RF REACTIONS OF AROMATIC COMPOUNDS

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ABSTRACT

The reactions of aromatic compounds in a 13.6 MHz discharge have been studied. Typical conditions are 0.05 Torr, 25 watts, and flow rates 1 mmole/min. Decarbonylations leading to strained hydrocarbons, benzocyclopropene and benzocyclobutene, have been achieved. Aromatic cyanation reactions have been performed by simultaneously flowing CH_3CN and an aromatic compound through the plasma zone. The effects of variations in flow rate and power are discussed.

INTRODUCTION

Preparative plasma chemistry has some intrinsic interest as a unique processing method. Our studies in this area have concentrated on discovering new reactions, developing them from a synthetic viewpoint and attempting to understand the kinetics of the overall reactions. In this paper are described two recent studies of the plasma reactions of aromatic compounds. One of these studies explores reactions which extrude CO or CO_2 from complex molecules producing strained hydrocarbons. The second describes a cyanation reaction involving coreaction of two compounds in the plasma zone. In each case the yields of products approach the levels required to make the processes of synthetic utility.

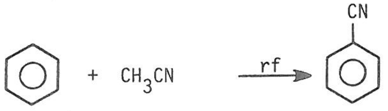
RESULTS

Cyanation

The apparatus is quite similar to that previously described.[1] The experiment involves simultaneously flowing acetonitrile and the aromatic compound through a plasma zone in a 30 cm x 2.5 cm id reactor tube. The flow rates of the two compounds are independently controlled. Energy is supplied by an inductively coupled 13.6 MHz rf reactor. The products are collected in a cold trap and eventually analyzed, usually by gas liquid chromatography (glc) and mass spectrometry (ms). The controlled variables are power (P), 10-100 W; flow rate of acetonitrile (r_A), 100-300 mmol hr^{-1}; and flow rate of aromatic (r_B), 20-200 mmol hr^{-1}. In general it was found that aryl cyanides were the major products.

Qualitatively, the extent of conversion of reactants depends directly on P and inversely on r. The yields of products are also dependent on P, r_A and r_B. It was established that no reaction occurs in the cold trap by coplasmolyzing benzene, acetonitrile with pyridine in the cold trap. No cyanopyridines resulted.

Benzonitrile was the major aromatic product from the reaction of benzene, acetonitrile mixtures and it was formed in surprisingly high yield under the proper conditions. For example, in one run where 76% of the benzene, reacted, a 61% yield of benzonitrile was obtained. This reaction is also effective with heterocyclic compounds and simple aromatic hydrocarbons. These reactions were performed on a scale of several grams. As demonstrated in Table 1, respectable yields on reacted aromatic can be obtained in several cases. These yields are improved by using a large ratio of acetonitrile to aromatic. In essence this demonstrates that acetonitrile when present in excess, provides a reagent which rapidly and selectively transforms the aromatic to the nitrile, thus avoiding the usual plasma pathways of the aromatic. The major competing pathway is methylation. Each of these reactions could involve radical reactions, i.e., $\dot{C}H_3$ or $\dot{C}N$ [2] attacking benzene to produce toluene or benzonitrile, but the data argue against this possibility. Thus, the positional selectivity found for thiophene or toluene plus acetonitrile is very different for methylation and cyanation. Furthermore, in the reaction of benzene with acetonitrile, the ratio of products $C_6H_5CN/C_6H_5CH_3$ varies from two to twenty as the conditions are varied.



ArH ArCN

where Ar = C_6H_5

Since some success has been recently achieved in resolving the dynamics of organic plasmolysis we have applied this approach to the present, more complex, problem. Our efforts center on the cyanation of benzene. It has been previously shown[1] that the rates of several rf discharge reactions follow the rate law

$$-\log \frac{A}{A_o} = k \frac{P}{r_T} + C$$

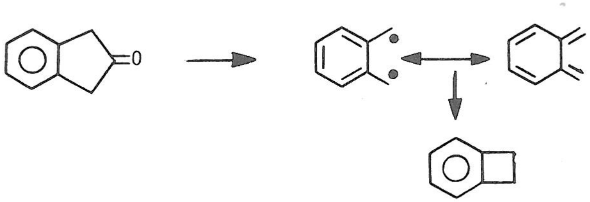
This rate law can be shown to be consistent with a scheme in which an initial electron impact on reactant is rate limiting, or other schemes which are essentially limited by energy input and are first order in reactant. In this situation the amount of reactant converted in a given run depends directly on the power and residence time and inversely on the total pressure of organic compounds. This rate law can be tested for acetonitrile conversion. If all the points are used, a linear regression analysis gives $-\log A/A_0 = 0.63\ Pr_T^{-1} + 0.08$ where k is expressed in units of mmol W^{-1} hr^{-1}. Using only the points at r_A/r_B of approximately six (see below) k = 0.63 mmol W^{-1} hr^{-1}. These rate constants are satisfactorily close to that previously estimated for acetonitrile alone using a similar reactor. Although the correlation coefficients are not high there are no obvious trends with P, r_A or r_B, and in particular k is nearly independent of r_A/r_B.

The kinetics for disappearance of benzene are quite different. A linear plot for $-\log(B/B_0)$ vs. Pr_T^{-1} is obtained for $r_A/r_B \approx 6$ (Figure 1). The regression analysis gives $-\log B/B_0 = 1.32\ Pr_T^{-1} + 0.02$. The rate constant so obtained is, however, much larger than that for benzene alone and it depends on r_A/r_B. At $r_A/r_B = 1.0\text{-}1.6$ the rate constant is some six times smaller and is closer to the rate for benzene alone. It is proposed, therefore, that there are two main routes for consumption of benzene.. One is direct plasmolysis to produce toluene, polymer, and other products with a rate which should be nearly independent of r_A/r_B. The other, dominant route, acts to increase the rate constant for disappearance of benzene as r_A/r_B increases and leads to benzonitrile. The rate law for this reaction can be described as pseudo-first order in benzene. Acetonitrile and benzene (or species derived from them) are both involved in the rate limiting step.

The competition between the two pathways for benzene consumption can be quantitatively expressed in terms of the relative yield of benzonitrile. As shown in Figure 2 the yield of benzonitrile based on benzene consumed is linearly related to r_A/r_T. Thus, benzonitrile formation and the benzene rate enhancement are both the results of one mechanistic phenomenon.

Extrusion of CO and CO_2

Decarbonylations and decarboxylations have been previously explored by Suhr and coworkers.[4] In the present study a number of ketones were reacted in the rf plasma in order to find routes to benzocycloalkenes. It was found that 2-indanone gave the cleanest conversion to benzocyclobutene. The yields in this case were as high as 50% based on reacted ketone.

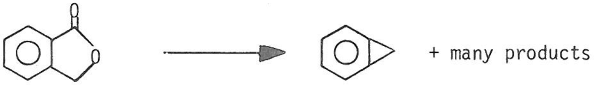


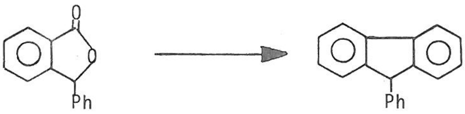
1-Indanone in contrast gave negligible yields of the desired product. A similar comparison of 2-tetralone, which produced bencocyclopentene and

1-tetralone which did not, indicates that formation of a relatively stable benzylic radical or ion is required for good yields.

In the 2-indanone reaction it was shown using a pulsed plasma that the yields were limited by the further reaction of the product, benzocyclobutene. It was also shown that "wall effects" were unimportant. Thus, the yields and reaction rates were virtually unaffected by packing the reactor with glass wool.

A similar approach to the formation of benzocycloalkenes is decarbonylation and the following schemes demonstrate our discoveries.





These can again be rationalized using diradical intermediates, but the mechanisms are in fact unknown.

ACKNOWLEDGEMENT

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2) $\dot{C}N$ have been detected spectroscopically in rf plasmas of acetonitrile. J.E. Nicholas and P. W. Smith, J. Phys. D., 9, 447 (1976).
3) The rate law implies that density of those electrons responsible for the initiating reactions is quite similar for different organic compounds. In this case it implies that the electron energetics are similar regardless of whether benzene, acetonitrile or the other products are present in the plasma zone.
4) See H. Suhr, Angew. Chem. Int. Ed. Engl. 11, 781 (1972); A. Szabo and H. Suhr, Liebigs Ann. Chem. 749 (1977).

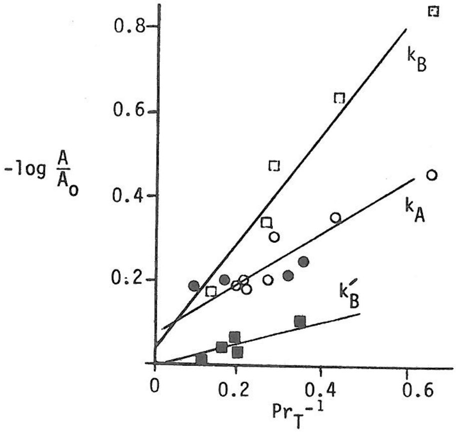

Fig. 1. Benzene, Acetonitrile Reaction Rates
○Acetonitrile at $r_A/r_B \approx 6$; ●Acetonitrile at $r_A/r_B = 1.0\text{-}1.6$
□Benzene at $r_A/r_B \approx 6$; ■Benzene at $r_A/r_B = 1.0\text{-}1.6$

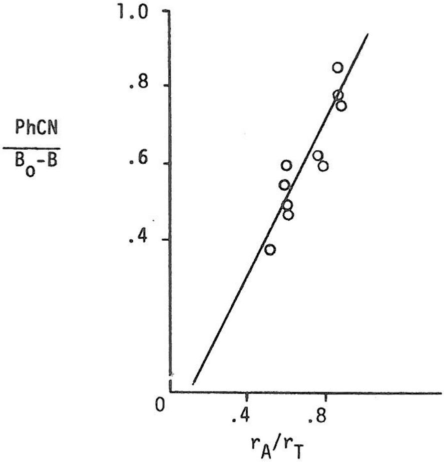

Fig. 2. Yield of Benzonitrile Based on Reacted Benzene vs. Acetonitrile Mole Fraction

Table 1. Yields of ArCN from ArH, CH_3CN

ArH	ArH conversion %	ArCN yield (%)[a]
Benzene	76 32	61 85
Toluene	81 50	21 38
Naphthalene	49	83
Pyridine	18	80
Thiophene	30	40

[a] Yields based on reacted ArH; sum of isomers, where appropriate.