



Quantifying hydrogen-deuterium exchange of meteoritic dicarboxylic acids during aqueous extraction

Megan FULLER and Yongsong HUANG*

Department of Geological Sciences, Brown University, Providence, Rhode Island 02912–1846, USA

*Corresponding author. E-mail: Yongsong_Huang@brown.edu

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Abstract—Hydrogen isotope ratios of organic compounds in carbonaceous chondrites provide critical information about their origins and evolutionary history. However, because many of these compounds are obtained by aqueous extraction, the degree of hydrogen-deuterium (H/D) exchange that occurs during the process needs to be quantitatively evaluated. This study uses compound-specific hydrogen isotopic analysis to quantify the H/D exchange during aqueous extraction. Three common meteoritic dicarboxylic acids (succinic, glutaric, and 2-methyl glutaric acids) were refluxed under conditions simulating the extraction process. Changes in δD values of the dicarboxylic acids were measured following the reflux experiments. A pseudo-first order rate law was used to model the H/D exchange rates which were then used to calculate the isotope exchange resulting from aqueous extraction. The degree of H/D exchange varies as a result of differences in molecular structure, the alkalinity of the extraction solution and presence/absence of meteorite powder. However, our model indicates that succinic, glutaric, and 2-methyl glutaric acids with a δD of 1800‰ would experience isotope changes of 38‰, 10‰, and 6‰, respectively during the extraction process. Therefore, the overall change in δD values of the dicarboxylic acids during the aqueous extraction process is negligible. We also demonstrate that H/D exchange occurs on the chiral α -carbon in 2-methyl glutaric acid. The results suggest that the racemic mixture of 2-methyl glutaric acid in the Tagish Lake meteorite could result from post-synthesis aqueous alteration. The approach employed in this study can also be used to quantify H/D exchange for other important meteoritic compounds such as amino acids.

INTRODUCTION

Dicarboxylic acids are abundant constituents of carbonaceous chondrites and have been described in the Murchison (Lawless et al. 1974; Cronin et al. 1993) and, more recently, the Tagish Lake meteorites (Pizzarello et al. 2001). In the Tagish Lake meteorite, they are the most abundant soluble organic species, with a concentration of over 75 nmol/gram of meteorite, and show molecular and isotopic distributions that are remarkably similar to those observed in the Murchison meteorite (Pizzarello and Huang 2002).

Pizzarello and Huang (2002) reported compound specific hydrogen and carbon isotopic measurements for several dicarboxylic acids found in the Tagish Lake and Murchison meteorites. Hydrogen isotopic ratio analysis is a particularly sensitive approach for identifying organic compounds that originated in cold interstellar space. Because of the large mass difference (100%) between hydrogen (H) and deuterium (D), the hydrogen isotope fractionation is the largest among all of

the stable isotope pairs, e.g., $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ (see Sanford, Bernstein, and Dworkin 2001 and references within). The δD values for succinic, 2-methyl succinic, glutaric, and 2-methyl glutaric acids from the Tagish Lake and Murchison meteorites were found to range from +389.5 to +1550.7‰, while $\delta^{13}\text{C}$ values varied from +5.5 to +28.1‰ (Pizzarello and Huang 2002). These isotopic enrichments are comparable to those described previously for other classes of meteoritic compounds, such as amino acids. These compounds have been attributed, particularly because of their high δD values, to partially altered, highly deuterated interstellar precursors (see Cronin and Chang 1993, for a review).

However, the δD values determined for several classes of meteoritic compounds may in fact be minimum values. Hydrogen atoms on meteoritic compounds could exchange with those in water used during the aqueous extraction process. For example, the carboxyl hydrogens on dicarboxylic acids exchange completely with the hydrogen in

the extraction water. Also, α -hydrogens, i.e., those bound to the carbon adjacent to the carboxyl carbon, are slightly acidic and could partially exchange with hydrogen in the extraction water (Epstein et al. 1987; Pizzarello and Huang 2002). The potential for isotopic exchange has been investigated for some amino acid compounds by Pereira et al. (1975), who used stable isotope mass fragmentography to estimate the amount of hydrogen-deuterium exchange on eight protein amino acids and found that the amino acids showed variable degrees of hydrogen exchange. Further work was done on the hydrogen exchange of amino acids by Lerner (1995). Lerner concluded that temperature and the amount of meteorite powder controlled the rate at which hydrogen exchange takes place. However, an accurate assessment of hydrogen exchange of individual compounds cannot be achieved without accurate measurements of D/H ratios at the molecular level.

The primary objective of this study is to use compound-specific hydrogen isotope analysis to quantify hydrogen isotope exchange caused by aqueous extraction for three common meteoritic dicarboxylic acids. Specifically, our goals are to: 1) quantify the hydrogen-deuterium exchange during extraction of dicarboxylic acids using deuterium oxide (D_2O); 2) obtain the exchange rate constant for each diacid and use the rate constant to compute the isotopic exchange caused by the aqueous extraction process; 3) assess changes in the hydrogen-deuterium exchange in the diacids under different extraction conditions (e.g., presence/absence of stirring, meteorite powder, and different alkalinities); and 4) compare the rate of hydrogen exchange between glutaric acid and 2-methyl glutaric acid and examine the role of hydrogen exchange in the possible racemization of 2-methyl glutaric acid. This fourth goal is important for understanding the origin of the racemic 2-methyl glutaric acid in the Murchison and Tagish Lake meteorites (Pizzarello and Huang 2002). If hydrogen exchange occurs at a chiral center (e.g., the chiral center in 2-methyl glutaric acid), it may conceal any previous enantioselective process that could have acted on the meteoritic molecule.

EXPERIMENTAL METHODS

Experimental Design

Soluble organic compounds are recovered from carbonaceous chondrites by powdering the stone, placing the sample into a vial with several milliliters of DI water, and evacuating and heating the sample to $\sim 100^\circ C$ for a period of 24 hr (Cronin, Grady, and Pizzarello 1981; Pizzarello and Cronin 2000; Epstein et al. 1987).

Three types of reflux experiments were conducted to simulate these extraction conditions. In each experiment, 200 μl aliquots of a stock solution containing succinic, glutaric, and 2-methyl glutaric acid standards ($\sim 10 \mu mole/ml H_2O$) of

known δD values were placed into vials and dried using a rotary evaporator. Each type of reflux experiment we performed is described below:

1. D_2O reflux: to measure the net exchange that occurred in the D_2O -dicarboxylic acid system, the compounds were refluxed in the presence of 2 ml D_2O (99.9%, Aldrich). The pH of the solution was 3.4.
2. D_2O + meteorite powder: to assess the affect of meteorite powder on the exchange process, approximately 700 mg of Murchison meteorite powder was added to a dicarboxylic acid/ D_2O solution. The rock:water ratio of 350 mg:1 ml is approximately what was used to extract the Tagish Lake meteorite (Pizzarello and Huang 2002). The powder was annealed at $550^\circ C$ before use to remove any organic compounds in the powder. The pH of the diacid/ D_2O /meteorite solution was 7.1.
3. D_2O + meteorite powder + pyridine: to assess the role of alkalinity on the exchange process, pyridine was added (6.8 μl pyridine/ml D_2O) to the diacid/ D_2O /meteorite solution. Pyridine creates a buffer solution with a pH of 8.1, similar to the pH of typical meteorite extractions.

Each vial was capped with a Teflon-lined lid and placed on a heating block at 100 – $110^\circ C$ for 24 hr. These experiments were run in duplicate. One set of samples were not stirred (referred to as Case 1) while the other set of samples were stirred continuously (Case 2) over the 24 hr reaction period. The samples were cooled and dried using a rotary evaporator. The samples containing meteorite powder were centrifuged, and the supernatant was decanted into a clean vial, along with subsequent rinses, and dried. Care was taken to ensure that there was no cross-contamination of samples via the rotary evaporator by rinsing with solvents between samples.

Sample Preparation and GC Analysis

The diacids were derivatized using acidified isopropyl alcohol (IPA). Approximately 200 μl of acidified isopropanol were added to the vials. The vials were capped and heated at $100^\circ C$ for 1 hr. The contents of the vials were dried and diluted in toluene for analysis. This procedure eliminates the carboxyl hydrogen which is fully exchanged with the extraction water. Therefore, it is unnecessary to include the carboxyl hydrogens in the calculation of exchange rates. We only report the exchange rates for the alkyl hydrogens (i.e., hydrogen on the carbon chain between the two carboxyl groups of the dicarboxylic acids) in this paper.

The GC analysis was conducted using a Hewlett-Packard 6890+ gas chromatograph fitted with an HP 7683 series auto sampler. The GC column used was HP-1MS (0.32 mm \times 0.25 μm \times 60 m). The temperature was programmed as holding at $40^\circ C$ for 2 min, then heating to $70^\circ C$ at $10^\circ C/min$, and subsequently ramping to $200^\circ C$ at $6^\circ C/min$. The

concentration of the target compounds was estimated using the peak area—FID response relationship established by an external standard (C₂₁ *n*-alkane).

Hydrogen Isotope Analysis

The hydrogen isotope analysis of the samples was performed using a gas chromatography-high temperature conversion-isotope ratio mass spectrometer (GC/TC/IRMS). An HP 6890+ GC equipped with an AS200 auto-sampler was interfaced via a high-temperature conversion reactor to a Finnigan MAT Delta +XL stable isotope spectrometer. The GC conditions are identical to those used for the GC analyses. The samples were carried into the pyrolysis reactor (1445°C) by a constant flow of helium gas (UHP grade) at 1.1 ml/min. The samples were then converted into H₂ and C or CO and carried into the IRMS. In the IRMS, an electrostatic filter in front of the mass 3 Faraday cup (for deuterium) suppressed the amount of scattered helium reaching the collector (Hilkert et al. 1999). The H₃⁺ factor was determined daily to ensure that it was stable and below 10. The samples were run in either triplicate or quadruplicate to ensure reproducibility, and external standards (5, α -androstande, myristic acid methyl ester, behenic acid methyl ester, and C₂₁ *n*-alkane) were run between every 6 to 8 sample injections to ensure accurate measurements. The hydrogen isotope ratios of organic compounds are expressed relative to VSMOW using the following equation.

$$\delta D = \left(\frac{[D/H]_{\text{sample}}}{[D/H]_{\text{SMOW}}} - 1 \right) \times 1000 \quad (1)$$

Because two isopropyl groups were added to each dicarboxylic acid prior to isotopic analysis, a correction for the measured hydrogen isotope ratios is needed to exclude the isotopic contribution from the isopropyl groups. To do this, we first determined the δD value of the isopropyl group by derivatizing a sodium succinate with a known δD value (after acidifying the salt and extracting the succinic acid with ethyl

acetate). The hydrogen isotope ratio of the isopropyl group is computed using the following equation:

$$\delta D_{\text{measured}} = 14/18 \delta D_{\text{IPA}} + 4/18 \delta D_{\text{succinate}} \quad (2)$$

where $\delta D_{\text{measured}}$, $\delta D_{\text{succinate}}$, and δD_{IPA} are hydrogen isotope values for the total molecule, the succinic salt, and the isopropyl group. We obtained a δD value of -141.7‰ for the isopropyl group used in our experiments.

Similar hydrogen isotope mass balance equations were used to calculate the δD values for the 4, 6, and 8 alkyl hydrogens of succinic, glutaric, and 2-methyl glutaric acid, respectively, from the measured δD values of isopropyl diesters:

$$\delta D_{\text{measured}} = 14/18(-141.7) + 4/18 \delta D_{\text{succinic acid}} \quad (3)$$

$$\delta D_{\text{measured}} = 14/20(-141.7) + 6/20 \delta D_{\text{glutaric acid}} \quad (4)$$

$$\delta D_{\text{measured}} = 14/22(-141.7) + 8/22 \delta D_{\text{2-methyl glutaric acid}} \quad (5)$$

RESULTS AND DISCUSSIONS

Unstirred Versus Stirred Experiments

Table 1 shows the initial “unprocessed” δD measurements for the three diacids as well as the δD measurements from Case 1, the unstirred experiments, and Case 2, the stirred experiments.

As seen in the highly positive δD values, it is evident that there was significant deuterium incorporation in all three of the dicarboxylic acids. Significant differences are observed between Case 1 and 2 (Table 1). The unstirred experiments show much less exchange than the stirred experiments. Both sets of experiments show a sequential increase in H/D exchange for the D₂O, D₂O + powder, and D₂O + powder + pyridine experiments. These results suggest that the stirring enhanced interaction between diacids, water, powder, and pyridine, and hence, caused an increase in hydrogen exchange. The addition of pyridine and the resulting increase in alkalinity may have enhanced the

Table 1. δD values for individual dicarboxylic acids, both unprocessed and after reflux experiments.^a

	Succinic	σ^b	Glutaric	σ	2-methyl glutaric	σ
Unprocessed	-404	2	59	5	-120	1
Case 1 (not stirred)						
D ₂ O	18770	37	7017	16	4672	5
D ₂ O + Murchison	24227	15	6772	7	3495	5
D ₂ O + Murchison + pyridine	22756	38	7728	14	4076	4
Case 2 (stirred)						
D ₂ O	26407	34	11177	89	7736	116
D ₂ O + Murchison	62334	96	18183	406	9292	36
D ₂ O + Murchison + pyridine	128838	14	35995	47	20221	65

^aMeasured by GC-C-IRMS, corrected for esterification, relative to SMOW and the average value of four data.

^b σ represents one standard deviation from the mean.

exchange rate because of the increased dissociation of the α -hydrogen of the dicarboxylic acids. For the purpose of this paper, we are interested in the maximum amount of exchange that could occur during the extraction process. Therefore, only the results from Case 2 will be further discussed. Because the water and powder are typically mixed either by a magnetic stir bar or by the turbulence of the boiling of the water during actual meteorite extractions, the stirred experiments should resemble real extraction more closely.

Influence of Molecular Structure

Hydrogen exchange on dicarboxylic acids is likely to occur at the α -hydrogen site. This site is slightly acidic because the conjugate base, formed as a result of deprotonation, is stabilized by resonance and inductive withdraw of the carboxyl group. We have not been able to find the pK_a , the dissociation constant, of the α -hydrogen on these dicarboxylic acids, although the pK_a of a hydrogen bonded to an α -carbon of a carboxylic acid methyl ester is ~ 25 (Bruice, 1995). The pK_a of the dicarboxylic acid α -hydrogen should be a few pK_a units less than 25. Other alkyl hydrogens on the dicarboxylic structure, i.e., the β -hydrogens in glutaric acid and 2-methyl glutaric acid and the hydrogens on the methyl group of 2-methyl glutaric acid are considered non-exchangeable (Sessions 2001). The following calculations only consider the exchange of α -hydrogens.

Succinic acid has 4 hydrogens (excluding those on the isopropyl derivatization groups), all of which are α -hydrogens (see Fig. 1). Glutaric acid also has 4 α -hydrogens, as well as 2 β -hydrogens. The additional β -carbon in glutaric acid decreases the acidity of the α -hydrogens slightly, relative to succinic acid, by inductively donating electrons to the α -carbons and increasing the distance between the 2 carboxyl groups. 2-methyl glutaric acid has 3 α -hydrogens and 2 β -hydrogens, as well as 3 hydrogens on the methyl group. The α -hydrogens on 2-methyl glutaric acid are thus less acidic than those on glutaric acid because the methyl substitute is also inductively electron donating. In general, more acidic hydrogens are expected to exchange at a greater rate than less acidic hydrogens. So, we expected that succinic acid would

exchange more than glutaric acid, which would exchange more than 2-methyl glutaric acid. Details of the exchange rate computation are discussed later.

Effect of Pyridine and Meteorite Powder

The aqueous solution during extraction of carbonaceous chondrites is often slightly basic (pH ~ 8.5) possibly because of the abundant soluble alkaline salts present. To ensure that we considered these effects in our extraction simulation experiments, the dicarboxylic acids were refluxed in the presence of Murchison powder. To assess the role of alkalinity on the exchange rates, we added pyridine (6.8 μ l pyridine/ml D_2O) to the D_2O -powder system to ensure a buffered solution with a pH of 8.1, similar to the pH values encountered during actual meteorite extractions.

The presence of both pyridine and meteorite powder increases the amount of H/D exchange compared to the D_2O experiment. Pyridine increases the alkalinity of the solution, which could in turn promote the removal of the acidic hydrogen and enhances the net H/D exchange. Because of its alkaline character, it is likely that the meteorite powder also increases the alkalinity of the solution, resulting in an increased exchange. However, the role of meteorite powder is not well understood. It is possible that the mineral surfaces could catalyze the exchange reaction (Pereira et al. 1975; Lerner 1995). It is well documented that clay surfaces have catalytic properties (Alexander, Kagi, and Larcher 1984; Larcher et al. 1986), particularly under acidic conditions. Annealing of the Murchison powder at 550°C may have caused some dehydration of clay minerals, although we do not have evidence that annealing affected the catalytic activity of the powder. Any acid-catalyzed exchange mechanisms should be relatively unimportant under the basic conditions of typical meteoritic extracts.

Exchange Rate

The net deuterium incorporation that occurs for each diacid over the 24 hr reaction period provides important kinetic data that can be used to determine the rate constants of the exchange. The H/D exchange reaction, $RH + D_2O \rightarrow RD + HDO$, which occurs between an organic compound and

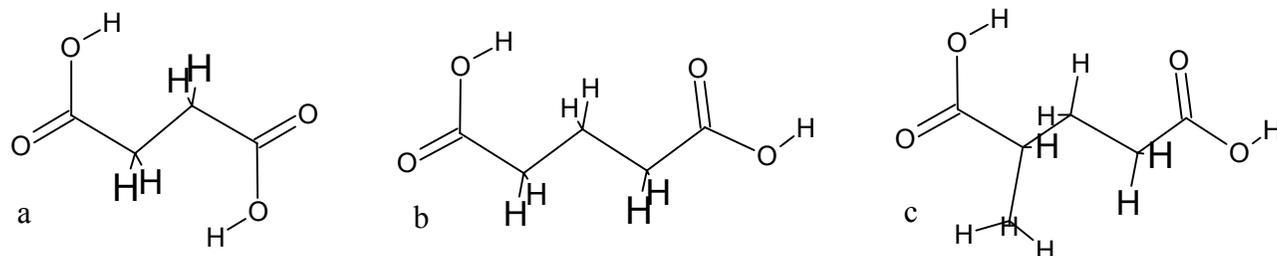


Fig. 1. The molecular structures of a) succinic, b) glutaric, and c) 2-methyl glutaric acid, where the bold Hs denote α -hydrogens.

water can be characterized by a pseudo-first-order-rate law equation (Wedeking and Hayes 1983; Sessions 2001).

$$kt = \ln[(F_i - F_e)/(F_t - F_e)] \quad (6)$$

where k is the rate constant, t is time, and F equals the fractional abundance of deuterium $[D/(D + H)]$ in the compound. F can be obtained by converting the δD values, using Equation 1, to D/H ratios (D/H ratio of SMOW = 155.67×10^{-6}). F_i is the initial (before the extraction process) fractional abundance of D in the compound. F_t is the fractional abundance of D in the compound at time t ($t = 24$ hrs at the end of extraction process). F_e is the fractional abundance of D in the compound when it reaches equilibrium. F_e is assumed to be approximately equal to the fractional abundance of D in the water used in the extraction, because the water is an infinite pool of exchangeable hydrogen relative to the quantities of compounds present (Wedeking and Hayes 1983).

Exchange Rates for the Whole Molecule

In order to apply corrections for the hydrogen isotope exchange for individual acids during aqueous extraction, we need to obtain rate constants for the diacids as whole molecules and consider all the hydrogen atoms present. Equation 5 was used to calculate rate constants for hydrogen exchange, where F_t was the maximum fractional abundance (Case 2, D₂O/Murchison powder/pyridine) achieved during the reflux experiments, F_e was the fractional abundance of deuterium in the D₂O (99.9%), and F_i was the initial fractional abundance of deuterium in the unprocessed diacids. The rate constants calculated for the individual diacids are shown in Table 2.

Using these rate constants, Equation 5 was used to model F_t values for meteoritic acids for a range of post-extraction δD estimates. When calculating the F_t values, F_e was assumed to be equivalent to the δD of previously measured laboratory DI water, -108‰ . Table 3 shows typical post-extraction meteoritic values for the three dicarboxylic acids and the model-simulated calculations for initial isotopic values. For example, assuming a post-extraction δD value of $+1800\text{‰}$ for succinic, glutaric, and 2-methyl glutaric acid, their initial δD values are 1838‰ , 1810‰ , and 1806‰ , respectively. These results indicate that the hydrogen exchange during the extraction process is, in the case of glutaric and 2-methyl glutaric acid, within the analytical error and of little concern to the robustness of the data. Succinic acid, despite showing a

Table 2. Rate constants for H/D exchange of each diacid as determined by the δD data from the Case 2 study, D₂O + Murchison powder + pyridine.

	Rate constant (k) hr^{-1}
Succinic	8.13×10^{-4}
Glutaric	2.33×10^{-4}
2-methyl glutaric	1.321×10^{-4}

slightly larger exchange, is still insignificant when compared to the degree of deuterium enrichment seen in typical extraterrestrial dicarboxylic acids (Pizzarello and Huang 2002). The isotope change during actual meteorite extraction is likely to be even smaller than our computed values because deuterium deprotonation from dicarboxylic acids in “light” terrestrial water is slower than hydrogen deprotonation in D₂O (due to slightly greater bond strength of R-D than R-H).

Exchange Rates for the α -Hydrogens

The exchange rates above for the three diacids are not directly comparable because of the “dilution” effect by the non- α -hydrogens. By making a simple assumption that only α -hydrogens exchange in our experiments, we can compute the exchange rates specifically for α -hydrogens, which then allow us to compare the exchange rates for the three dicarboxylic acids. Mass balance equations for the hydrogens on the diacids are as follows:

$$\text{Succinic acid} \quad F_t = F_{\alpha t} \quad (7)$$

$$\text{Glutaric acid} \quad F_t = (4/6)F_{\alpha t} + (2/6)F_{\beta t} \quad (8)$$

$$\text{2-methyl glutaric acid} \quad F_t = (3/8)F_{\alpha t} + (5/8)F_{\beta t} \quad (9)$$

where $F_{\alpha t}$ and $F_{\beta t}$ are the fractional abundances of deuterium for the α - and β -hydrogens, respectively, which sum to equal the total F_t for the whole molecule. The $F_{\alpha t}$ values for glutaric acid and 2-methyl glutaric acid can be calculated using Equations 8 and 9 by assuming that $F_{\beta t}$ is equal to the initial value F_i of the respective diacids. The rate constants for exchange at α -hydrogens of individual diacids can then be calculated using Equation 6 (see Table 4). Succinic acid exchanges more than twice as fast as glutaric and methyl glutaric acid, while the latter two acids show similar exchange rates. This indicates that the methyl substitute present on the α -carbon of 2-methyl glutaric acid does not significantly change the α -hydrogen’s reactivity.

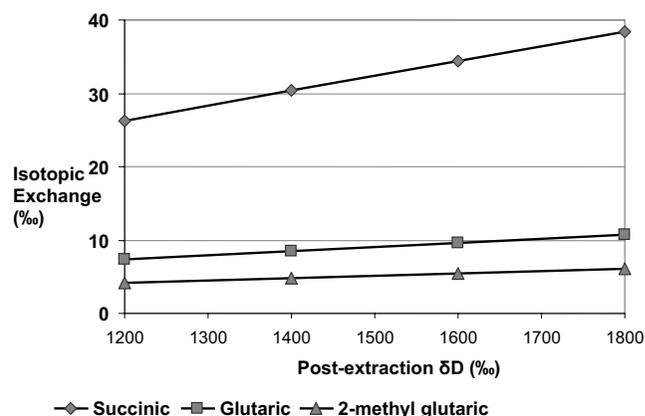


Fig. 2. Plot of typical post extraction δD values versus isotope exchange introduced by the extraction procedure, as calculated from the rate constants shown in Table 2.

Table 3. Typical post-extraction meteoritic δD values compared to the model-simulated “initial” δD values as predicted by Equation 1.^a

Typical post-extraction meteoritic δD values (‰)	Model-simulated initial δD values (‰)
Succinic acid	
1200	1226
1400	1430
1600	1634
1800	1838
Glutaric acid	
1200	1207
1400	1408
1600	1610
1800	1811
2-methyl glutaric acid	
1200	1204
1400	1405
1600	1605
1800	1806

^a“Initial” values were calculated using the rate constants from Table 2 and an F_e value equivalent to a DI water with a δD of -108% .

Table 4. Rate constants for the exchange of α -hydrogens ($k_{\alpha t}$) for succinic acid, glutaric acid, and 2-methyl glutaric acid.

	Succinic acid	Glutaric acid	2-methyl glutaric acid
D ₂ O + powder + pyridine	8.13×10^{-4}	3.565×10^{-4}	3.527×10^{-4}

Hydrogen Exchange at Chiral Centers and Racemization

If the removal of an α -hydrogen occurs on a chiral carbon, the resulting carbanion has a pyramidal geometry that inverts rapidly. This inversion leaves the anion open for attack from either side as long as the inverted structure is not stabilized by the nature of the substituents (Lowry and Richardson 1987). If this hydrogen exchange occurs on the chiral carbon of a meteoritic compound with an enantiomeric excess, racemization will occur. Given the importance of chirality when studying meteoritic organic compounds (Cronin and Pizzarello 1997; Pizzarello and Cronin 2000), we examined the hydrogen exchange at the chiral α -carbon in 2-methyl glutaric acid. This compound was the only chiral dicarboxylic acid present on the Tagish Lake meteorite that was resolvable by GCMS (Pizzarello and Huang 2002) and was found to be racemic. The important question is whether this racemic mixture is a direct result of abiotic synthesis or is an artifact of post-synthesis aqueous alteration. To answer this question, we need to estimate the hydrogen exchange rate for the α -hydrogen on the chiral carbon of 2-methyl glutaric acid.

The $k_{\alpha t}$ constants for glutaric acid and 2-methyl glutaric acid in the D₂O + powder + pyridine experiment are nearly

identical (Table 4). If the exchange of the hydrogen bound to the methyl-substituted α -carbon was inhibited, the rate constant for the α -hydrogens of 2-methyl glutaric acid should be significantly smaller than that of glutaric acid. This result indicates that the α -hydrogen exchange occurs at approximately the same rate despite the presence of the methyl substitute on the α -carbon of 2-methyl glutaric acid. The exchange at the chiral α -carbon, although shown to be a small amount during the aqueous extraction process, could be important during the aqueous alteration of the parent body where an aqueous environment could exist for thousands, if not millions, of years (Grimm and McSween 1989; Cohen and Coker 2000). For example, if enantiomeric excess was originally present in a meteoritic compound when it was first synthesized, post-synthesis aqueous alteration could lead to complete racemization of the compound.

CONCLUSIONS

This study demonstrates that compound-specific hydrogen isotopic study of simulated extraction experiments can provide a quantitative assessment of artificial hydrogen isotopic changes caused by the aqueous extraction procedure. Molecular structure controls the degree to which hydrogen can be exchanged during the aqueous extraction process. The three dicarboxylic acids contain acidic α -hydrogens that are susceptible to exchange. Using the δD changes measured in the simulated extractions, a pseudo-first-order rate equation was established to calculate rate constants for the exchange reactions. These rate constants were used to determine the degree of hydrogen exchange that can be expected during actual meteoritic extraction of succinic, glutaric, and 2-methyl glutaric acids. Our results indicate that the artificial isotope change caused by the meteoritic aqueous extraction procedure is negligible for the three dicarboxylic acids. The exchange rates for the α -hydrogens of the three dicarboxylic acids follow the sequence of succinic acid > glutaric acid \approx 2-methyl glutaric acid. In addition, the exchange rate is enhanced in alkaline solutions and in the presence of meteorite powder.

Our results also indicate that the methyl substitute on the chiral α -carbon in 2-methyl glutaric acid does not inhibit the exchange of the remaining α -hydrogen. In fact, the rate constants for the α -hydrogens on both glutaric acid and 2-methyl glutaric acid are remarkably similar. This suggests that any original enantiomeric excess in 2-methyl glutaric acid as a result of asymmetric abiotic synthesis could have been racemized by the post-synthesis aqueous processing (e.g., parent body aqueous alteration).

The approach developed in this paper can also be used to determine H/D exchange on other meteoritic compounds (e.g., amino acids) obtained by aqueous extraction.

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