Reports and Letters

Volatility of Metallo-Porphyrin Complexes

Small quantities of heavy metals are associated with crude oils. During refining these metals tend to pass overhead with the heavier distillates. The presence of vanadium, nickel, copper, and iron in distillate charge stocks greatly increases gas and coke yields and reduces gasoline production (*1*).

There are two hypotheses regarding the mechanism of occurrence of metals in distillates. One is that mechanical entrainment of residua is responsible (*1, 2*), and the other that the metals distill in the form of volatile metallo-organic compounds. (*3, 4*).

The demonstration of the presence of metallo-porphyrin complexes in crude oils (*5*) has been taken as evidence for the latter hypothesis (*4*). Reports of the sublimation of etioporphyrin (*6, 7*), monoimido- and diimido-etioporphyrin II (*8*), and octapropylporphine (*9*) indicate that these compounds possibly possess sufficient vapor pressure to distill with crude oils. No reference, however, could be found to the sublimation or other direct determination of the volatility of the heavy-metal complexes.

This paper describes the sublimation of the vanadium, nickel, copper, and iron (ferric chloride) complexes of etioporphyrin I under conditions that permitted the free porphyrin to sublime, thus demonstrating that these heavy-metal complexes may equally well distill with the heavier fractions of crude oils. The results of trial distillations of mixtures of metals-free petroleum fractions and pure synthetic porphyrin complexes will be reported in the near future.

Etioporphyrin I was selected as representative of the alkyl-substituted porphyrins that occur in crude oils. The procedure for the preparation of the etioporphyrin I was essentially that of Fischer (*6*), except that the product was purified chromatographically. The preparation of the nickel, copper, and iron complexes was performed in the usual manner. A description of the method for the preparation of the vanadium complex is in preparation.

The apparatus consisted of a sublimation cell, a vacuum system, a microscope equipped with a Leitz-Weygand hot stage, and equipment for cooling one surface of the cell. The sublimation cell was a hollow, glass cylinder of inner diameter 14 mm and inner height 10 mm; the end-pieces of the cylinder were optically flat. A mechanical forepump, an oil diffusion pump, a trap, and a Pirani gage for measuring pressure comprised the vacuum system. One flat base of the cell rested on the microscope hot stage, and the walls of the cell were surrounded with a washer of crumpled aluminum foil as insulation. A hypodermic needle connected with narrow copper tubing to a cylinder of carbon dioxide was arranged to direct a jet of expanding gas onto the exposed flat surface of the cell.

The porphyrin sublimand was placed in the cell and was distributed in an even layer over the entire surface of the base. Heating was begun only after a pressure of approximately 0.4 μ had been attained in the system. When the cell had cooled, the unsublimed residue was completely removed from the cell, and the weight of sublimate was determined. The results are summarized in Table 1.

The spectra of the sublimates were determined over the range 220 to 700 mμ, using a Beckman DU spectrophotometer. In all cases it was demonstrated that the metal complexes had sublimed and that the sublimate and sublimand were the same substance. There was no indication of significant thermal decomposition or dissociation of the metal complexes.

Table 1. Summary of sublimation data.

Substance	Wt. sample (mg)	Temperature range (°C)	Wt. sublimate (mg)	Duration of run (hr)
Etioporphyrin I	0.5	220–316	0.5	1.0
Etioporphyrin I—Copper complex	0.7	225–305	0.4	6.5
Etioporphyrin I—Nickel complex	0.6	210–305	0.6	3.3
Etioporphyrin I—Vanadium complex	6.6	220–316	5.6	3.5
Etioporphyrin I—Ferric chloride	0.6	225–298	0.6	3.5

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* Multiple fellowship of Gulf Research and Development Company.

19 September 1955

Transformation of Normal Human Fibroblasts into Histologically Malignant Tissue in vitro

On 18 Sept. 1953, fragments of a 4-day-old infant's foreskin were explanted into sponge matrix tissue culture. The most luxuriant cultures were used in studies on the invasion of HeLa cells into the connective tissue outgrowth (*1*). The least vigorous culture, now designated as strain D, was incubated at 37°C and fed at intervals as indicated by changes in the *p*H of the medium. The nutrient was composed of human serum, beef embryo extract, and Hanks' balanced salt solution in the ratio of 5/1/10 with penicillin and streptomycin at a concentration of 50 μg/ml.

Growth was very poor, and as an extreme measure before discarding the culture, the area of the explant was incised with a scalpel and patched. Subsequently spindle-shaped cells grew out into the new clot and soon extended into the old, granular clot, filling up the area of implantation as well as much of the surrounding cellulose sponge with new connective tissue.

Explants from this culture, cemented with a plasma clot on the surface of other slices of cellulose sponge, grew and were