Selectivity of Organic Plasma Reactions

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Most organic plasma reactions can be described as a sequence of three steps:

$$M \xrightarrow{\text{excitation}} M^* \xrightarrow{\text{bond breaking}} I \xrightarrow{\text{stabilisation}} P$$

where M^* is an excited neutral or ionic species and I an intermediate. A selective conversion of the starting material M into the product P is only possible if all three steps are selective.

The excitation normally is acchieved through electrons with a Boltzmann energy distribution. This step will only be selective if either one excitation process requires considerably less energy then all others, or if there is a rapid intermolecular exchange of energy.

The conversion $M^* \longrightarrow I$ in most cases involves a unimolecular bond rupture. Since always the weakest bond in the molecule is broken preferably, the selectivity in this step depends on the relative bond strengths within the excited molecules.

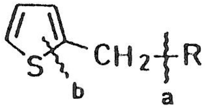
The stabilisation $I \longrightarrow P$ might involve neutralisations, radical combinations or disproportionations. The selectivity of such processes depends on the specific system under investigation and no generalisations are possible.

The selectivities of excitation and bond breaking can be visualised as intermolecular and intramolecular selectivities. The intermolecular selectivity describes to what extent a species with a favourable excitation process could be diluted with other molecules and still determine the product formation. The intramolecular selectivity would indicate in a series of homologue compounds up to what molecular weight a single weak bond would be broken preferably.

To study selectivity eliminations were chosen because they are the most important organic plasma reactions 1). Eliminations where both bond breaking and stabilizations are selective are useful in synthetic work. Eliminations with selective bond ruptures but unselective stabilization steps are of importance in the desulphurisation of petroleum or petroleum fractions. Such processes are possible because most C-S-bonds are weaker than C-C- and C-H-bonds and thus are broken preferably 2). Since petroleum is composed of a variety of sulphur compounds and hydrocarbons problems of intermolecular and intramolecular selectivities are of special importance for this field.

To study intramolecular selectivity a series of alkylthiophenes from $C_4H_3S\text{-}CH_3$ to $C_4H_3S\text{-}C_9H_{19}$ was treated in plasmas. Since the desulphurisation of organic vapours often is greatly enhanced by addition of oxygen 3) a similar series was carried out in the presence of this additiv.

In 2-alkylthiophenes the two most favourable processes of bond breaking are the cleavage of the side chain between the α- and β-positions (a) and the cleavage of the C-S bond in the thiophene ring (b).



Since both processes have similar energy requirements alkylthiophenes are especially sensitive models to study intramolecular selectivity.

Process a leads to thienyl radicals which stabilize to various thienyl derivatives. The bond breaking at b leads to carbondisulfide, acetylene, and various hydrocarbons.

All alkylthiophenes on plasma treatment yield complex mixtures of saturated and unsaturated hydrocarbons as well as new sulphur compounds. Among the hydrocarbons ethene and ethine are predominant. Most new sulphur compounds are thienyl derivatives. Occasionally elementary sulphur and carbondisulfide is found.

The yield of new thienyl compounds might be taken as a measure for process a. An exception is vinylthiophene which is formed by a different mechanism. The relative importance of process b cannot be measured by a single compound, however, the total hydrocarbon yield can be taken as a reasonable estimate for this process.

In the experiments without additives all alkylthiophenes yield 70±20 mMole/kWh of thienyl-compounds and 70±20 mMole/kWh of hydrocarbons. There is some scatter in the data but no dependance on molecular weight.

In the experiments with oxygen (3 l/h) the toal yield in increased by a factor of 2,2±0,2, the yield of thienyl-compounds by a factor of 1,6±0,3, the hydrocarbon yield by 3,5±1,1. Thus the relative importance of the two main fragmentation processes are approximately 1:1 without additives and 1:2,2 in the presence of oxygen. Also in the experiments with oxygen there is no dependance on molecular weight.

To study intermolecular selectivity mixtures of 2-n-butylthiophene or di-n-hexylthioether with various hydrocarbons were treated in plasmas. Special experimental arrangements prevented separation of the starting materials during vaporisation. Some of the results obtained for mixtures of n-butylthiophene and hexadecane are summarized in Table 1.

Table 1 Plasma treatment of mixtures at 60 W

Starting mixture				
hexadecane/butylthiophene	2/1	5/1	10/1	15/1
converted mMole/kWh				
hexadecane	102	86	67	63
butylthiophene	84	46	26	18
relative yields				
butylthiophene/hexadecane	1.6	2.7	3.9	4.4

In these experiments the relative amounts of the products roughly parallel the relative concentrations in the starting mixtures. Especially at low dilution the preference of the butylthiophene reaction over the hydrocarbon reaction is easily recognizable. The relative rates of butylthiophene and hydrocarbon conversions reveal in interesting tendency. The thiophene derivative always reacts faster than the hexadecane and this preference increases with increasing dilution by the hydrocarbon.

Mixtures of butylthiophene with other hydrocarbons or with hexylthioethers with hydrocarbons show the same tendency.

The prefered reaction of the butylthiophene indicates that this compound is more easily excited then the hydrocarbon. The enhancement of this intermolecular selectivity by dilution indicates that a fraction of excited hydrocarbon molecules do not decompose but transfer their energy to butylthiophene molecules. The dependance of this energy transfer on total pressure is presently being investigated.

In recent years a number of plasma syntheses have been developed. The success in this area already demonstrates the existence of selectivities in excitations, bondruptures and stabilizations. However, most of these syntheses were carried out with small molecules of high stability. The present study uses fairly complex molecules with 12 to 50 atoms. The results indicate that the intramolecular selectivity is a very effective principle in organic plasma chemistry. The two main processes of bondruptures have the same relative and absolute rates independent whether there are 10 or 30 additional bonds. Probably even larger molecules would show selective bond breaking.

The intermolecular selectivity as effective in the plasma treatment of mixtures has never been studied previously. The present data show clearly the existence of this effect, though in the pressure range of Torr it is not very important. Even at a given pressure this intermolecular selectivity is not a constant but increases with dilution. This observation is of special value for all plasma processes which aim at the destruction of impurities.

Literature

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