

CRACKING KINETICS OF PRISTANE AND PHYTANE IN A SET OF CRUDE OILS FROM THE PANNONIAN BASIN (HUNGARY)

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The objective of our research was to study the effect of maturation on distributions of C₉-C₂₀ isoprenoids in different crude oils, and to determine the activation energies and pre-exponential factors for the thermal degradation of two ubiquitous acyclic isoprenoid alkanes present in sedimentary rocks, crude oils and coals: pristane (Pr; 2,6,10,14-tetramethylpentadecane) and phytane (Ph; 2,6,10,14-tetramethylhexadecane) in oil.

Former analysis of a crude oil resulted in the following cracking parameters of pristane and phytane: $E_{aPr}=64$ kcal/mol, $A_{Pr}=1.5741E+16/\text{min}$, and $E_{aPh}=63$ kcal/mol, $A_{Ph}=8.1392E+15/\text{min}$. Calculations were carried out using Kinetics05 software (GeoIsoChem Corporation), with Discrete analysis method based on cumulative reacted data, and with fixed E-spacing of 1 kcal/mol (Sajgó and Fekete, 2015). We applied 0.1, 0.7 and 5°C/min heating rates.

In the frames of the recent study we have performed heating experiments on 17 crude oil samples originating from the Pannonian Basin. The aim was to gather more information on possible kinetic parameters and to compare the data gained from oils of various origin, maturity and biodegradation state. Heating rate was 0.7°C/min from 250°C to 505°C, and samples were taken in 10°C or 20°C steps above 370°C. After thermal treatment whole oils were examined in a full blown MSSV Kinetics system (Hall Analytics). The products of the experiments were measured by gas chromatography. The compositional determination of the compounds was accomplished based on retention times, utilising the acyclic regular isoprenoid alkanes in the iC₉-iC₂₀ (2,6-dimethylheptane-2,6,10,14-tetramethylhexadecane) molecular range (nC₈-nC₂₀ normal alkanes).

As only one heating rate per sample was applied, a fixed A range of $1 \times 10^{14} - 1 \times 10^{17}$ was used in the Kinetics05 software, based on our former results. 25 reactions (activation energies) were searched with the middle value of 64 kcal/mol for pristane, and 63 kcal/mol for phytane.

Activation energy distributions of three samples are shown in Figure 1 (pristane cracking: upper line, phytane cracking: lower line). A part of the samples show Gaussian-like distribution of numerous peaks, while in others only 1-3 major peaks can be observed. The increased number of reactions may be the result of ongoing pristane and phytane generation (release) from the asphaltene fraction. Activation energies are somewhat higher (66-68 kcal/mol) than in the former one crude oil sample (64 and 63 for pristane and phytane, respectively).

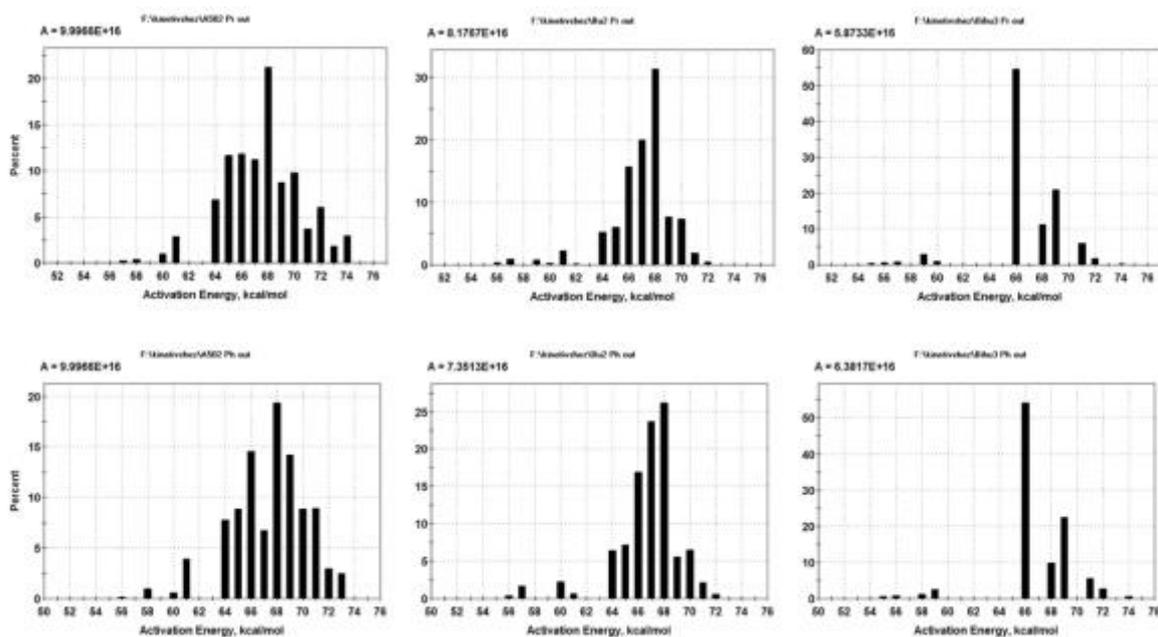


Figure 1 Activation energy distributions in 3 samples (pristane: above, phytane: below).

In severely biodegraded oils the calculations cannot be performed, because the generation of C₉-C₂₀ isoprenoids can be considered continuous up to the intense cracking temperatures, resulting in irregular hump-shaped or saw-toothed reaction curves.

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