

**HYDROGEN ISOTOPIC EXCHANGE RATES BETWEEN DEUTERIUM-RICH SOURCES (UV IRRADIATED MOLECULAR HYDROGEN AND LIQUID WATER) AND AN ORGANIC MOLECULE: IMPLICATIONS FOR THE CONDITIONS OF FORMATION OF THE INSOLUBLE ORGANIC MATTER IN THE EARLY SOLAR SYSTEM.** A. Thomen<sup>1</sup>, F. Robert<sup>1</sup>, S. Derenne<sup>2</sup>, <sup>1</sup>LEME, MNHN-CNRS (athomen@mnhn.fr, robert@mnhn.fr), Paris, France, <sup>2</sup>LCBOP, CNRS, Paris, France (sylvie-derenne@enscp.fr).

### Introduction.

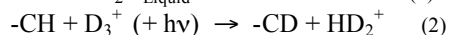
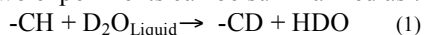
The mechanism of formation of the Insoluble Organic Matter (IOM) isolated from the carbonaceous meteorites is pending. The recent identification of H isotopic fractionation between the different organic C-H bonds (benzylic, aliphatic, aromatic), suggests that formation processes and secondary alteration events (in parent bodies?) are isotopically recorded at a molecular scale [1]. The most remarkable feature of such isotopic distribution is the negative correlation between the D/H ratios of the C-H bonds and their bonding energies. This pattern is interpreted as resulting from an isotopic exchange between IOM and a deuterium-rich source. It was suggested that this source was H<sub>3</sub><sup>+</sup> produced H<sub>2</sub> at T<50K by UV irradiation [1].

Several questions arise from this interpretation: (1) Does this isotopic enrichment take place in the ISM or in the proto-planetary disk? (2) How can this correlation survive the possible isotopic exchange with water during parent body hydrothermalism?

These two questions are linked to a precise determination of the kinetics of isotopic exchange between organic hydrogen and H<sub>2</sub>D<sup>+</sup> or liquid H<sub>2</sub>O. Ultimately, it should be possible to reproduce the observed correlation in laboratory conditions.

**Laboratory experiments.** We have conducted hydrogen isotopic exchange experiments between a model organic compound, namely, the 2-ethylnaphthalene and (i) liquid D<sub>2</sub>O, and (ii) D<sub>2</sub> gas submitted to a RF discharge.

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



As far as the calculation of the rate constant for these 2 experiments is concerned, note that the reverse reactions are always negligible.

The enrichment in D was measured through an *organic* GC-mass spectrometer (GC-MS). This analytical technique offers several advantages compared with the classical geochemical mass spectrometry: (1) The fragmentation of the 2-ethylnaphthalene in the source of the MS permits the analyzes in the same spectrum of the D/H ratio in the aromatic, benzylic and aliphatic C-H bonds. (2) The enrichment in D in each organic fragment produced in the source of the MS, can be quantitatively measured assuming the isotopic selection during the fragmentation can be neglected in regards of a huge enrichment in D. (3) Possible

contaminations by D-rich products such as water or other organics are separated by the GC column. (4) The detection limit of the method (D/H  $\approx 5 \times 10^{-4}$  i.e.  $\approx 2500\text{‰}$  in the usual  $\delta\text{D}$  units) turns out to be compatible with the deuteration rates of the here studied reactions (1) and (2).

2-ethylnaphthalene has C<sub>10</sub>H<sub>7</sub> - CH<sub>2</sub> - CH<sub>3</sub> as molecular formula. It comprises a naphthalene moiety, C<sub>10</sub>H<sub>7</sub>, i.e. two fused aromatic cycles with 7 aromatic C-H bonds with an ethyl group CH<sub>2</sub> - CH<sub>3</sub> as side chain. The latter contains 2 benzylic C-H bonds (CH<sub>2</sub>) and 3 aliphatic C-H bonds in the terminal methyl group (CH<sub>3</sub>).

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

- at mass 115 (n) and 116 (n+1) for aromatic C-H (the ion 115, C<sub>9</sub>H<sub>7</sub>, results from the classical  $\beta$ -cleavage – yielding the ion at mass 141 – followed by elimination of acetylene). The mass 115 thus contains all the aromatic C-H bonds of the 2-ethylnaphthalene.

- at mass 141 and 142 (n+1) for C<sub>10</sub>H<sub>7</sub>-CH<sub>2</sub>

- at mass 156 and 157 (n+1) for the molecular ion, C<sub>10</sub>H<sub>7</sub>-CH<sub>2</sub>-CH<sub>3</sub>

The mass spectrum of 2-ethylnaphthalene before deuteration was run as a reference value. We have checked that the reference spectrum yields the nominal <sup>13</sup>C/<sup>12</sup>C ratio, insuring in turn that no isobaric interference is present on mass n+1. After deuteration, 2-ethylnaphthalene shows a systematic enrichment at mass 116, 142 and 157 relative to the reference.

### Reaction (1)

A mixture of 1mL of D<sub>2</sub>O and 1mL of pure 2-ethylnaphthalene (2-ethylnaphthalene is a liquid at room temperature) was refluxed in a sealed vessel with 10 mg of Na<sub>2</sub>CO<sub>3</sub> and 50 mg of NaCl for 7 and 38 days at 380K. The organic product is extracted with dichloromethane immediately after the quench of the mixture in air and injected in the column of a GC-MS.

### Reaction (2)

A continuous D<sub>2</sub> gas flow (0.15 mbar, 330K) was submitted to a 2450 Mz discharge (70 watt). This discharge yields a UV flux of  $\approx 10^{15}$  photons cm<sup>-2</sup> sec<sup>-1</sup>. 2-ethylnaphthalene absorbed in a thin layer chromatography plate, is located at 2 cm from the discharge and is directly exposed to the UV's. The main species produced in the gas by the discharge are D and D<sub>3</sub><sup>+</sup>. The duration of the irradiation experiments was 30 min. The 2-ethylnaphthalene is then extracted from the plate with dichloromethane, and analysed through GC-MS.

## Results

Contrary to previous published experiments [2, 3, 4], no isotopic exchange was observed for reaction (1). Such a difference is likely caused by the lack of -OH groups in 2-ethylnaphthalene and/or by absorption (oxidation ?) of water in the IOM. These processes were modelled by [2].

For reaction (2), we measure:

$$\begin{aligned} (D/H)_{\text{Benzylic}} &= 1.4 (\pm 0.5) \times 10^{-2} \\ (D/H)_{\text{Aromatic}} &= 1.3 (\pm 0.2) \times 10^{-2} \\ (D/H)_{\text{Bulk}} &= 8.8 (\pm 0.6) \times 10^{-3} \end{aligned}$$

These D/H ratios stand for each individual C-H bond and not for the isotopomers ratios. Note however that there is a slight inconsistency between the three ratios since the bulk value of C<sub>10</sub>H<sub>7</sub> - CH<sub>2</sub> - CH<sub>3</sub> is too low to account for the D/H ratio of the 3 aliphatic H. It is thus possible that an isotopic fractionation occurs during fragmentation. The analysis of the reproducibility of this inconsistency is under progress.

## Rate constants

The rate constants  $k^+$  for the forward reactions (1) and (2) are expressed via :

$$-\ln F = n k^+ t$$

with  $n$  standing for the number of D in the deuterium-rich source ( $n=2$  for D<sub>2</sub>O and  $n=3$  for D<sub>3</sub><sup>+</sup>),  $t$  the duration of the exchange and  $F$  the usual *exchange fraction* :

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

with  $R$  the D/H ratio. 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.  $1.5(\pm 0.5) \times 10^{-4}$ . Due to the high D/H ratios obtained after deuteration ( $\approx 10^{-2}$ ), the uncertainty of the terrestrial value ( $\pm 0.5 \times 10^{-4}$ ) has a negligible effect on the calculated  $k^+$ .

For reaction (1), since no exchange was observed we took our detection limit for  $R_t$ . That is:  $R_t = 5 \times 10^{-4}$ , yielding  $k^+_{\text{Reaction 1}} < 4 \times 10^{-11} \text{ sec}^{-1}$

For reaction (2), we assume that the reaction rate is proportional to the density of H<sub>2</sub>D<sup>+</sup>; that is:

$$-\ln F = 3 [H_2D^+] k^+ t$$

A precise calculation of the density of [H<sub>2</sub>D<sup>+</sup>] in our experiment is in progress. As a first order of approximation we assume that the density of H<sub>2</sub>D<sup>+</sup> is close to the degree of ionization ( $\approx 10^{-6}$ ). This gives, for D<sub>2</sub>=1.5 mbar, H<sub>2</sub>D<sup>+</sup>=  $4 \times 10^9 \text{ cm}^{-3}$  yielding  $k^+_{\text{Reaction 2}}$  between  $4.0 \times 10^{-16}$  and  $6.3 \times 10^{-16} \text{ cm}^{-3} \text{ sec}^{-1}$  for the observed D/H variations between  $1.4 \times 10^{-2}$  and  $8.8 \times 10^{-3}$ , respectively. Note that this value is based on several assumptions namely, the linearity of  $k^+$  with the pressure, the role of the ion D<sub>3</sub><sup>+</sup> in the exchange. The validity of these approximations will be checked in future experiments. The calculated  $k^+$  should thus be regarded as maximum values.

## Cosmochemical implications

If the source of D (or of H for a reverse reaction) is infinite, the evolution of the D/H ratio is:

$$R_t = R_\infty + [R_0 - R_\infty] \exp(-k^+ t)$$

with  $R_0$  the initial composition of the organic molecule before exchange and  $R_\infty$  the equilibrium value between the isotopic composition of the source ( $R_{\text{source}}$ ) and the organic molecule:  $R_\infty = \alpha R_{\text{source}}$  with  $\alpha$  the isotopic fractionation factor (see [5] for example).

In the case of hydrothermalism, since no exchange was observed, the possible duration of an isotopic exchange between D-rich organic matter and water, was not calculated.

For an exchange in the gas phase between C-H bonds and H<sub>2</sub>D<sup>+</sup>, we took the conditions prevailing at the surface of the protosolar disk around 5 AU [6] : H<sub>2</sub>=  $5 \times 10^{15} \text{ cm}^{-3}$ , [H<sub>3</sub><sup>+</sup>] =  $2 \times 10^8 \text{ cm}^{-3}$ , [H<sub>2</sub>D<sup>+</sup>] =  $3 \times (1.5 \times 10^{-2}) \times (2 \times 10^8) \text{ cm}^{-3}$  ( $1.5 \times 10^{-2}$  stands for the D/H ratio measured in the organic radicals of the IOM by EPR [7];  $1.5 \times 10^{-2} = R_{\text{source}}$  in the previous equation), the UV flux  $\phi$  is  $\phi = 3 \times 10^6 \phi_{\text{ISM}}$  with  $\phi_{\text{ISM}}$  the canonical value of the UV field ( $10^8 \text{ photon cm}^{-3} \text{ sec}^{-1}$ ), with  $R_0=10^{-4}$  i.e. the isotopic ratio of the IOM before its deuteration (assumed to be the measured D/H ratio in the *cold spots* of NanoSims images [7]) and with  $\alpha=1$  for simplicity. We assume that the rate of exchange is proportional to the density of H<sub>2</sub>D<sup>+</sup>, to the flux of UV photons and independent of the temperature of the neutral species in the gas phase. Under these assumptions, the calculated duration for the exchange stands for a maximum value. The calculated duration to increase the D/H ratio of the IOM from  $10^{-4}$  to its measured value in meteorites ( $\delta D \approx + 1000\%$  i.e.  $D/H \approx 3 \times 10^{-4}$ ) is extremely short (few  $10^3$  hours).

If we extrapolate this calculation to the ISM (with a UV flux  $3 \times 10^6$  times less intense than at the surface of the protosolar disk), the time needed for the deuteration of the IOM C-H bonds is  $10^{12}$  years.

## Conclusions

These preliminary experiments confirm our interpretation [1] according to which IOM could get its deuterium enrichment at the surface of the protosolar disk, in a dense and UV irradiated gas. The rate of such an exchange seems too slow to take place in the ISM. However, the origin of the relation between the D/H ratio and the organic C-H bonds is still a pending experimental issue.

## References

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