REACTION MECHANISMS IN NONEQUILIBRIUM PLASMAS STUDIED BY ISOTOPIC LABELLING

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ABSTRACT

For studies of reaction mechanisms a reactor was developed which permitted working in a closed system and which rapidly quenched all reaction products. Experiments were carried out with C_6H_6 and equimolar mixtures of C_6H_6 and C_6D_6. Analysis of isotope distribution in the products yields information about the mechanisms of formation. The reaction studies show no analogies to pyrolysis, photolysis or mass spectrometry, but rather follow different, plasmaspecific mechanisms.

1. INTRODUCTION

Though plasma reactions have been studied extensively, their mechanisms are practicaly unknown. In a typical plasma experiment initial and final states are well defined, however, the steps inbetween are unknown and depend on a number of variables like electron density, electron energy, pressure, concentration and nature of the intermediates, cross sections, life times of excited species etc. Measurement of such parameters in a reacting system is difficult because most analytical methods (e.g. probes) change the plasma properties. Because of these difficulties it is general praxis not to study mechanisms of plasma reactions but rather to postulate analogies to pyrolysis, photolysis or mass spectrometry. The present study demonstrates the absence of such analogies.

2. EXPERIMENTAL

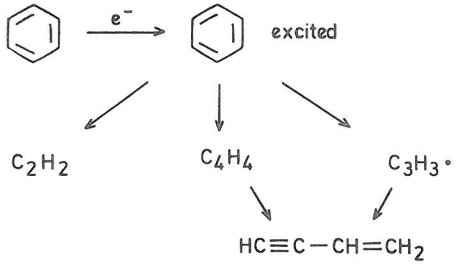
Experiments were carried out in a reactor (Fig. 1), the walls of which were cooled by liquid nitrogen. In the experiments first benzene was placed in the destillation flask and cooled with liquid nitrogen. Then the system was evacuated and sealed. By raising the temperature in the destillation flask the starting material was vaporized. The organic vapors immediately after passing the Rf-glow discharge condense at the reactor walls. This rapid

quenching increases the yields of temperature sensitive compounds and reduces polymerisations. Rates of destillation were ~0,1 mole/h, conversion 10 - 30%. Product analyses were made by VPC and VPC/MS. The deuterium concentration in the products was determined by mass spectrometry using the signal of the molecular ion.

3. RESULTS AND DISCUSSION

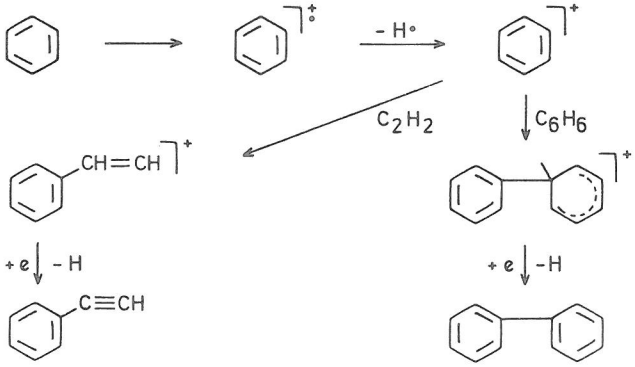
The reaction of benzene in glow discharges has been studied by many authors. Products are biphenyl, terphenyl, and polymers. With rapid quenching several additional products and also low boiling materials are obtained. Under such conditions the main products are acetylene, diacetylene, vinylacetylene, cyclohexadiene, toluene, phenylacetylene, biphenylene, biphenyl, 3 benzene dimers, and polymeric material. Mixtures of C_6H_6/C_6D_6 yield products which in many cases have typical deuterium distributions and thus give information on the reaction mechanisms. Different mechanisms exist for low molecular weight products ($M < 78$) and for larger molecules ($M > 78$). The first is discussed for acetylene and vinylacetylene, the later for phenylacetylene, biphenylene, biphenyl, and the benzene dimers.

Acetylene consists mainly of C_2H_2 and C_2D_2 with little contribution of C_2HD. This indicates an acetylene formation mainly by monomolecular decomposition of benzene. Vinylacetylene consists of C_4H_4, C_4H_3D, C_4D_3H, and C_4D_4 in a ratio of 2:1:1:2 but has no $C_4H_2D_2$. This result is consistent with two reactions leading to vinylacetylene. About one third of the compound is formed directly by monomolecular decomposition of benzene. The rest stems from C_4H_3 and C_4D_3-radicals which also are formed by monomolecular decomposition of benzene. These radicals form vinylacetylene by disproportionation or hydrogen abstraction. The absence of $C_4H_2D_2$ rules out any formation of vinylacetylene by dimerisation of acetylene.



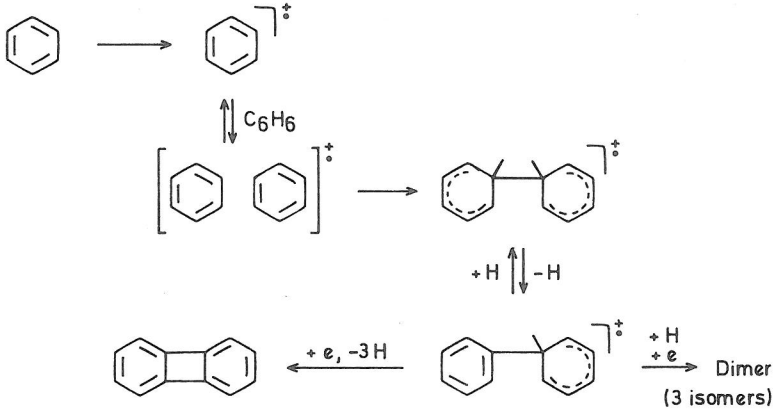
The excited state from which the monomolecular decomposition of benzene occurs, can be determined by comparison

with other methods of energy transfer. A thermal excitation is very unlikely due to the low temperature in the reactor. Photochemical excitations also are not to be expected because the plasma is optically thin. Besides in pyrolysis and photolysis of C_6H_6/C_6D_6-mixtures products are formed with a pronounced isotope effect which is not observed in the plasma reaction. Excitation processes like those in mass spectrometry can also be excluded in plasma chemistry. The main fragments in mass spectrometry of C_6H_6/C_6D_6-mixtures are $C_6H_5^+$ and $C_6D_5^+$. On neutralisation they would form phenylradicals which through hydrogen abstraction lead to C_6H_6, C_6H_5D, C_6HD_5, and C_6D_6. The unreacted benzene recovered from the experiments shows no C_6H_5D and C_6D_5H. The only process which ressambles plasma reactions is the fragmentation of neutrals excited by electron collision (1) which mainly leads to C_2H_2, C_4H_2, C_4H_4, and C_3H_3. Because of the strong similarity it may be assumed that in plasma the monomolecular decomposition occurs also from highly excited neutral states.
Of the larger molecules obtained from C_6H_6/C_6D_6-mixtures phenylacetylene consists only of $C_6H_5C_2H$, $C_6H_5C_2D$, $C_6D_5C_2H$, and $C_6D_5C_2D$. The yields of $C_6H_5C_2H/C_6D_5C_2H$ or $C_6H_5C_2D/C_6D_5C_2D$ show an isotope effect for the formation of the phenyl moiety of 1,45±0,02. A similar ratio of $C_6H_5^+/C_6D_5^+$= 1,45 is found in the mass spectrum of equimolar C_6H_6/C_6D_6-mixtures. Deuterium distribution and isotope effect indicate a reaction sequence involving phenyl cations and their attack on acetylene. Several alternatives can be ruled out on bases of the deuterium distribution.



Biphenyl is the main volatile product of benzene reactions in plasma, pyrolysis, photolysis, radiolysis and electrochemical oxidation. The deuterium distributions and the isotope effects, however, depend strongly on the method of preparation. A formation of biphenyl in plasma via phenyl radicals (as in pyrolysis and photolysis) can be ruled out

on bases of the isotope effect. The isotope effect of the plasma product, the product of electrochemical oxidation and the ratio of $C_6H_5^+/C_6D_5^+$ in mass spectrometry, however, are in close agreement. This indicates a biphenyl formation in plasma via phenyl cations which react with benzene and stabilize by neutralisation and loss of hydrogen.
The deuterium distribution of biphenylene from plasma which is quite distinct from that in pyrolysis, shows characteristic similarities to the benzene dimers. Both, the biphenylene and the dimers show no significant isotope effect and probably are formed by the reaction of benzene radical ions with benzene. Initially an ion-molecule-complex is formed inside of which C-C-bond formation occurs followed by neutralisation and hydrogen migration or hydrogen loss.



The two main pathways in the plasma reaction of benzene are the monomolecular decomposition of highly excited neutrals and the reaction of phenyl cations or benzene radicals ions with neutrals. Both have no analogies in pyrolysis, photolysis or mass spectrometry and are specific for reactions under plasma conditions. Similar results have been obtained from other systems when studied by isotopic labelling.

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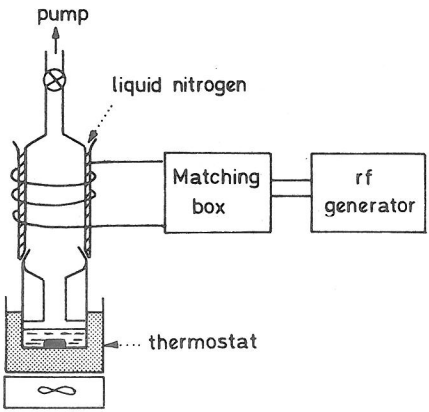
Fig. 1


pump
liquid nitrogen
Matching box
rf generator
thermostat