The photochemical reaction of hydrocarbons under extreme thermobaric conditions

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Abstract. The photochemical reaction of hydrocarbons was found to play an important role in the experiments with the synthetic petroleum conducted in Diamond Anvil Cell (DAC). Raman spectroscopy with a green laser (514.5 nm) was used for in situ sample analysis. This photochemical effect was investigated in the pressure range of 0.7-5 GPa, in the temperature interval from the ambient conditions to 450°C. The power of laser used in these experiment series was from 0.05 W to 0.6 W. The chemical transformation was observed when the necessary threshold pressure (~2.8 GPa) was reached. This transformation correlated with the luminescence appearance on the Raman spectra and a black opaque spot in the sample was observed in the place where the laser focus was forwarded. The exposure time and laser power (at least in the 0.1-0.5 W range) did not play a role in the 0.1-0.5 GPa range.

1. Introduction

Hydrocarbon photochemistry has received serious attention in the last few years due to its importance in the chemistry of cosmic water ices in space [1] and the higher layers of Jovian planets [2], [3]. High pressure studies have also touched on this problem. Interesting results were found for unsaturated hydrocarbons, especially butadiene. It was found that using laser radiation at 488 nm or 458 nm and 20 mW for 2-3 hours switched the dimerization pathway of the butadiene transformation to a selective polymerization [4]. While special experiments are still rare in which significant efforts are made to change the reaction pathways, the use of laser radiation as an analytical tool is a standard procedure.

Raman laser spectroscopy became a routine analytical technique for DAC experiments very long ago due to its high sensitivity to most components and relatively low diamond quality requirements. Heating from Raman laser is typically almost negligible, even for rubies, which have a high absorption rate. A couple degrees of temperature rise during ruby irradiation with a 150 mW (~75 mW) green laser (532.8 nm) was found to occur during the investigation of ethane (which will be published elsewhere). At the same time, if a chemical reaction takes place, laser radiation should accounted for, especially if thermobaric stability limits are being investigated.

Acetylene was studied by [5] in which a few milliwatts of laser light was used above 3 GPa. Exceeding this low threshold led to polymerization. Below this pressure and the corresponding ambient
temperature orthorhombic phase, the cubic phase was stable with several tens of milliwatts of 530.9 and 647.1 nm Kr laser irradiation.

A uniform acetylene color change [6] due to the polymerization was observed at 3.5 GPa and ambient temperature inside an Inconel X-750 gasket between diamonds. Laser radiation with a 0.3 mm focus diameter radiated the entire sample hole. The effects of radiation on the polymerization products were investigated at -196°C using laser strengths of a few milliwatts at different wavelengths. No spectral change was observed with 676.4 nm and 647.1 nm wavelengths, while the background intensity increased with 476.2 nm.

[7] paid great attention to give away the photochemical and heating potential of the laser radiation of the benzene phase and chemical transformations. The Raman laser point was defocused, and the laser power was 20 mW (it was optimal to have Raman signals). To confirm the hypothesis concerning the benzene transformation line in the phase diagram found by laser testing, separate experiments were carried out without Raman laser radiation. The laser effect was found to shift the reaction pressure threshold from 23 to 16 GPa when the sample was radiated for 23 hours with 70 mW using a 458 nm laser [8].

[9] emphasized that it was the Raman laser that caused methane to change into graphite-like soot at 2.5-5.0 GPa, 639°C and a hard, clear solid film at 10-13 GPa, 675°C. Blue 488 nm and 458 nm lasers were used. Soot formation was observed using a 458 nm laser with a 40 mW power output. This formation occurred more quickly using a 488 nm laser at 200 mW. The paper did not describe whether the wavelength, power, or the combination of the two accelerated the transformation. The formation of a brown spot of soot correlated with the incident laser spot. It was observed that with color change it was not possible to find the soot signals. Therefore, there is a possibility that soot was not the first substance formed, though soot signals were observed after cooling the samples to the ambient temperature.

[10] did not mention the laser properties, but Raman spectroscopy was the only analytical technique used for the methane resistive heating experiments. The methane dissociation temperatures in their experiments were even lower than in [9]. The reactions were observed at 3.17 GPa and 520°C, 7.36 GPa and 450°C, as well as at 560°C and 0.86 GPa.

[11] did not observe a n-heptane reaction using a 532 nm laser at 120 mW power. The authors measured the laser power near the sample, and it appeared to be 30 mW. This difference between the output laser power value and the power that reached the sample is a typical issue in experiments where the optical pathway diminishes the laser power output. The question in this case is how much it diminishes. [11] reported no chemical changes in n-heptanes with pressures up to 16 GPa at ambient temperature. The same setup was used for two further studies [12], [13], and no photochemistry effects were noted for n-hexane and n-pentane. For pentane, 15 mW of laser power reached the sample at the highest pressure tested (17 GPa) and ambient temperature.

It is difficult to estimate the influence of a Raman laser on the transformation of samples in experiments in which infrared lasers were used to heat the sample. Raman laser irradiation of the same incident point of on the sample as the heating laser may have some influence, but this question has not been investigated thus far. In some papers, the type of Raman laser used was not mentioned [14], and in others [15], [16], no laser power information was presented.

In experiments in which the synthetic petroleum stability was investigated under the Earth’s crust at thermobaric conditions (to be published elsewhere), the photochemical reaction was found to play an important role.

2. Experimental details

Synthetic petroleum synthesized in Fischer-Tropsch process (figure 1) and (table 1) was received from ZAO “Zeosit”.

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Figure 1. Chromatogram of synthetic petroleum using in Fischer-Tropsch process

Table 1. Components of synthetic petroleum using in Fischer-Tropsch process

| Symbol | Compounds                                      | Symbol | Compounds                                      |
|--------|------------------------------------------------|--------|------------------------------------------------|
| 3      | propane C₃H₈                                  | 8      | n-C₈, n-octane, C₈H₁₈                           |
| i4     | i-C₄, i-butane, CH(CH₃)₃                      | MCG    | methycyclohexane                               |
| 4      | n-C₄, n-butane, C₄H₁₀                         | B      | benzene, C₆H₆                                  |
| 4=     | butylenes, C₄H₈                              | i9     | i-C₉, i-nonanes                                |
| i5     | i-C₅, i-pentane (2-methylbutane)              | 9      | n-C₉, n-nonane, C₉H₂₀                          |
| 5      | n-C₅, n-pentane, C₅H₁₂                        | T      | toluene, C₆H₅-CH₃                             |
| 5=     | pentenes, C₅H₁₀                              | i10    | i-C₁₀, i-decanes                               |
| G      | 2,2-dimethylbutane                           | M      | ethylbenzene+meta-xylene+para-xylene, C₆H₅-C₂H₅+ meta-C₆H₅-(CH₃)₂+ para-C₆H₅-(CH₃)₂ |
| G1     | 2,3-dimethylbutane                           | i11    | i-C₁₁, i-undecanes                             |
| G2     | 2-methylpentane                              | O      | ortho-xylene, ortho-C₆H₅-(CH₃)₂                 |
| 6      | n-C₆, n-hexane, C₆H₁₄                        | P      | ethyltoluens                                   |
| 6=     | hexenes, C₆H₁₂                               | i12    | i-C₁₂, i-dodecanes                             |
| i7     | i-C₇, i-heptanes                             | PC     | pseudocumene, 1,2,4-trimethylbenzene           |
| MCP    | methycyclopentane                             | A1     | ethylxlenes                                    |
| 7      | n-C₇, n-heptane, C₇H₁₆                      | A2     | durol, 1,2,4,5-tetrarmethylbenzene             |
| i8     | i-C₈, i-octanes                               | A      | aromatic hydrocarbons Cₑ₁             |
| CG     | cyclogexane, C₆H₁₂                            |        |                                                 |

This synthetic petroleum was loaded in the Diamond Anvil Cells (DACs) with internal resistive heaters made of platinum wires. The temperature was measured by Pt/Pt-Rh thermocouples. Ruby and Sm:YAG were used as internal pressure and temperature sensors. Raman spectroscopy with a green Ar⁺-laser (514.5 nm) was used for in situ sample analysis. The temperature increased slowly during the experiments (60-70°C/h). Periodically, the pressure was checked and corrected if necessary. The temperature range was 25-450°C, and the pressure range was 0.5-1.5 GPa. The details of the experiments are described in [17].

3. Results and discussion
A series of experiments with the synthetic petroleum was performed with starting pressures of 1, 3 and 5 GPa. Without laser radiation, the synthetic petroleum remained stable over the entire thermobaric
range investigated in this study, from 25 to 450°C and 1-5 GPa. During the experiments, it was discovered that the hydrocarbons only reacted to the laser radiation at specific thermobaric conditions. This observation was noticed because the appearance of luminescence in the Raman spectra showed that the hydrocarbon peaks were no longer visible (figure 2 b,c).

Figure 2. Fluorescence in Raman spectra during the heating of the synthetic petroleum at 2.8 GPa.

This fluorescence phenomenon was also observed by [16] when methane was heated above 2700°C without a coupler at 23.1 GPa. This was interpreted as the formation of ultra-dispersive diamonds.

A black opaque spot in the hydrocarbon sample was found by optical observations of the focal point of the laser on the sample. If the sample was a liquid at certain thermobaric conditions, the black spot began to dissolve in the sample after a certain amount of time, and in this case, the sample color did not change (figure 3).

Figure 3. Reaction of the synthetic petroleum during heating at 170°C, 2.8 GPa in response to 0.5 W Raman Ar⁺-laser radiation. a) Solid sample and black spot after one laser shot; b) brownish
area around Sm:YAG and ruby main spots during the dissolving process; c) fully liquefied sample and multiple black dots in radiated spots.

Laser induced transformations took place during loading runs at 100°C and 4.5 GPa (0.2 W laser power), 160°C and 5.0 GPa (0.15 W), and 170°C and 2.8 GPa (0.5 W). At the same time, with lower pressures, much higher temperatures were reached without synthetic petroleum transformations: 220°C at 1.2 GPa (0.5 W), 320°C at 0.7 GPa (0.4 W), and 420°C at 1.15 GPa (0.5 W).

The initiation of a photochemical reaction in the sample depended on the pressure, temperature and laser power. The key factor was the pressure inside the cell. The photochemical reaction took place at very high pressures (10 GPa and more) even at an ambient temperature and with a low laser power (0.15 W). However, no reactions occurred at low pressures (less than 1.5 GPa) even at 450°C and with a laser power of 0.3-0.4 W.

The hydrocarbon photochemical reactions were more intense when the Raman laser was focused on ruby and Sm:YAG that was placed in the DAC to control the pressure and temperature. Both the ruby and Sm:YAG were more opaque and better absorbers of laser radiation. The background intensity of the spectra increased with each successive accumulation.

The time of exposure of the laser radiation was not found to play a role. If the threshold pressure was overcome, even a second of radiation with 0.1 W power was enough to cause the reaction. On the contrary, at a pressure of 1.15 GPa, the sample was radiated with a 0.5 W laser for 2 hours without any sign of transformation, and the Raman spectra did not change.

4. Conclusions
During the investigation of the synthetic petroleum received from Fischer-Tropsch, laser radiation was observed to induce chemical transformations if the necessary threshold pressure (~2.8 GPa) was reached. The exposure time and laser power did not play a role in the 0.1-0.5 GPa range. The temperature appeared to be important, and its critical value changed with the pressure. More experiments are necessary to find a clear correlation between the pressure and critical temperature as well as to identify fluorescent reaction products.

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