Ordovician marine marls and mudstone (Tian et al., 2010). NG3 has relatively

high wet gas content and a propane (C3) concentration of 2.1% (v/v). The composition and CSIR values of this natural gas for methane (C1), ethane (C2), and propane (C3) are respectively as follows: C1: 71.9%, –43.6‰ VPDB; C2: 3.6%, –40.2‰ VPDB; and C3: 2.1%, –33.8‰ VPDB (Dai et al., 2012).

2.2. Methods

2.2.1. Overview of the analysis

Our general approach is shown in Fig. 1, where terminal methyl carbons are termed as position *a* and the center or carbonyl carbon is position *b*. Propane is purified from a gas mixture and converted enzymatically first to 2-propanol, then to acetone, and finally to acetic acid. The enzymatically catalyzed reaction from C3 to 2-propanol could suffer from isotopic fractionation, due to discrimination between ^{12}C and ^{13}C by the biological catalyst, and/or a failure for equilibrium to be established between C3 in the reaction vial headspace and that dissolved in the aqueous reaction medium. Therefore, it is essential that the compound-specific $\delta^{13}\text{C}$ value of all reaction species be measured after each reaction or processing step to allow monitoring and calculations as described below. For reaction steps from propane to acetone, only the experimental runs that preserved the same CSIR value for propane, 2-propanol, and acetone are chosen to carry onto the next reaction or processing step. In the last step from acetone to acetic acid, the conversion rate must be sufficiently high for the method to be valid; in our case this conversion rate was ensured to be at least 85%, and preferably at least 90%.

The CSIR value of C3 ($\delta^{13}\text{C}_{\text{C3}}$) is an average of PSIR $\delta^{13}\text{C}$ values of two position *a* carbons ($\delta^{13}\text{C}_a$) and one position *b* carbon ($\delta^{13}\text{C}_b$), i.e.:

$$\delta^{13}\text{C}_{\text{C3}} = \frac{2 \times \delta^{13}\text{C}_a + 1 \times \delta^{13}\text{C}_b}{3} \quad (1)$$

The CSIR values of both the 2-propanol and acetone are also averages of two position *a* carbons ($\delta^{13}\text{C}_a$) and one position *b* carbon ($\delta^{13}\text{C}_b'$). The $\delta^{13}\text{C}$ for the position *b* carbon was initially designated $\delta^{13}\text{C}_b'$, since isotopic fractionation at this position is possible in the enzymatic conversion from C3 to 2-propanol, as this is the carbon that is attacked by the enzyme to form 2-propanol. We assume no isotope fractionation going from C3 to acetone (i.e., $\delta^{13}\text{C}_b = \delta^{13}\text{C}_b'$), as long as we obtained the same $\delta^{13}\text{C}_{\text{C3}}$, $\delta^{13}\text{C}_{2\text{P}}$, and $\delta^{13}\text{C}_{\text{Acetone}}$ values from the same series of reactions. We do not expect isotopic fractionation in the 2-propanol to acetone reaction, as long as the reaction is complete, i.e.:

$$\delta^{13}\text{C}_{2\text{P}} = \frac{2 \times \delta^{13}\text{C}_a + 1 \times \delta^{13}\text{C}_b}{3} = \frac{2 \times \delta^{13}\text{C}_a + 1 \times \delta^{13}\text{C}_b'}{3} = \delta^{13}\text{C}_{\text{Acetone}} \quad (2)$$

The two-carbon acetic acid inherited one position *a* carbon and one position *b* carbon from acetone. The CSIR of acetic acid ($\delta^{13}\text{C}_{\text{AA}}$) is thus

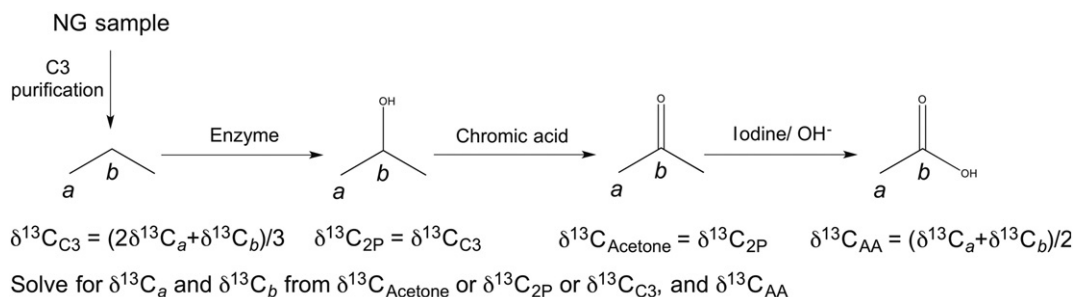


Fig. 1. An overview of the method to determine position-specific $\delta^{13}\text{C}$ values of propane's methyl and methylene carbons, *a* and *b* respectively, in propane.

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