OXIDATION OF ORGANIC COMPOUNDS WITH RF PLASMA

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ABSTRACT

The reactions of organic compounds with oxygen in a 13.56 MHz glow discharge have been studied. Aromatic hydrocarbons are effectively oxidized to yield the volatile products due to hydroxylation on aromatic ring, C-H oxidation of alkyl groups and/or epoxidation of olefinic double bonds. Associated with mechanism, the effects of variations in reaction conditions are discussed.

1. INTRODUCTION

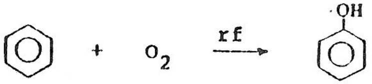
Non-equilibrium plasma is of interest to organic chemists, because it provides a unique reaction media, where the energetic electron impact is the most responsible for the initiation step of the over-all reaction. Recently, some approach for preparative plasma chemistry have been attempted, where two or more substrates were simultaneously subject to discharge. Thus, direct cyanation of aromatics was achieved in respectable yields.[1] This approach seems of significance from not only synthetic but mechanistic viewpoints. In these years, our efforts have centered on elucidating the roles of organic or inorganic additives in the organic plasma reactions. This paper is related to the reactions of organic compounds, in particular aromatic hydrocarbons with oxygen in 13.56 MHz glow discharge. Molecular oxygen is known to be readily converted to O, $^1O_2$ or O_3 in plasma. Therefore, coexisting organics might undergo the attack by these oxidizing reagents in addition to their own plasma reactions.

2. EXPERIMENTAL

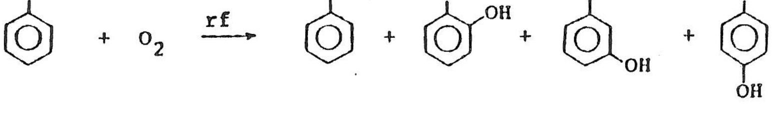
The apparatus and procedure are quite similar to those described previously.[2] The experiment involves simultaneously flowing oxygen and the organic substrate through a plasma zone in a 40 cm x 4.5 cm id reactor tube. Each flow rate is independently controlled. Energy is supplied by an inductively coupled 13.56 MHz RF generator. The products and recovered starting material are collected in cold traps on liquid nitrogen and eventually analyzed by gas chromatography and mass spectrometry. The controlled variables are power, 10-50 W; oxygen flow rate, 1-10 mmol/min; and organic flow rate, 0.5-5 mmol/min. The product yields are based on moles of organic starting materials consumed.

3. RESULTS AND DISCUSSION

Phenol was the only volatile organic product from the reaction of benzene with oxygen in RF plasma. The yield, for example, was 25% at 10% conversion. Generally, high conversion resulted in low yield. A considerable amount of polymeric product deposited on reactor wall throughout all runs. Formation of toluene and biphenyl, major products in benzene plasmolysis without oxygen, was completely suppressed when oxygen was fed sufficiently. Direct derivation of phenol from benzene has of synthetic interest, although our yield might be unsatisfactory. The effects of variation in power or flow rates on benzene conversion and phenol yield are shown in Figs. 1-3. Conversion increases linearly with power, while it decreases exponentially with benzene flow rate(see Figs 1 and 2). This relationship between the reactant conversion and power or the flow rate is essentially the same as those observed in the plasmolyses of various organics with or without additives.[3] Fig. 3 indicates more notable fact that the conversion and yield are entirely independent of oxygen flow rate. This implies that oxygen or its derivatives are not involved in the rate-determining step of benzene disappearance and the autoxidation of the intermediate species from benzene plasmolysis, possibly phenyl radical yields phenol. The hydroxylation on aromatic ring is so general that naphthalene gives naphthols as major volatile products with somewhat less yield than that of phenol from benzene. The isomeric ratio of naphthols (1-/2-) was ca. 1.7.



The oxidation of alkyl side chain competes with aromatic hydroxylation in the reactions of monoalkylbenzenes with oxygen (Table 1). Thus, toluene gives benzaldehyde and benzyl alcohol, methyl oxidation products, as well as phenol and three isomeric cresols, aromatic hydroxylation products, in a comparative ratio. Secondary or tertiary alkylbenzene yields acetophenone as another major product. The alkyl oxidation takes place on α-carbon atom exclusively. It is true even in the reaction of tert-butylbenzene which has no α-hydrogen. With the size of alkyl groups, side chain oxidation gets favorable. These suggest that benzyl radical is the most likely precursor of side chain oxidation products. Similar oxidation of C-H bond was performed with cyclohexane, giving cyclohexanone and cyclohexanol in considerable yields. With aromatic hydroxylation of alkylbezenes, it should be noted that ipso substitution to phenol was preferred to hydrogen substitution to



alkylphenols, the positional selectivities of which appeared lower than those found in the reactions with ^3O.[4] The ipso substitution got predominant with aromatics having plasma-labile substituents. The selectivities of phenol were 67% (benzaldehyde), 74% (acetophenone), 47% (anisole) and 24% (chlorobenzene).

Another type of products were obtained in the oxidation of substrates with olefinic double bond. Cyclohexene yielded cyclohexene oxide and cyclohexanone. Similar epoxidation occurred in the styrene oxidation, producing styrene oxide. Other major products were benzaldehyde and acetophenone. In this case, aromatic hydroxylation was not substantial. Unless oxygen was supplied sufficiently, phenylacetylene was also one of major products. However, it diminished abruptly with the increase in oxygen flow rate. On the other hand, styrene oxide or acetophenone predominated in an excess of oxygen. This contrasts with the results in the cases of benzene and alkylbenzenes, where product yields as well as conversions were virtually unaffected by oxygen flow rate, suggesting that styrene could be attacked by species resulting from O_2 plasmolysis, namely oxygen atom. The product pattern was in essence identical to that in the reaction in condensed phase with O generated by means of microwave discharge.[5]

Further investigation is in progress to elucidate the mechanism and to explore unique reactions in the present system.

ACKNOWLEDGEMENT

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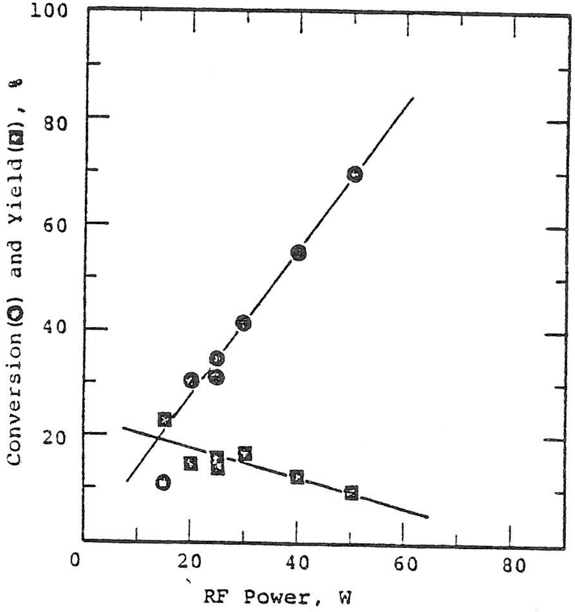

Fig.1. Effect of RF Power on Benzene Oxidation
[Flow rate: O_2, 9.4; Benzene, 1.2 mmol/min.]

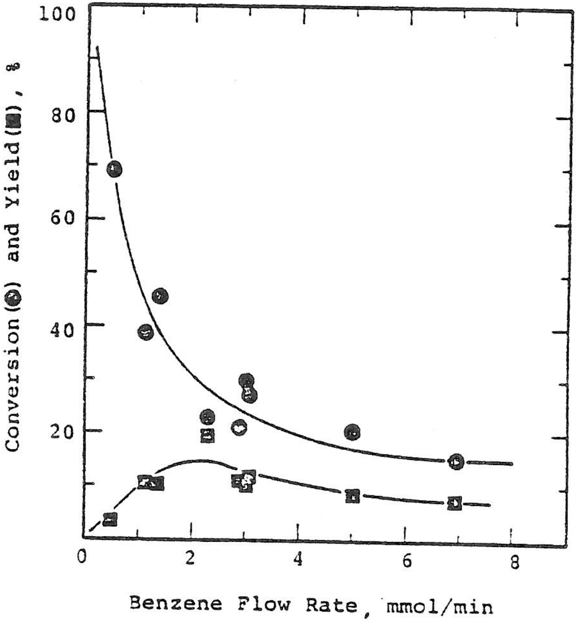

Fig.2. Effect of Benzene Flow Rate on Benzene Oxidation
[RF power: 30W, O_2 flow rate: 9.3 mmol/min.]

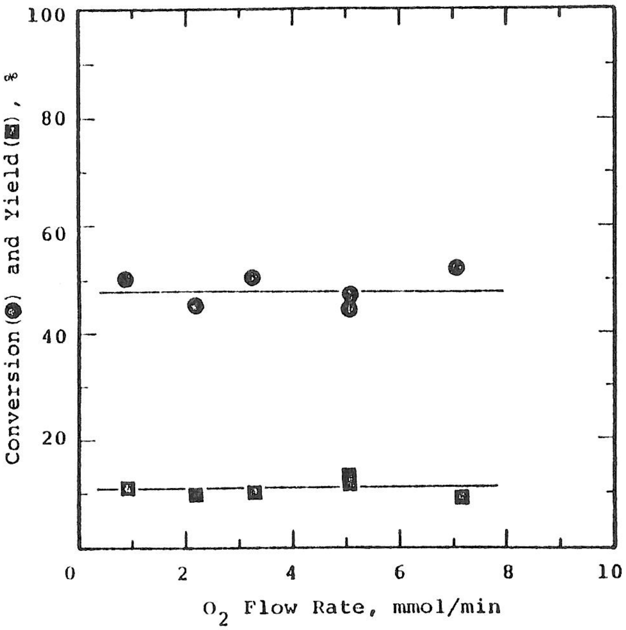

Fig.3. Effect of O_2 Flow Rate on Benzene Oxidation

[RF power: 30W, Benzene flow rate 0.8 mmol/min.]

Table 1. Oxidation of Monoalkylbenzenes in RF Plasma with O_2[a]

Substrate	Conversion (%)	Total Yield (g/kWh)	Total Yield (%)[b]	Oxidation Products (mol %) alkyl	Oxidation Products (mol %) ring
Toluene	33	22.1	13	Benzaldehyde(37)	Phenol(22)
				Benzyl Alcohol(13)	Cresols
					(o,m,p=14,12,2)
Ethylbenzene	25	32.6	25	Benzaldehyde(53)	Phenol(11)
				Benzyl Alcohol(9)	Ethylphenols
				Acetophenone(6)	(o,m,p=8,4,2)
				Phenylethanol(8)	
Cumene	73	15.8	11	Benzaldehyde(33)	Phenol(19)
				Acetophenone(32)	iso-Propylphenol
				Cumyl Alcohol(7)	(o,m,p=3,5,2)
tert-Butylbenzene	34	28.8	15	Benzaldehyde(3)	Phenol(9)
				Acetophenone(25)	tert-Butylphenol
				α-Methylstyrene(35)	(o,m,p=4,3,3)
				Cumyl Alcohol(19)	

[a] RF power: 20-30W, O_2 flow rate: 5-9 mmol/min and substrate flow rate: 1-2 mmol/min.

[b] Based on moles of the reacted substrate.