

Carbon and hydrogen isotope fractionation of acetic acid during degradation by ultraviolet light

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Low molecular-weight carboxylic acids, such as acetic and propionic acids, are abundant organic compounds in carbonaceous chondrites, and are generally enriched in heavy stable isotopes (i.e., ^{13}C and D) relative to terrestrial organic compounds. In this study, we have determined carbon and hydrogen isotopic fractionation of acetic acid, and site-specific carbon isotopic fractionation of acetic acid, during degradation by ultraviolet (UV) light. Acetic acid became enriched in ^{13}C and D with increased UV exposure times. The isotopic fractionation factors (α) of total, methyl and carboxyl carbon of acetic acid were 0.9922, 1.0022 and 0.9823 respectively, and the α value for hydrogen was 0.9875. These results suggest that UV degradation could be a process for yielding ^{13}C - and D-enrichment of acetic acid in natural environments.

Keywords: acetic acid, isotope, fractionation, UV, degradation

INTRODUCTION

Various low molecular-weight carboxylic acids are found in carbonaceous meteorites, with acetic acid (CH_3COOH) being the most abundant (Yuen *et al.*, 1984; Epstein *et al.*, 1987; Shimoyama *et al.*, 1989; Naraoka *et al.*, 1999; Huang *et al.*, 2005). Acetic acid has a central role in various biological activities, including energy production for metabolism and membrane lipid synthesis. Mechanisms to generate acetate have been proposed for the environment of the early Earth. For example, acetic acid could have been synthesized from CO or CO_2 with sulfides under hydrothermal conditions (Huber and Wächtershäuser, 1997). Furthermore, we recently demonstrated that hydrous pyrolysis of macromolecular organic matter hosted by the Murchison carbonaceous meteorite yields ~400 ppm acetic acid (Oba and Naraoka, 2006). Therefore, carbonaceous meteorites might have carried this important building block of life to the early Earth (Chyba and Sagan, 1992; Bada, 2004).

Generally, carboxylic acids in carbonaceous chondrites are enriched in ^{13}C (+4.5 to +22.7‰) and deuterium (D) (+19 to ~+2000‰) relative to terrestrial organic compounds (Yuen *et al.*, 1984; Krishnamurthy *et al.*, 1992;

Huang *et al.*, 2005). The D-enrichment suggests that they were derived, at least partly, from interstellar molecules (Krishnamurthy *et al.*, 1992; Huang *et al.*, 2005). Carbon and hydrogen isotope distributions in extraterrestrial environments have been summarized elsewhere (e.g., Geiss and Reeves, 1981). Although carbon isotopic compositions of carboxylic acids in the Murchison meteorite suggest that the long-chain acids were kinetically produced from short-chain ones (Yuen *et al.*, 1984), the detailed mechanisms for the ^{13}C - and D-enrichment of meteoritic carboxylic acids remain unclear.

Spectroscopic observation demonstrates that acetic acid is present in the interstellar environment (Mehring *et al.*, 1997). Therefore, interstellar acetic acid might partly contribute to the presence of this material in some meteorites. In contrast, organic molecules are extensively exposed to UV radiation in interstellar environments and also quickly destroyed (e.g., Bernstein *et al.*, 2004). Because UV degradation of organic molecules generally causes isotopic fractionation (e.g., Poulson and Naraoka, 2006), UV degradation of acetic acid has the potential for the ^{13}C - and D-enriched occurrence of the residual acid.

In contrast to extraterrestrial environments, UV radiation above the Earth is important in three distinctive wavelength ranges: UVC (200–280 nm); UVB (280–315 nm) and UVA (315–400 nm). At the surface of the modern Earth, solar UV radiation is less effective in degrading small organic molecules because atmospheric ozone and

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molecular oxygen absorb most of the UVC and UVB (Okabe, 1978). The absorption band of acetic acid also lies within the UVC wavelengths, at ~215 nm, ~172 nm, ~159 nm and ~150 nm (Wilkerson and Guillory, 1977) and therefore acetic acid on the present-day Earth is not subjected to UV-mediated photolysis. However, since atmospheric oxygen levels were very low on the early Earth, UVC radiation could have reached the surface and might have been one of the energy sources to promote chemical reactions.

So far, no study has investigated the isotopic fractionation of carboxylic acids during UV degradation. In this study, we have conducted UV exposure experiments of acetic acid, with measurements of carbon and hydrogen isotopic compositions of total acetic acid and site-specific carbon isotopic fractionation. The primary goal of this study was to reveal carbon and hydrogen isotope behavior of acetic acid during UV degradation.

EXPERIMENTAL METHODS

Acetic acid was procured from Wako Pure Chemical Industries (Osaka, Japan, 99.7%). The carbon isotope composition of the acetic acid was reported previously (Yamada *et al.*, 2002). Acid (5 μ l) was added to quartz tubes (2.2 cm i.d. $\times$ 26 cm long, ~100 mL by volume, Poulson and Naraoka, 2006) by syringe through a Mininert valve (Vici Precision Sampling Co. Inc., Baton Rouge, LA) immediately after helium purging. The sample in the reaction tube was allowed to vaporize for about 1 hour before measuring the concentration and isotope ratios of the acid.

The sample was exposed to UV light from a high pressure mercury lamp (450 W, Model UM-452, USHIO Inc., Japan) for 1 to 5 hours at room temperature. The wavelengths produced by this lamp were centered at ~300, ~350, ~450 and ~550 nm (UVA and visible), with weak emission at between 200 and 300 nm (mostly UVC). The wavelength of the absorption bands for acetic acid and the photon wavelength from this lamp coincide at ~215 nm. The photon flux of the lamp was not measured. A control experiment, with the reaction tube tightly wrapped with aluminum foil, was conducted using acetic acid under the same experimental conditions.

Quantification of acid concentrations was performed using a Hewlett-Packard (HP) 5890II gas chromatograph/flame ionization detector (GC/FID) equipped with a DB-FFAP capillary column (30 m length $\times$ 0.32 mm i.d., 0.25 μ m film thickness; J&W). Gas samples (0.1 ml) were taken from the reaction tubes every hour using a Pressure-Lok gastight syringe (Vici Precision Sampling Co. Inc., Baton Rouge, LA) and analyzed by GC with splitless injection. The He flow rate was 1.0 ml/min. The oven temperature was programmed at 40°C for 2 min, then

20°C/min to 100°C, 2°C/min to 130°C, and 20°C/min to 200°C. Standard deviation of the acid concentration analyses was better than 5%.

The carbon isotope composition of the acid ($\delta^{13}\text{C}_{\text{TOTAL}}$) was measured by GC/combustion/isotope ratio mass spectrometry (GC/combustion/IRMS) with split injection, using a Finnigan MAT delta S mass spectrometer interfaced with a HP5890II GC, which was equipped with a DB-FFAP capillary column (60 m length $\times$ 0.32 mm i.d., 0.25 μ m film thickness). The gas sample (0.025–0.2 ml) of acid, separated by GC, was combusted through a microvolume combustion furnace (0.5 mm i.d. $\times$ 34 cm) at 940°C, with copper and nickel oxide wires as oxidants and platinum wire as a catalyst. The GC oven temperature was programmed at 50°C for 2 min, then 10°C/min to 100°C, 2°C/min to 130°C, and 10°C/min to 200°C. The carbon isotopic composition of carboxyl carbon (-COOH, carboxyl-C) was measured by GC/pyrolysis/IRMS (after Dias *et al.*, 2002a; Yamada *et al.*, 2002), using a Thermo Finnigan DELTA plusXL mass spectrometer. The latter was interfaced with a HP6890 GC via a microvolume pyrolysis furnace (0.5 mm i.d. $\times$ 34 cm), operated at 1000°C. In this arrangement, acetic acid was thermally decarboxylated into CH₄ and CO₂, and the $\delta^{13}\text{C}$ value of the generated CO₂ was directly measured (modified after Yamada *et al.*, 2002). The GC condition and sample amounts were identical to those used during the $\delta^{13}\text{C}_{\text{TOTAL}}$ analyses. $\delta^{13}\text{C}$ of methyl carbon (CH₃-, methyl-C) was calculated by isotopic mass balance:

$$\delta^{13}\text{C}_{\text{methyl}}(\text{‰}) = 2 \times \delta^{13}\text{C}_{\text{TOTAL}} - \delta^{13}\text{C}_{\text{carboxyl}} \quad (1)$$

where $\delta^{13}\text{C}_{\text{methyl}}$ and $\delta^{13}\text{C}_{\text{carboxyl}}$ are $\delta^{13}\text{C}$ of the methyl- and carboxyl-C in acetic acid, respectively. $\delta^{13}\text{C}$ values were calibrated with a CO₂ gas standard and are reported in per mil (‰) relative to Vienna-Peedee Belemnite (VPDB). Standard deviations of $\delta^{13}\text{C}_{\text{TOTAL}}$ and $\delta^{13}\text{C}_{\text{carboxyl}}$ analyses were better than 0.6‰ and 0.9‰, respectively.

The hydrogen isotopic ratio (δD) of the acid was measured using a Thermo Finnigan DELTA plusXL mass spectrometer interfaced with a HP6890 GC. The analytical conditions were identical to those used for the site-specific $\delta^{13}\text{C}$ analysis, except for the pyrolysis furnace conditions (1440°C, with graphite as a catalyst). δD was calibrated with a reference H₂ gas, and values are reported in per mil (‰) relative to Vienna-Standard Mean Ocean Water (VSMOW). Standard deviation of the δD analyses was better than 6‰.

Since the carboxyl hydrogen in acid may undergo exchange with hydrogen in the stationary phase of the GC capillary column, an isotopic correction is needed to eliminate the contribution of the carboxyl hydrogen (Huang *et al.*, 2005). δD of the carbon-bound hydrogen in acetic

acid (δD_{methyl}) can be calculated on the basis of:

$$\delta D_{\text{methyl}} = (4/3) \times \delta D_{\text{TOTAL}} - (1/3) \times \delta D_{\text{carboxyl}} \quad (2)$$

where δD_{TOTAL} is the hydrogen isotopic ratio of total acid, measured by GC/pyrolysis/IRMS, and $\delta D_{\text{carboxyl}}$ is the hydrogen isotopic ratio of the labile hydrogen. To measure δD_{methyl} of acid before UV irradiation, the acetic acid was converted into the sodium salt and then its δD value determined using a thermo-conversion elemental analyzer (TC/EA, ThermoFinnigan) interfaced to a DELTA plusXL mass spectrometer (Hilkert *et al.*, 1999; Huang *et al.*, 2005). The initial δD_{methyl} value of acetic acid was -85‰ . Consequently, $\delta D_{\text{carboxyl}}$ was calculated using initial δD_{methyl} and δD_{TOTAL} values to be $+169\text{‰}$. The $\delta D_{\text{carboxyl}}$ value was assumed to be constant during isotopic measurement.

RESULTS

Rate of photolysis

If the UV degradation rate of acetic acid is assumed to be unimolecular, the decrease of acetic acid concentration vs. time may be fitted to a first-order (simple exponential) decay using

$$\ln F = -kt \quad (3)$$

where F is the fractional abundance of the acetic acid remaining at time t (i.e., concentration at time t relative to the initial concentration), and k is a rate constant.

Concentration of the acetic acid decreases logarithmically with increasing UV exposure time, as shown in Fig. 1. This result supports the notion that the UV degradation of acetic acid is unimolecular. The control experiment revealed that degradation of the acid occurred only in the presence of the UV irradiation (Fig. 1). The half-life of acetic acid is ~ 130 minutes under our experimental conditions, with rate constant $k = 9.2 \pm 0.3 \times 10^{-5} \text{ s}^{-1}$.

Isotopic fractionation during UV degradation

If isotopic compositions of acetic acid follow a Rayleigh fractionation during UV degradation, the relationship between δ values and F is given by the following equation:

$$\delta = (\delta_i + 1000)F^{(\alpha-1)} - 1000 \quad (4)$$

where δ is the isotopic composition of the acid at time t , δ_i is the initial isotopic composition of the acid, and α is the isotope fractionation factor associated with UV degradation. Re-arranging equation (4) yields

$$\ln[(\delta + 1000)/(\delta_i + 1000)] = (\alpha - 1)\ln F \quad (5)$$

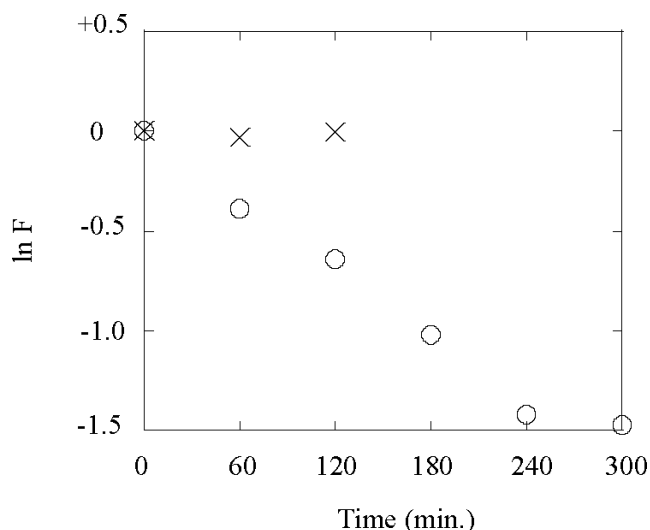


Fig. 1. Rate data for the UV photolysis of acetic acid. The graph also contains data of the control experiment. F is the fraction of acid remaining. Circle and cross symbols denote acetic acid and acetic acid-control experiments, respectively.

which indicates that a plot of $\ln[(\delta + 1000)/(\delta_i + 1000)]$ vs. $\ln F$ should give a straight line with a slope of $(\alpha - 1)$.

A time-sequence of $\delta^{13}\text{C}$ and δD values is presented in Tables 1 and 2. The averaged value of $\ln[(\delta + 1000)/(\delta_i + 1000)]$ vs. $\ln F$ yields good values of r^2 for the linear least-squares fit, with r^2 values from 0.86 to 0.99 for $\delta^{13}\text{C}_{\text{TOTAL}}$, $\delta^{13}\text{C}_{\text{carboxyl}}$ and δD (Tables 1 and 2). The value of α for carbon (α_C) associated with UV degradation of total acetic acid is 0.9922, with the corresponding enrichment factor (ϵ_C or ϵ_H) of -7.8 , where $\epsilon = 1000(\alpha - 1)$. The carboxyl-C becomes more enriched in ^{13}C relative to the total-C as UV irradiation proceeds (Fig. 2). This intramolecular carbon isotopic ordering is consistent with that of carboxylic acids generated by hydrous pyrolysis of terrestrial kerogen (Dias *et al.*, 2002b) and with that expected from a thermodynamically-controlled isotope fractionation (Galimov, 1985). The α_C value of carboxyl-C calculated from the slope of Eq. (5) is $0.9823 (\pm 0.0025)$, with the corresponding ϵ_C of -17.7‰ . Two data sets of $\delta^{13}\text{C}_{\text{carboxyl}}$ value yield corresponding $\delta^{13}\text{C}_{\text{methyl}}$ values (from Eq. (1)) to give α_C values of methyl-C in each data set. The averaged α_C value of methyl-C is $1.0022 (\pm 0.0018)$, with the corresponding ϵ_C of $+2.2\text{‰}$. In contrast to the $\delta^{13}\text{C}_{\text{TOTAL}}$ and $^{13}\text{C}_{\text{carboxyl}}$ changes, the $\delta^{13}\text{C}_{\text{methyl}}$ value was little changed during the degradation, indicating that carbon isotopic change of this study is attributable to the $\delta^{13}\text{C}_{\text{carboxyl}}$ change (see below).

Values of $\ln[(\delta + 1000)/(\delta_i + 1000)]$ for hydrogen vs. $\ln F$ are plotted in Fig. 3. The value of α for hydrogen (α_H) associated with UV degradation of acetic acid is

Table 1. Change of $\delta^{13}\text{C}$ with $\ln[(\delta_i + 1000)/(\delta + 1000)]$ values and fractional abundance, and carbon isotope fractionation factor of acetic acid during UV degradation

Expt.		0 min	60 min	120 min	180 min	240 min	α (1 σ)	r^2
Total acetic acid (CH_3COOH)	$\ln F$	0.000	-0.3931	-0.6452	-1.0213	-1.4214		0.98
	$\delta^{13}\text{C}$ (‰, vs. VPDB)	-32.2	-30.1	-26.6	-24.2	-21.8		
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	0.0021	0.0057	0.0083	0.0107	0.9922	
Carboxyl-carbon ($-\text{COOH}$)								0.98
	$\delta^{13}\text{C}$ (‰, vs. VPDB)	-29.1	-22.3	-15.4	-10.3			
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	0.0069	0.0140	0.0192		0.9841	
	$\delta^{13}\text{C}$ (‰, vs. VPDB)	-29.2	-21.6	-17.3	-13.1	-8.4		
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	0.0074	0.0131	0.0178	0.0211	0.9806	
	averaged $\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	0.0071	0.0136	0.0185	0.0211	0.9823 (0.0025)	
Methyl-carbon (CH_3^- , calculated value)	1 σ	0.0000	0.0003	0.0007	0.0010	—		0.99
	$\delta^{13}\text{C}$ (‰, vs. VPDB)	-35.3	-37.9	-37.9	-38.0			
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	-0.0027	-0.0027	-0.0028		1.0035	
	$\delta^{13}\text{C}$ (‰, vs. VPDB)	-35.3	-38.3	-37.0	-36.6	-35.0		
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	-0.0032	-0.0017	-0.0014	0.0002	1.0010	
	averaged $\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	-0.0030	-0.0022	-0.0021	0.0022		0.02
	1 σ	0.0000	0.0003	0.0007	0.0010	—	1.0022 (0.0018)	

Table 2. Change of δD with $\ln[(\delta + 1000)/(\delta_i + 1000)]$ values and fractional abundance, and hydrogen isotopic fractionation factor of acetic acid during UV degradation

Expt.	$\ln F$	0 min	60 min	120 min	180 min	240 min	300 min	α (1 σ)	r^2
Acetic acid (CH_3^- , calculated value)									
1	δD (‰, vs. VSMOW)	0.0000	-0.3931	-0.6452	-1.0213	-1.4214	-1.4698		0.98
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	-89	-87	-76	-76	-74	-68	0.9858	
2	δD (‰, vs. VSMOW)	0.0000	0.0026	0.0140	0.0148	0.0161	0.0232		
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	-91	-89	-90	-79	-80	-84	0.9926	
3	δD (‰, vs. VSMOW)	0.0000	0.0025	0.0013	0.0126	0.0116	0.0078		
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	-79	-74	-61	-59	-56	-67	0.9839	
	$\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	0.0059	0.0196	0.0218	0.0255	0.0135		
	averaged $\ln[(\delta + 1000)/(\delta_i + 1000)]$	0.0000	0.0037	0.0116	0.0164	0.0177	0.0148	0.9875 (0.0046)	0.86
	1 σ	0.0000	0.0019	0.0094	0.0048	0.0071	0.0078		

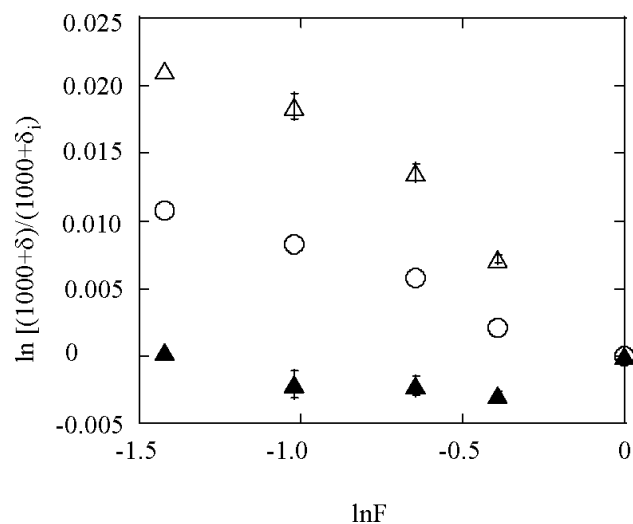


Fig. 2. Total- and site-specific-carbon isotope fractionation data of acetic acid, presented as $\ln[(1000 + \delta)/(1000 + \delta_i)]$, vs. extent of reaction ($\ln F$) during UV photolysis of acetic acid. Circle, filled and open triangles symbols denote “total” acetic acid, methyl-C and carboxyl-C, respectively.

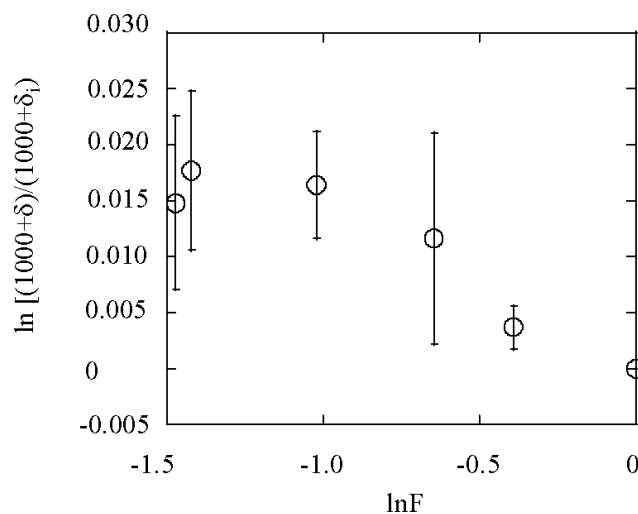


Fig. 3. Total-hydrogen isotope fractionation data of acetic acid, presented as $\ln[(1000 + \delta)/(1000 + \delta_i)]$, vs. extent of reaction ($\ln F$) during UV photolysis of acetic acid.

calculated to be 0.9875 (± 0.0046), with the corresponding ϵ_H value of -12.5‰ (Table 2). The averaged values of $\ln[(\delta + 1000)/(\delta_i + 1000)]$ for hydrogen in each experiment are less consistent than that for carbon (Figs. 2 and 3). This is probably because the precision of δD analysis is lower than that of $\delta^{13}C$ analysis ($<6\text{‰}$ and $<0.9\text{‰}$, respectively).

DISCUSSION

Characteristics of $\delta^{13}\text{C}$ and δD changes in acetic acid during UV degradation

Concentration of acetic acid decreases exponentially with UV exposure time, consistent with a previous study (Bernstein *et al.*, 2004). The half life of acetic acid in the previous work, conducted under interstellar conditions (e.g., at ~ 15 K, Ehrenfreund *et al.*, 2001; Bernstein *et al.*, 2004), is ~ 5 min, i.e., much shorter than that of our study, probably because the previous study employed more effective UV wavelengths (121.6 and ~ 160 nm) for acetic acid degradation. Although the experimental conditions of our study are very different from interstellar conditions, the first order decay of the acid is consistent with previous studies on the photodecomposition of acetic and amino acids under interstellar conditions.

Although the degradation of acetic acid by UV irradiation has been investigated previously (e.g., Wilkerson and Guillory, 1977; Bernstein *et al.*, 2004), our study is the first to measure isotope enrichment factors of ^{13}C and D associated with the UV degradation. It is apparent that acetic acid becomes enriched in ^{13}C with increasing UV exposure (Fig. 2), because UV degradation of acetic acid is a kinetically controlled process.

In addition to total carbon and hydrogen isotopic compositions, site-specific carbon isotope analysis of organic compounds may be helpful to evaluate chemical processes found in natural environments (e.g., Galimov, 1985; Dias *et al.*, 2002b). The slightly positive $\epsilon_{\text{C-methyl}}$ value ($+2.2 \pm 1.8\text{‰}$ in Table 1) indicates that the methyl-C is isotopically unchanged, or a little depleted in ^{13}C , with increasing UV exposure. The $^{13}\text{C}_{\text{methyl}}$ value is calculated using two measured values ($\delta^{13}\text{C}_{\text{TOTAL}}$ and $\delta^{13}\text{C}_{\text{carboxyl}}$), both of which have individual analytical errors. In addition, values of $\ln[(\delta + 1000)/(\delta_i + 1000)]$ for $\delta^{13}\text{C}_{\text{methyl}}$ vs. $\ln F$ yield an extremely low value of r^2 (0.02), suggesting that the $^{13}\text{C}_{\text{methyl}}$ change is independent of UV exposure time. Probably, the α value of the methyl-C is very close to 1 (within the limits of the analytical precision of this study), which would indicate that there is no mass dependence inherent to the process during UV degradation. The large value of $\epsilon_{\text{C-carboxyl}}$ vs. small value of $\epsilon_{\text{C-methyl}}$ in acetic acid indicates that the $\delta^{13}\text{C}$ change of acetic acid is largely controlled by that of the carboxyl-C.

Degradation mechanisms of acetic acid during vapor phase photolysis have been studied previously (e.g., Wilkerson and Guillory, 1977 and references therein). The primary process of acetic acid degradation can give $\text{CH}_4 + \text{CO}_2$ (Eq. (6)), as well as $\text{CH}_3\text{COO}^* + \text{H}$ (Eq. (7)). In addition, acetic acid could degrade to $\text{CH}_3 + \text{COOH}^*$ (Eq. (8)) and $\text{CH}_3\text{CO}^* + \text{OH}$ (Eq. (9)), thus the reaction pathway is not simple to predict. Active chemical species such

as H, OH and methyl radicals are produced during the degradation, which may also be involved in reactions with acetic acid.



Usually, when a C–C bond breaks kinetically, the isotope effect occurs in both carbons (Eqs. (6) and (8)). It is expected that both carboxyl and methyl carbons of the remaining acetic acid will be ^{13}C -enriched. Therefore, the apparently negligible $\delta^{13}\text{C}$ change of methyl-C in this study is unusual isotope behavior and contrasts to the significant ^{13}C -enrichment of the carboxyl-C. This unusual behavior may be explained by ^{13}C -depleted CH_3 and COOH^* formation during photolysis, followed by CO_2 formation from ^{13}C -depleted COOH , while the CH_3 could recombine with the residual ^{13}C -enriched COOH^* to produce acetic acid by back reaction:



If the degradation of COOH is the rate-determining step, it makes sense that $^{12}\text{COOH}$ would be preferentially broken relative to $^{13}\text{COOH}$. In this case, carboxyl-C would show ^{13}C -enrichment but there would be little change for methyl-C. Another possible mechanism is based on an alternative different cleavage pattern of acetic acid during photolysis. As shown by Wilkerson and Guillory (1977), acetic acid could be fragmented to $\text{CH}_3\text{CO}^* + \text{OH}$ as an additional primary process (Eq. (9)). If this fragmentation occurred, $\delta^{13}\text{C}$ of methyl-C should change little, but the carboxyl-C should be ^{13}C -enriched.

Our study also reveals that acetic acid becomes more enriched in D with longer UV exposure times. This is also consistent with kinetic control, involving the preferential breaking of a C–H bond rather than a C–D bond. The isotopic fractionation factor (α) is relatively large (0.9875 ± 0.0046), although no evidence is directly observed for C–H bond cleavage of methyl group in acetic acid during photolysis, as described above. In this case, acetic acid containing D-depleted methyl group could be cleaved preferentially into CH_3 and COOH compared to the D-depleted one. In addition, the D-enrichment of the remaining acetic acid might be associated with isotopic exchange by the hydrogen produced during photolysis. In this study, we only analyzed carbon and hydrogen isotope compositions of the remaining acetic acid. Indeed, we need to determine isotope compositions of the photolysis prod-

ucts in order to understand fully the isotope systematics of acetic acid degradation.

Application of isotope changes in acetic acid to natural environments

Ultraviolet degradation of acetic acid could be a factor in controlling the carbon and hydrogen compositions in carbonaceous chondrites, although formation mechanisms of meteoritic acetic acid are not yet understood. If 99% of acetic acid is decomposed by UV, this study suggests that the corresponding changes in $\delta^{13}\text{C}$ and δD are +36.4 and +59‰, respectively. Thus, UV degradation has the potential to yield large carbon and hydrogen isotope enrichments of acetic acid, as seen in the Murchison meteorite (+22.7 and +19‰, respectively, Yuen *et al.*, 1984; Huang *et al.*, 2005).

This result implies that carboxyl-C in interstellar acetic acid is expected to be enriched in ^{13}C relative to methyl-C, by UV degradation. Therefore, if carboxyl-C in meteoritic acetic acid is more enriched in ^{13}C relative to methyl-C, acetic acid in meteorites may have been derived, at least in part, from UV degradation of interstellar acids. In addition, the site-specific $\delta^{13}\text{C}$ fractionation of acetic acid suggests that carboxylic acids potentially become enriched in heavy isotopes, relative to hydrocarbons, by UV degradation. Therefore, in the Murchison meteorite, the observation that the $\delta^{13}\text{C}$ values of carboxylic acids are higher than those of hydrocarbons (Yuen *et al.*, 1984) suggests that isotopic compositions may have been affected by UV degradation, although there may be other mechanisms—such as oxidation of hydrocarbons—that could produce similar isotope fractionations in meteoritic organic compounds. Of course, the UV radiation process is not all encompassing for all organic compound distributions in carbonaceous chondrites.

SUMMARY

We have measured the degradation rates and isotopic fractionation factors of acetic acid during UV degradation. $\delta^{13}\text{C}$ and δD of acetic acid increase with increased UV exposure times. Position-specific carbon isotopic analysis reveals that the $\delta^{13}\text{C}$ change of acetic acid during UV degradation is mainly controlled by the behavior of carboxyl carbon. Whether carbon and hydrogen isotopic distributions in acetic acid present in carbonaceous meteorites are a result of UV irradiation remains unclear at present, although the results presented here indicate that UV degradation has the potential to change significantly the abundance and the isotopic composition of acetic acid in natural environments which experience UV fluxes.

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