

**HYDROGEN ISOTOPIC EXCHANGE RATES BETWEEN  $D_3^+$  AND ALIPHATIC, AROMATIC AND BENZYLIC C-H BONDS.** F. Robert<sup>1</sup>, A. Thomen<sup>1</sup>, Ch. Anquetil<sup>2</sup>, S. Derenne<sup>2</sup>, K. Hassouni<sup>3</sup> <sup>1</sup>LEME, MNHN-CNRS (robert@mnhn.fr, athomen@mnhn.fr), Paris, France, <sup>2</sup>BioEMCo, CNRS-UPMC, Paris, France (sylvie.derenne@upmc.fr), <sup>3</sup>LIMHP, CNRS-UPR 1311, Institut Galilée, Université Paris 13 (hassouni@limhp.univ-paris13.fr).

### Introduction.

The mechanism of organo-synthesis of the Insoluble Organic Matter (IOM) isolated from the carbonaceous meteorites remains an unsolved issue. The identification of an internal H isotopic fractionation between the different organic C-H bonds (benzylic, aliphatic, aromatic), suggests that this process is recorded at a molecular scale [1]. At the first order, the magnitude of the fractionation (up to 950‰ between the aromatic and the benzylic bonds) precludes an isotopic exchange with liquid water circulating in the meteorite parent bodies. However, this conclusion is not in conflict with a possible late and partial re-equilibration with liquid water taking place in parent bodies (as proposed by [2]).

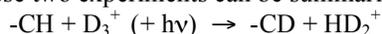
The most remarkable feature of this internal isotopic distribution is the negative correlation between the D/H ratios of the C-H bonds and their bonding energies. This pattern was interpreted as resulting from an isotopic exchange between IOM and a deuterium-rich source. It was suggested that this source was  $H_2D^+$  produced by UV irradiation at  $T < 50K$  [1].

The aim of the present work is to test experimentally the validity of this interpretation through a precise determination of the kinetics of isotopic exchange between organic hydrogen and  $D_3^+$ . To summarize the main results of the present study, the correlation observed in the IOM is in quantitative agreement with (1) the measured fast rate of isotopic exchange and (2) with the internal isotopic fractionation factor between the 3 types of C-H bonds identified in the IOM.

### Laboratory experiments.

We have conducted hydrogen isotopic exchange experiments between  $D_3^+$  and several organic molecules: the 2-ethylnaphthalene, the 1- and 2- methylnaphthalene. These molecules are liquid at room temperature. The organic liquids are absorbed on a chromatographic plate, located 2 cm away from the discharge. A continuous  $D_2$  gas flow (0.2 mbar, 330K) was submitted to a 2450 Mz discharge (70 watt). This discharge yields a UV flux of  $\approx 10^{15}$  photons  $cm^{-2} sec^{-1}$ . The main species produced in the gas by the discharge are D and  $D_3^+$  ( $D_3^+/D_2=1.1 \times 10^{-3}$ ). The 2-ethylnaphthalene is then extracted from the plate with dichloromethane and analysed through GC-MS.

The isotopic exchange reactions corresponding to these two experiments can be summarized as :



As far as the calculation of the rate constant for these experiments is concerned, note that the reverse reaction is negligible.

The enrichment in D of the molecules was measured by an *organic* GC-mass spectrometer (GC-MS). This analytical technique offers several advantages compared with the classical geochemical isotope mass spectrometry (GCiRMS): (1) The fragmentation of the molecules in the source of the MS permits the analysis in the same run of the D/H ratio in the aromatic, aromatic+benzylic and aromatic+benzylic+aliphatic molecular fragments. (2) The detection limit of the method ( $D/H \approx 2 \times 10^{-4}$ ) turns out to be compatible with the deuteration rates studied here.

2-ethylnaphthalene has  $C_{10}H_7-CH_2-CH_3$  as molecular formula. It comprises a naphthalene moiety,  $C_{10}H_7$ , i.e. two fused aromatic cycles with 7 aromatic C-H bonds with an ethyl group  $CH_2 - CH_3$  as side chain. The latter contains 2 benzylic C-H bonds ( $CH_2$ ) and 3 aliphatic C-H bonds in the terminal methyl group ( $CH_3$ ).

The D/H ratios of these 3 organic bonds can be measured via the following m/z fragments in the mass spectrum:

- at m/z 115 (n) and 116 (n+1) for aromatic C-H (the 115 ion,  $C_9H_7^+$ , results from elimination of acetylene from the benzotropylium ion at m/z 141). The fragment 115 thus contains all the aromatic C-H bonds of the 2-ethylnaphthalene.

- at m/z 141 and 142 (n+1) for  $C_{10}H_7-CH_2^+$ , resulting from the classical  $\beta$ -cleavage

- at m/z 156 and 157 (n+1) for the un-fragmented molecular ion,  $C_{10}H_7-CH_2-CH_3^+$ .

For the 1- and 2-methylnaphthalene ( $C_{10}H_7-CH_3$ ), the fragments are at m/z 115 for the aromatic ion and at m/z 142 for the molecular ion,  $C_{10}H_7-CH_3^+$ .

The mass spectrum of 2-ethylnaphthalene before deuteration is used as a reference value for calculating the isotopic ratios. We have checked that the reference spectrum yields the nominal  $^{13}C/^{12}C$  ratio, insuring in turn that no isobaric interference is present on n+1 fragment. After deuteration, 2-ethylnaphthalene shows a systematic enrichment at m/z 115+1, 141+1 and 156+1 relative to the reference. Similarly at mass 116 and 143 for the 1- and 2-methylnaphthalene.

The D/H ratio of each organic fragment can be calculated from the measured intensity  $^mI$  at the different m/z fragments. The deuterated molecular isotopomer ratio is:

$$\Delta(D/H)_{\text{molecular}} = (R_{\text{std}} - R_{\text{spl}}) / (1 + R_{\text{std}})$$

with  $R_{\#} = ({}^{m+1}I/{}^mI)_{\#}$  and with # standing for the standard (std) or the sample (spl). The factor  $(1 + R_{\text{std}})$  stands for the correction of the dominant isobaric interference at  $m+1$ ; the other possible isobaric interferences are neglected. The D/H ratio of the individual C-H bond  $\Delta(D/H)_m$  is :

$$\Delta(D/H)_m = \Delta(D/H)_{\text{molecular}} / n$$

with  $n$  being the number of H involved in the molecule present at mass  $m$ . By GC-MS we have access to  $\Delta(D/H)_{115}$  ( $n=7$ ),  $\Delta(D/H)_{141}$  ( $n=9$ ),  $\Delta(D/H)_{156}$  ( $n=12$ ) corresponding to the molecular fragments  $C_9H_7$ ,  $C_{10}H_7-CH_2$  and  $C_{10}H_7-CH_2-CH_3$ , respectively.

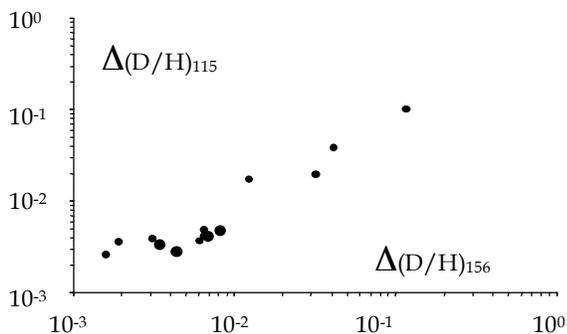
The possible isotopic selection during the fragmentation has also been measured precisely using industrial  $C_{10}H_7-CH_2-CD_3$ .

### Results

A heuristic representation of the results can be achieved using the following graphs:

$$\Delta(D/H)_{115} = f\{\Delta(D/H)_{141}\} \quad (1) \quad \text{and}$$

$$\Delta(D/H)_{115} = f\{\Delta(D/H)_{156}\} \quad (2) \quad (\text{Figure here after})$$



The relations (1) and (2) are linear since the molecule at mass 115 contributes on both masses at  $m=141$  and  $m=156$ . The slopes of the two correlations give an access to the isotopic fractionation factor between the three CH bonds via the two mass balance equations between Aromatic, Benzylic and Aliphatic D/H ratio:

$$9 (D/H)_{141} = 7 (D/H)_{\text{Aro}} + 2 \alpha_{\text{Benz-Aro}} (D/H)_{\text{Aro}}$$

$$12 (D/H)_{156} = 7 (D/H)_{\text{Aro}} + 2 \alpha_{\text{Benz-Aro}} (D/H)_{\text{Aro}} + 3 \alpha_{\text{Ali-Aro}} (D/H)_{\text{Aro}}$$

with - by definition:

$$\Delta(D/H)_{115} = (D/H)_{\text{Aro}}$$

$$\alpha_{\text{Benz-Aro}} = (D/H)_{\text{Benz}} / (D/H)_{\text{Aro}}$$

$$\alpha_{\text{Ali-Aro}} = (D/H)_{\text{Ali}} / (D/H)_{\text{Aro}}$$

The slopes of the two linear correlations defined by the relation (1) and (2) gives (2 sigma) :

$$\alpha_{\text{Benz-Aro}} = 1.68 \pm 0.14$$

$$\alpha_{\text{Ali-Aro}} = 1.07 \pm 0.02$$

In the IOM isolated from the Orgueil meteorite, Remusat et al. found :

$$\alpha_{\text{Benz-Aro}} = 1.96 \pm 0.05$$

$$\alpha_{\text{Ali-Aro}} = 1.35 \pm 0.05$$

The present experimental data confirm the previous assumption according to which the degree of exchange is related to the energy  $\Delta E$  of the chemical C-H bond. That is to say  $\Delta E_{\text{Aro}} > \Delta E_{\text{Ali}} > \Delta E_{\text{Benz}}$  yields  $(D/H)_{\text{Benz}} > (D/H)_{\text{Ali}} > (D/H)_{\text{Aro}}$ .

### Rate constants

The rate constants  $k^+$  for the forward reactions are expressed via [3, 4]:

$$-\text{Ln } F = n k^+ t$$

with  $n$  standing for the number of D in the deuterium-rich source ( $n=3$  for  $D_3^+$ ),  $t$  the duration of the exchange and  $F$  the usual *exchange fraction* :

$$F = [R_t - R_{\infty}] / [R_0 - R_{\infty}]$$

with  $R = x_D / (x_D + x_H)$  with  $x_D + x_H = 1$ . In a pure deuterated source,  $R_{\infty} = 1$ . We took the initial value  $R_0$  – the isotopic composition of the 2-ethylnaphthalene – at its nominal terrestrial value i.e.  $1.5(\pm 0.5) \times 10^{-4}$  (a more precise estimate is in progress). The duration of the experiments varies between 780 and 8200 sec. The half time  $t_{1/2}$  of the reaction is defined as:  $t_{1/2} = \text{Ln}(2) / k^+$

Most experiments yield  $t_{1/2}$  lying between 10 and 70 days. The corresponding  $k^+$  is  $3 (\pm 2) \times 10^{-7} \text{ s}^{-1}$ . It has been experimentally verified that the rate of exchange is the same if the samples are exposed or not to the UV light. Therefore the dominant parameter for the exchange is the density of  $D_3^+$ . The results with 1- and 2-methylnaphthalene are undistinguishable from those with 2-ethylnaphthalene, indicating that at our level of precision on D/H ratios, the exchange rate is dominated by the chemical nature of the CH bond and not by the molecular configuration.

### Cosmochemical implications

In our experiment  $[D_3^+]/[D_2]$  has been precisely computed:  $1.1 \times 10^{-3}$ . With a  $D_2$  pressure of 0.3 mbar, this gives a  $[D_3^+]$  density =  $8.8 \times 10^{12} \text{ cm}^{-3}$ .

Taking the conditions prevailing at the surface of the protosolar disk [5, 6] around 5 AU [6] :  $H_2 = 5 \times 10^{15} \text{ cm}^{-3}$ ,  $[H_3^+] = 2 \times 10^8 \text{ cm}^{-3}$ ,  $[H_2D^+] = 3 \times (2 \times 10^{-2}) \times (2 \times 10^8) \text{ cm}^{-3}$  ( $2 \times 10^{-2}$  stands for the measured D/H ratio in  $H_3^+$ ) and assuming that the rate of exchange is proportional to the density of  $H_2D^+$ , the calculated duration to increase the D/H ratio from  $10^{-4}$  to its average measured value in meteorites ( $D/H \approx 3.5 \times 10^{-4}$ ) should not exceed few  $10^4$  years.

If we extrapolate this calculation to the ISM ( $[H_3^+] = 100 \text{ cm}^{-3}$ ), the time needed for the deuteration of the C-H bonds is  $\geq 5 \times 10^9$  years.

### References

- [1] Remusat L. et al. (2006) *EPSL*, 243, 15-25. [2] Alexander et al., (2007) *Cosmochim. Acta*, 71, 4380-4403 [3] Lecluse C. & Robert F. (1994) *Cosmochim. Acta*, 58, 2927-2939 [4] Sessions A. et al., (2004) *Geochim. Cosmochim. Acta*, 68, 1545-1559. [5] Glassgold A.E. et al. (1997) *Ap. J.*, 480, 344-350. [6] Chunhua Qi et al., (2008) *Ap. J.*, 681, 1396-1407.