DESULFURATION OF SULFONES *

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ABSTRACT

The plasmachemistry of a number of sulfones of various structural types (aliphatic, aromatic, cyclic) was studied using highfrequency glow discharges and pressures of 1 - 5 Torr. Though sulfones are inert in pyrolysis and photolysis they are very reactive in plasmas. Products are hydrocarbons and sulfur dioxide. The reaction mechanism involves ionic intermediates. The plasma desulfuration is highly selective, nearly quantitative and has very high yields.

1. INTRODUCTION

When vapors of organic substances are subjected to glow discharges various reactions occur. Most frequently observed are isomerizations, eliminations, and polymerizations. Elimination reactions are of special interest to synthetic chemistry because of high selectivity and yields. In elimination reactions normally the weakest bond in the molecule is broken preferably. Best suited in preparative chemistry are eliminations which liberate molecules of low energy content like N_2, CO, and CO_2. Since the carbon sulfur bond in sulfones is considerably weaker then carbon-carbon and carbon-hydrogen bonds and since SO_2 has a low energy content sulfones are specially suited for plasma treatment.

2. EXPERIMENTAL

All experiments were carried out in laboratory scale equipment using a 300 W Rf generator (International Plasma Corporation) coupled to a matching network the coil of which surrounded the reactor. To prevent condensation of vapors at the walls, the reactor was placed in a thermostated box. Sulfones were vaporized in a stirred thermostated destillation flask. The rate of destillation was adjusted to 0,1 - 0,3 moles /h at pressures of 1 - 5 Torr. Products and unreacted starting material were collected in cool traps at the temperature of liquid nitrogen. Conversion rates and product distributions were determined by VPC (Hewlett Packard 5750 with automation system 3385 A) and VPC/MS (Varian Mat 111).

3. RESULTS

All sulfones react readily in plasma forming mainly saturated and unsaturated hydrocarbons and SO_2. In none of the experiments plymers were formed.

Di-n-butylsulfone at low conversion rates produces mainly butene-1, n-butane, and ethylene. At high conversion rates ethylene yields drop. Di-n-octylsulfone yields n-octene and n-octane, ethylene and propene as main products. At high conversion rates mixtures of several hydrocarbons are obtained. Tetramethylenesulfone at low conversion ra--tes forms ethylene almost exclusively. At higher conversion rates mixtures of ethylene and acetylene are obtained. 2,4-Dimethyl-tetramethylenesulfone yields propene, ethylene, and acetylene as main products. At low conversion rates propene dominates, at high conversion rates acetylene. Diphenylsulfone forms benzene and biphenyl as the main products. In addition small amounts of phenol and diphenylether are observed. At low conversion rates some diphenylthioether and diphenylsulfoxid is observed which disappears at higher power levels. p-tolyl-phenylsulfone behaves similar forming benzene, toluene, biphenyl, methylbiphenyl, and ditolyl as main products. Methyl-tolylsulfone yields benzene, toluene, ethylbenzene, and ditolyl and small amounts of tolylmercaptane and tolylmethylsulfide. Dibenzylsulfone at low conversion rates forms dibenzyl almost exclusively. At higher power levels benzene, toluene, and dihydrophenanthrene are formed in comparable amounts. The plasma reaction of phenyl-benzyl-sulfones ressambles those of diphenylsulfone and dibenzylsulfone. Thionaphthene-1,1-dioxide forms phenylacetylene as the main product and in addition some benzene, naphthalene, and thionaphthene. Dibenzylthiophene-5,5-dioxide reacts in plasmas to biphenylene, some benzofurane and traces of dibenzylthiophene.

The aliphatic sulfones are disulfurized almost quantitatively. No oxygen compounds and only traces of sulfides are obtained. Large aliphatic residues in part fragmentate during plasma treatment. With aromatic sulfones disulfuration is incomplete. About 5 - 10 percent sulfur containing products are formed. In some cases also phenols and diarylethers are obtained in minute quantities. The yields are high in all cases and reached 1 - 1,5 mole/kWh in several cases.

4. DISCUSSION

Sulfones are very stable molecules. They hardly decompose at high temperatures and they do not react in photolysis. This is in sharp contrast to the facile reaction under conditions of glow discharges. This indication of ionic reaction intermediates is further supported by comparison with mass spectroscopic data.[1] Under conditions of mass spectroscopy aliphatic sulfones loose SO_2, SO_2H, and SO_2H_2. Arylsulfones after isomerization to aryl-arene-sulfinate esters form ArO^+ and $ArSO^+$-fragments. Similarily in plasmas aliphatic sulfones always produce more unsaturated then saturated hydrocarbons. This indicates that besides SO_2 also HSO_2 and H_2SO_2 are eliminated. The isomerization of aromatic sulfones also occurs in plasmas. Sulfinates are sometimes identified in minor quantities among the reaction products. The phenol and diphenylether obtained from diphenylsulfone also are an indication of the rearrangement and subsequent decomposition.

The yields of desulfuration of sulfones are considerably higher then decarbonylation yields of the corresponding ketones. Some plasmadecarbonylations are attractive one-step alternatives to conventional multistep syntheses. Since their yields are higher sulfones may serve even better for this purpose. For example biphenylene is prepared from fluorenone by decarbonylation in 0,3 mole/kWh,[2] from the dibenzylthiophene-5,5-dioxide in 0,5 mole/kWh.[3] Furthermore the separation of unused starting material and product is always much easier for sulfones because of their high polarity.

The plasma desulfuration is the easisiest method to eliminate sulfur from organic molecules. Mercaptanes, thioethers, disulfides, and sulfoxides also can be desulfurized by plasma treatment, however, the yields are lower then in the case of sulfones. For some sulfides oxidation to sulfones and subsequent plasma treatment may be the best method for desulfuration.

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