

Mass Spectrometric Volatilization Studies of Oil Shale

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Utilization of oil shale as a fuel is a two-fold problem for high temperature chemistry: controlled pyrolysis of organic material, and high temperature sublimation-decomposition reactions of inorganic residues. Because shale differs from petroleum, in that nature's decomposition of the organic matter "kerogen" is incomplete, a vast technology of the conditions^{1,4} (e.g., pressure, steam, air, and temperature) for the destructive distillation of kerogen has evolved. Realization of the disposal problem associated with the inorganic residues has also been the impetus for numerable technical studies^{1,4} concerned with the effective use of inorganic silicates, carbonates, sulfates, phosphides, etc. found to be present in the shale.

High temperature mass spectrometry has been effectively used for both hydrocarbon studies^{5,6} and numerous inorganic vaporization studies.^{7,8} While the technique provides direct detection without condensation or possible intermediate reactions of the volatilized species, it is usually limited by the medium mass resolution of the spectrometers and complex introduced mixtures which do not permit unambiguous identification of specific hydrocarbons present. Nevertheless, qualitative and semi-quantitative estimates regarding the types of organic compounds evolved can be made because various functional groups of organic compounds lead to characteristic common ions in the mass spectra.^{6,9,10} This technique has recently been applied to a similar problem of compounds found to be present in predominantly inorganic materials such as tektites, meteorites and natural glasses.¹⁰

Experimental

Samples (approx. 0.1 g) of Colorado oil shale were vaporized from tantalum Knudsen cells (with boron nitride and high purity alumina crucible liners) into both a Bendix, model 14-206A, time-of-flight mass spectrometer and a 60° magnetic sector field instrument. The crucibles were resistively heated to temperatures of approximately 700°C; higher temperatures were obtained by electron bombardment of the cells. Temperatures were measured with a Pt-Pt-10% Rh thermocouple peened into the base of the cell. A movable beam-defining slit "shutter", located between the furnace and ion source regions of the spectrometer, permitted differentiation of molecular species arising in the reactor from residual background gases in the instrument. Ions were monitored at 20 and 40 eV and the spectra scanned at pressures of $\sim 1 \times 10^{-6}$ torr in the ion source region. Mass spectra were monitored at selected time intervals with strip chart recorders during the heating cycle period. Continual oscillographic display of the spectra provided by the time-of-flight instrument insured that significant changes due to the evolution of trapped gases would not go unobserved.

Results and Discussion

Ions up to ~ 400 amu were monitored between room temperature and 1250°C. Neutral molecular progenitors of these ions have been assigned on the basis of mass-to-charge ratios, common fragment ions,^{6,9,10} isotopic abundance, shutter profiles, and appearance potentials.

Over the temperature range investigated, the observed mass spectra suggest three distinct regions of volatility: (1) room temperature to $\sim 350^\circ\text{C}$, where only small amounts of hydrocarbons are evolved, (2) $350\text{-}450^\circ\text{C}$ where large quantities of organic material are being released and (3) above 450°C for which inorganic species

are generally the most significant. The mass spectra reproduced in figures 2-4 are typical of these three categories; a background (room temperature) spectrum in figure 1 may be used for comparison. All four spectra were taken at 20 eV electron energy and have some ions that were off-scale with the sensitivity used.

Temperature range 25-350°C

Room temperature spectra obtained with mass spectrometers have characteristic residual peaks resulting primarily from pump fluids, air leaks, and condensation of various gases. Figure 1 shows such a spectrum obtained on the magnetic sector instrument. Nearly all ions attributed to pumping fluids (31, 108, 135, 169, 198-204) become smaller with heating as can be observed by comparison with figure 2. The scan at 160°C (figure 2) shows some significant changes in the hydrocarbon "envelopes"^{6,10} which correspond to different numbers of carbon atoms in the fragment ions. Since comparison of numerous spectra of organic compounds indicates that those with different levels of unsaturation or functional groups frequently give different characteristic ions, the change between figures 1 and 2 is indicative of a change in the hydrocarbon species present. Monitoring several of these ions (m/e 78, 92, 106, 111, 159) with the shutter indicated they arose from the sample; thus at temperatures below 200°C, principal ions of aromatic (m/e 78, benzene; 92, toluene; 106, xylene) or hetero-aromatic (78, 92, 106 pyridyl; 111, thiophenes) molecules are released from the shale. At ~200°C an increase of ions characteristic to those of alkanes, alkene and alkynes suggest that a large variety of hydrocarbons are beginning to be released from the sample.

Temperature range 350-450°C

Ion intensities for most organic species increased by a factor of 10. A spectrum taken at 400°C (figure 3) shows the large characteristic hydrocarbon envelopes observed. In general, there is relatively little evidence for nitrogen or oxygen containing organics. A number of thiophenes but not mercaptans seem to be present. In addition to the organics, H₂S (m/e 34), COS (m/e 60), and H₂O also showed large shutterable increases. These sulfur-containing species eventually disappeared at lower temperatures and more quickly than did the hydrocarbons. As the temperature was increased in this range, a distinct trend towards greater unsaturation was observed; at 350°C, alkane common ions were the largest in the spectra but by 400°C, alkene ions were larger than the alkane fragments.

Temperature range 450-1250°C

Most hydrocarbons have been volatilized at these temperatures. A significant feature between 500-700°C is the gradual increase in the CO⁺ ion intensity with a corresponding decrease in the CO₂⁺-ion intensity. These molecules probably result from thermal decomposition of carbonates present in the shale matrix. At ~550°C, relative intensities of m/e 15-18 suggest that small amounts of ammonia were being evolved from the sample; evidence for release of this by-product of oil shale is generally missing from most of this series of mass spectra. At ~1000°C, Na⁺ (m/e 23) and P₂⁺ (m/e 62) were observed as significant, highly shutterable ions in the spectrum; at slightly higher temperatures, SiO₂⁺ (m/e 60), Mg⁺ (m/e 24) and Al⁺ (m/e 27) were identified as well.

Sample residue of oil shale heated to 700°C retained their original shape but became black in color; a residue of shale heated to 1250°C changed to a dark, glassy bead.

In general, the results obtained in these studies agree with those found in previous oil shale technology. The most favorable temperature for hydrocarbon processing has been found to be 320°C. Greater unsaturation of the hydrocarbons with increasing temperature agrees with previous experimental work. The approximate 1% sulfur has been observed as thiophenes and H₂S but not as mercaptans. In agreement with the small theoretical yield of nitrogen from Colorado oil shale, only small amounts of nitrogen-containing species can be identified in these experiments.

Fig. 1, 25°C



Fig. 2, 160°C



Fig. 3, 400°C (Scale 1/3)

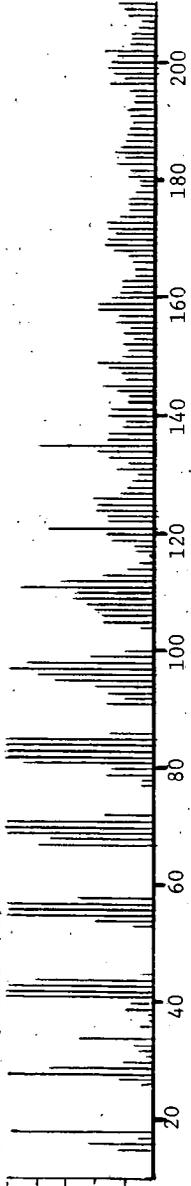
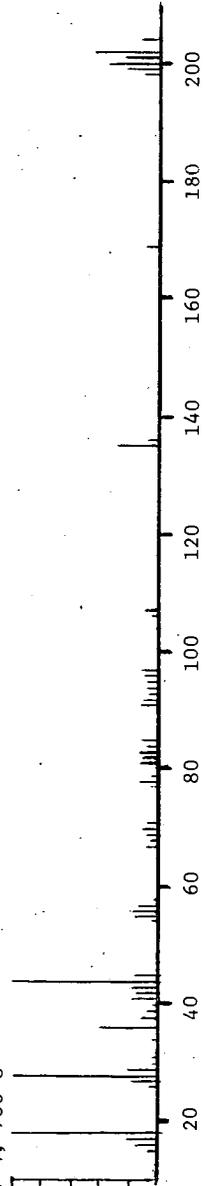


Fig. 4, 700°C



Acknowledgments

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