PLASMA OXIDATION OF LIQUID THIOETHERS

A NEW APPROACH TO THE DESULPHURISATION OF CRUDE OIL AND PETROLEUM FRACTIONS

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ABSTRACT

Oxygen plasmas convert liquid thioethers either neat or in mixtures with hydrocarbons into sulfones which form a separate phase easily being separated. Rates and selectivities of sulphur oxidation and various competing processes have been determined.

1. INTRODUCTION

Petroleum and high boiling petroleum fractions which contain nickel and vanadium are difficult to desulphurize by conventional techniques because these impurities poison the catalysts used in these methods. The nonvolatile components of petroleum cannot be desulphurized at all. They remain in the residue oils which have a very high sulphur content and when burnt cause severe problems of contamination or require complex and expensive installations of flue gas treatment. In search for alternative methods a plasma desulphurisation has been proposed (1) and has been studied extensively in laboratory scale. Vapors of neat dialkyl sulfides, of alkylthiols, and of alkylthiophenes, when subjected to glow discharges are easily desulphurized and partially cracked at the same time (2). Similar results are obtained starting with mixtures of sulphur compounds and hydrocarbons. The efficiency of plasma desulphurisation is considerably enhanced when oxygen passes jointly with the organic material through the glow discharge (3). Though giving satisfying results this plasma treatment is restricted to material which can be vaporized. A modification of the plasma oxidation using liquid starting materials, however, is equally suited for volatile and nonvolatile materials.

Plasma liquid interactions which have recently drawn considerable attention (4,5) are of great practical interest due to the high yields and excellent selectivities.

2. EXPERIMENTAL PART

Reactions have been carried out in perpendicular glass tube
reactors the lower part of which submerged into thermostatic baths. Liquids in the reactor were stirred magnetically. The plasma was generated by a 13.5 MHz generator and a copper coil placed around the reactor about 20 cm away from the surface of the liquid. The temperatures of the liquids were kept low enough to avoid vaporisation of the sulphur compounds. Power levels of 50-150 W and flow rates of oxygen and oxygen-helium mixtures of 0.5-10 l/h have been applied. Gas pressure in the reactor was varied from 0.1 to 3.0 mbar.

3. RESULTS

A desulphurization in the liquid state is achieved when oxygen plasmas are in direct contact with the liquids or when these are in the afterglow region. Under both conditions sulfides are oxidized to sulfoxones. Small amounts of water which are also formed in the process drastically reduce the solubility of the sulfoxones in the starting materials causing the formation of a second phase of higher specific gravity.

When for example neat thiokane at -90°C is exposed to a plasma of oxygen the main product is sulfolane, accompanied by some water and carbon dioxide. The amount of the heavier phase increases with power and time of exposure. It also depends strongly on the oxygen flow rate. From 1 l/h to 8 l/h there is a tenfold increase (Fig. 1). When at total gas flow rate the oxygen is diluted by 60-90% helium the yields are lower, however, in mixtures with 20-50% helium sulfolene yields are higher than in pure oxygen (Fig. 2). Independent of experimental conditions the heavy phase contains 18% sulphur corresponding to 70% sulfolane and 30% water.

Similar results are obtained when mixtures of sulfides and hydrocarbons are exposed to an oxygen plasma. Conversion rates and relative amounts of sulfoxones and byproducts depend on pressure, flowrate, power density, temperature of the liquid and distance between discharge and liquid.

4. CONCLUSIONS

The oxygen plasmas consist predominantly of groundstate and vibrational excited molecules, of singlet molecular oxygen \( O_2^+ \Delta \) and a small fraction of oxygen atoms \( O \sp{3P} \) (6). Ozone concentrations are negligible at the low pressures used in these experiments. Singlet oxygen is known to convert sulfides into sulfoxones but not or hardly attacks C-H-bonds (except in allylic positions) (7). Oxygen atoms, however, easily oxidize C-H-bonds to alcohols. Due to the different energies of formation (1 eV versus 6 - 8,4 eV) and lifetime \( \Delta \gg \sp{3P} \) the ratio singlet oxygen versus atomic oxygen strongly depends on experimental parameters and thus can easily be controlled. The competing or consecutive reactions occurring in contact of oxygen plasmas with sulfide-hydrocarbon mixtures are
R-S-R → R-SO₂-R
\text{-C-H} → \text{-C-OH}
\text{-C-OH} → \text{CO} + \text{H₂O}
\text{=}O → \text{-COOH}
\text{-COOH} → \text{CO₂} + \text{H₂O}

All of these have been studied separately. Their relative importance depends on experimental conditions. If the discharges are optimized for a \text{Î} \text{O₂} formation hydrocarbon oxidation is widely suppressed.

The results are promising for the desulphurisation of heavy crudes and residues of distillation especially in view of the easy formation of singlet oxygen, its long lifetime and selectivity. Metals do not interfere with this reaction but may quench reactions of oxygen atoms. The method furthermore is energy saving because vaporisation is not required and the sulfoxides separate easily from hydrocarbons due to their small solubility and their high specific gravity.

5. ACKNOWLEDGEMENT

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6. REFERENCES

Fig. 1 Plasmaoxidation of thiolane (C₄H₈S). Percent of lower phase after 1 hour treatment at 130 W in function of oxygen flow.
Fig. 2 Plasmaoxidation of thiolane. Percent of lower phase (1 hour, 130 W, 6 l/h) for various helium oxygen mixtures.