

A POSSIBLE MECHANISM OF ALKENE/ALKANE PRODUCTION IN OIL SHALE RETORTING

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INTRODUCTION

Alkene/alkane ratios have been used extensively as indicators of oil-shale retorting conditions. Jacobson, Decora and Cook (1) developed a "retorting index" which relates the ethene/ethane ratio to the retorting temperature. Campbell and coworkers developed relationships between ethene/ethane and propene/propane ratios (2), C₇ to C₁₂ 1-alkene/n-alkane ratios (3), and total 1-alkene/alkane ratios (4) and the logarithm of the heating rate during retorting. Raley (5) developed a relationship between the ethene/ethane and propene/propane ratios and the yield loss in the Livermore combustion retorts. Uden and co-workers (6) demonstrated the dependence of the C₂ to C₅ alkene/alkane ratios on the presence of oxygen during retorting. Finally, Burnham (7) related the ethene/ethane ratio to the temperature at which shale oil cracking occurs.

The purpose of the work reported here is to clarify the reaction mechanisms which determine the observed alkene/alkane ratios under various conditions. When oil shale is pyrolyzed either isothermally or nonisothermally, the hydrocarbon and hydrogen concentrations are all time-dependent. To determine if the alkene-alkane-hydrogen system is in equilibrium, we have measured the C₁ to C₃ hydrocarbons and hydrogen as a function of time for oil shale heated at a constant rate. We have also determined the effect of an inert sweep gas on the time-dependent ethene/ethane and propene/propane ratios and the integral 1-alkene/n-alkane ratios in the oil. We demonstrate that the C₂H₄-C₂H₆-H₂ system is not in thermal equilibrium. We interpret our results in terms of a nonequilibrium free radical mechanism proposed by Raley (8).

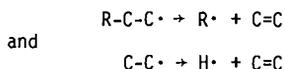
Pyrolysis of both kerogen and shale oil is basically a process of breaking larger molecules into smaller molecules. For the alkene-alkane-hydrogen system to be in equilibrium, the reactions which lead to equilibrium must be faster than those which produce the smaller molecular fragments. For equilibrium to be satisfied, the ethene/ethane ratio must satisfy the condition

$$\frac{[{}^P\text{C}_2\text{H}_6]}{[{}^P\text{C}_2\text{H}_4][{}^P\text{H}_2]} = K_{\text{eq}}$$

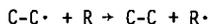
The enthalpy change of 34 kcal/mole (9) for the C₂H₄ plus H₂ reaction requires that the ethene/ethane ratio be a function of temperature with other conditions constant. Since the equilibrium expression has units of reciprocal pressure, the ethene/ethane ratio should be proportional to the amount of inert diluent if the system is at or near equilibrium.

From a more general viewpoint, an alkene/alkane ratio is determined by the relative rates of production of the alkene and alkane. In the pyrolysis of alkane moieties via a free-radical cracking mechanism, alkenes are formed by unimolecular decomposition of free radicals, and alkanes are formed by the free radical abstracting a hydrogen from another source. For example, ethene is formed from the decomposition of primary radicals (including ethyl), i.e.,

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Ethane forms from ethyl by hydrogen abstraction, i.e.,



Similarly, propene forms from decomposition of secondary free radicals and propyl while propane forms from propyl by hydrogen abstraction.

The free radical hypothesis leads to two interesting predictions:

- (a) The alkene/alkane ratios should depend on total organic concentration since alkene formation is a unimolecular reaction and alkane formation is a bimolecular reaction.
- (b) The alkene/alkane ratios should depend on retorting temperature because the activation energies for alkene formation are greater than the activation energies for alkane formation.

Therefore, both the equilibrium and free-radical hypotheses predict that the ethene/ethane ratio should depend on pyrolysis temperature and inert diluent. However, the predictions are quantitatively different and can be tested.

EXPERIMENTAL

The oil shale used in these experiments was a 22 gal/ton sample of Anvil Points shale which was ground and sieved to <0.84 mm. Aliquots from 14 to 40 g were held in a stainless steel can which had a porous frit in the bottom to allow gas and oil to escape. The sample was heated at a constant rate of 1.0 or 1.5°C/min in a programmable furnace. A constant flow of N₂ or Ar entered the system either near the bottom of the sample can or through the top of the sample can. The former configuration caused the retorting to occur under autogenous conditions (a self-generated atmosphere). The latter configuration caused the sweep gas to pass directly through the sample. Hydrocarbons were detected by a flame ionization gas chromatograph. H₂, N₂, and CO were detected by a thermal conductivity gas chromatograph. Ice water and dry ice-isopropanol traps preceded the chromatographs.

RESULTS

The rate of ethene and ethane evolution, ethene/ethane ratio and hydrogen partial pressure (relative evolution rate of hydrogen to total gas) are shown in Figure 1 for oil shale heated at 1.5°C/min under an autogenous atmosphere. The ethene/ethane ratio reaches a first minimum before the peak C₂ evolution rate. It then increases slightly before reaching a second minimum about 540°C. More pronounced results for the propene/propane ratio at 1°C/min are shown in Figure 2. We are able to combine the ethene/ethane ratios with the hydrogen partial pressures to demonstrate that the ethene-H₂-ethane system is far from thermal equilibrium under these conditions (typically 100 times too much ethene). Therefore a nonequilibrium explanation of the observed alkene/alkane ratios is required.

To form an alkane by the free-radical mechanism, there must be a source of reactive hydrogen. If this source is constant, the ethene/ethane ratio would increase continuously with temperature. However, the compositions of the gas and the solid are continuously changing which makes the problem more difficult. The first minimum in the ethene/ethane ratio occurs prior to the maximum in oil

evolution but near the temperature of a maximum in H₂S evolution (10). H₂S is a good donor of hydrogen to free radicals (11). Perhaps the second ethene/ethane minimum occurs because of a new source of reactive hydrogen in the char. The maximum rate of H₂ evolution from secondary char pyrolysis (2) occurs at about the same temperature as the second minimum observed in the alkene/alkane ratios.

The free-radical mechanism also predicts that the ethene/ethane ratio should be increased by the addition of inert diluent. This effect is demonstrated in Figure 3. The addition of an inert sweep causes both the instantaneous values above 450°C and the integral values of the ethene/ethane ratio to increase. The integral value of the ethene/ethane ratio increased from 0.21 under autogenous conditions to 0.29 in the slow sweep experiment and to 0.33 in the fast sweep experiment. A value of 0.34 for the ethene/ethane ratio is obtained by extrapolating the ethene/ethane ratios of the two sweep experiments to zero sample size/sweep rate.

The 1-alkene/n-alkane ratios in the oil as measured by capillary column GC/MS also increase with the addition of inert diluent as shown in Figure 4. This effect as well as the previously demonstrated dependence on heating rate is consistent with a free-radical mechanism. However, the alkene/alkane ratio in the presence of a sweep seems to show an even-odd dependence for reasons which we do not presently understand.

DISCUSSION

The general observation that temperature and inert diluent affect the ethene/ethane ratio is useful for correlating various data in the literature. An Arrhenius plot demonstrating the dependence of the ethene/ethane ratio on both temperature and sweep gas is given in Figure 5. In making this plot we used the temperature of maximum evolution rate as the effective temperature of retorting for the nonisothermal experiments (7). The ratio from all retorting and cracking experiments under autogenous conditions (or nearly so) can be described to within 20% by a single Arrhenius expression with an activation energy of 11 kcal/mole. This energy is substantially lower than the ethalpy of the ethane-H₂-ethene reaction (34 kcal/mole).

The ethene/ethane ratio from the Bureau of Mines entrained solids retort (12) lies substantially (2 to 3 times) above this line. We do not agree with the original interpretation of Jacobson et al (1) that residence time and extent of secondary cracking causes this effect. We have previously shown (7) that the ethene/ethane ratio during cracking is not a strong function of residence time at constant temperature. Instead, the effect is most likely caused by the steam diluent as outlined in prediction (a) above. To confirm our explanation, we show the ethene/ethane ratio from the infinite dilution extrapolation of our N₂ sweep experiments. This point shown as a black circle in Figure 5 is roughly consistent with an extrapolation of the entrained solids data to low temperature.

These findings have certain implications for the use of ethene/ethane ratios as an indicator of retorting conditions. The retorting index of Jacobson et al (1) should work well for retorting under autogenous conditions as in a Tosco or Lurgi process. It does not work in a retorting process where inert diluent is added. The case of a combustion retort is more complicated. For particle sizes greater than about 2 or 3 centimeters, retorting occurs under autogenous conditions, regardless of sweep, because of diffusion limitations. When oil combustion occurs, shale oil cracking also occurs at the interface of the combustion and kerogen pyrolysis zones. This produces locally high ethene/ethane ratios due to high temperatures, inert diluent and perhaps oxidative dehydrogenation. The ethene/ethane ratio at the exit depends on the amounts of C₂'s produced by both kerogen pyrolysis and shale oil cracking at the combustion-oil generation interface and the conditions existing at both locations. Low ethene/ethane ratios produced at low heating rates when intraparticle coking occurs can be negated by high ratios produced during oil cracking in the gas stream. Therefore, any empirical relationship between oil destruction in a combustion retort and the ethene/ethane ratio must be used with caution when both coking and cracking occur.

ACKNOWLEDGEMENT

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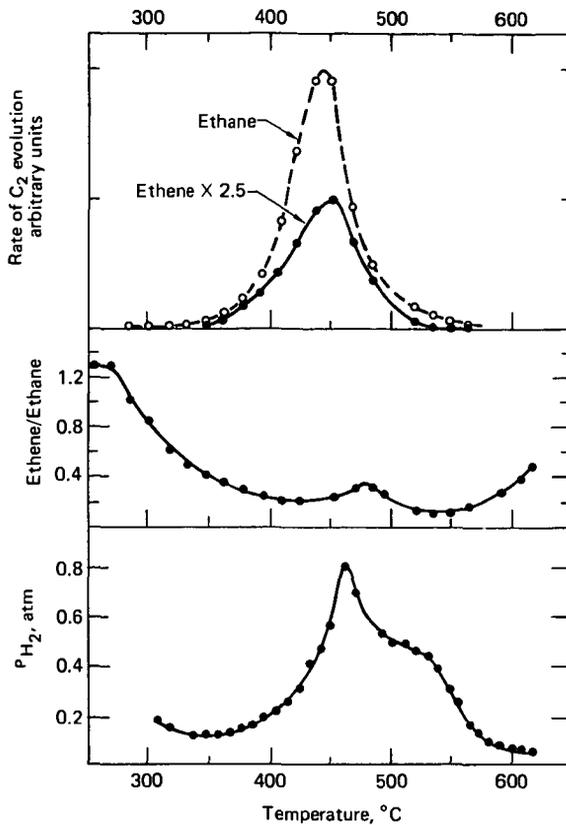


Figure 1. C₂ evolution rates, ethene/ethane ratio, and hydrogen partial pressure for oil shale heated at 1.5°C/min under an autogenous atmosphere.

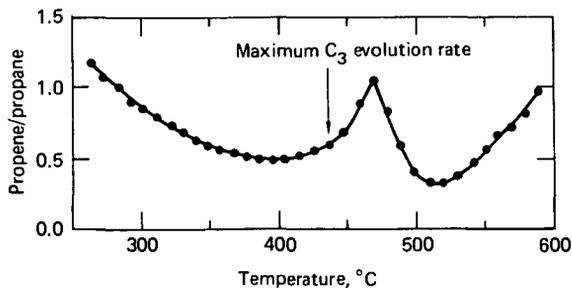


Figure 2. Propene/propane ratio from oil shale heated at 1°C/min under an autogenous atmosphere.

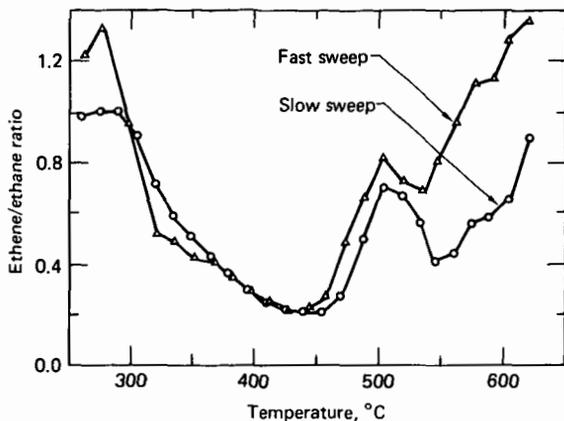


Figure 3. Effect of inert sweep gas on the time-dependent ethene/ethane ratio for oil shale heated at 1.5°C/min. The sample size and N₂ flow rate for the slow sweep experiment were 28 g and 50 cm³/min. The sample size and flow rate for the fast sweep experiment were 14 g and 100 cm³/min. Nearly all of the ethene and ethane is evolved between 400 and 500°C (see Fig. 1).

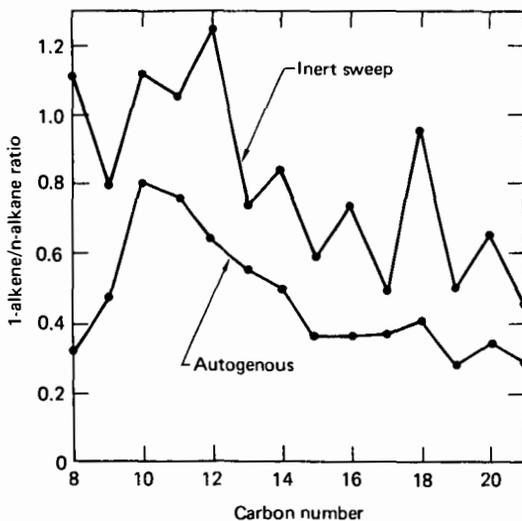


Figure 4. Effect of inert sweep gas on the 1-alkene/n-alkane ratios in shale oil. Peak height ratios were determined from capillary-column GC/MS total-ion chromatograms.

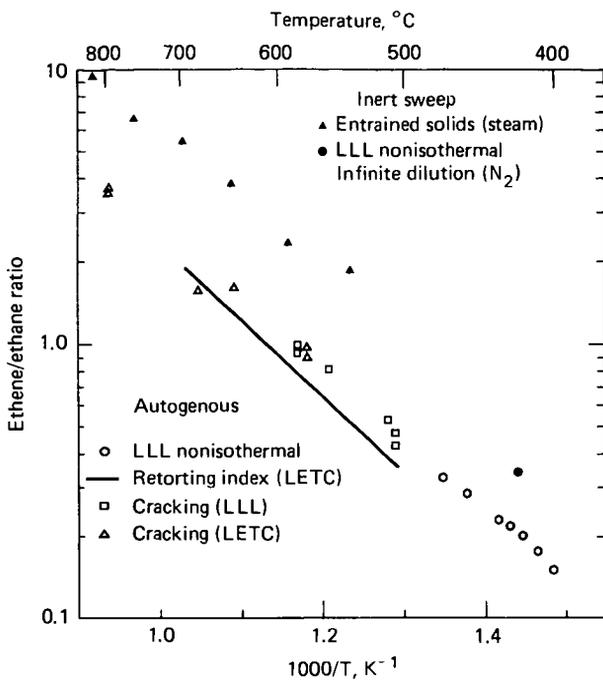


Figure 5. Demonstration of the effect of temperature and inert sweep gas on the ethene/ethane ratio from oil shale retorting. The temperature dependence of the ethene/ethane ratio can be described by an activation energy of about 11 kcal/mole.