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DIRECT HYDROXYLATION OF AROMATIC COMPOUNDS IN AN RF PLASMA

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The hydroxylation of aromatic compounds was carried out in the plasma generated by a radiofrequency discharge. Benzene and naphthalene yielded phenol and naphthols, respectively, as single volatile products. With respect to alkylbenzenes, the oxidation of the side-chains competed with the aromatic hydroxylation.

Non-equilibrium plasma provides a unique reaction medium, where the energetic electron impact is the most important initiation step of the overall reaction. Recently, several approaches for preparative plasma chemistry have been developed, in which two or more substrates were simultaneously subject to the discharge1); these approaches are of not only synthetic but also mechanistic significance. Therefore, in order to get further understanding of organic plasma chemistry and exploit a novel synthetic method, we undertook the studies relating to the effects of inorganic or organic additives on plasma reactions. In the present paper, it is reported that aromatic compounds are effectively oxidized in the plasma containing oxygen to give the hydroxylated products in respectable yields. Although it is well-known that molecular oxygen is readily converted to the reactive species such as atomic oxygen, singlet oxygen or ozone in the plasma, there are few systematic studies regarding the reactions of organics, particularly aromatic hydrocarbons, existing together with oxygen in the gaseous plasma.

The apparatus and procedure are quite similar to those described previously.2) The organic substrates and oxygen were simultaneously passed through the plasma zone in a 40 cm x 4.5 cm i.d. reactor tube; each flow rate was independently controlled. Energy was supplied by an inductively coupled 13.56 MHz rf generator. The products and recovered starting materials were collected in dual cold traps at liquid nitrogen temperature and eventually analyzed by gas chromatography and mass spectrometry. The controlled variables were: rf power(10-50 W), oxygen flow rate (1-10 mmol/min) and organic flow rate(0.5-5 mmol/min). The product yields were based on moles of organic starting materials consumed.

Non-substituted aromatic hydrocarbons were oxidized to give the hydroxylated compounds as single volatile organic products. Thus, phenol was obtained in the oxidation of benzene. The yield was, for example, 25% at 10% conversion. Generally, higher conversion resulted in lower yield. Water and carbon dioxide were formed in considerable amounts as well as polymeric deposit on the reactor wall. Formation of toluene and biphenyl, major products in benzene plasmolysis

Table 1. Oxidation of Monoalkylbenzenes in Gaseous Plasma with Oxygen[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) Benzyl alcohol(13)	Phenol(22) Cresols (o,m,p=14,12,2)
Ethylbenzene	25	32.6	25	Benzaldehyde(53) Benzyl alcohol(9) Acetophenone(6) Phenylethanol(8)	Phenol(11) Ethylphenols (o,m,p=8,4,2)
Cumene	73	15.8	11	Benzaldehyde(33) Acetophenone(32) Cumyl alcohol(7)	Phenol(19) iso-Propylphenols (o,m,p=3,5,2)
tert-Butylbenzene	34	28.8	15	Benzaldehyde(3) Acetophenone(25) α-Methylstyrene(35) Cumyl alcohol(19)	Phenol(9) tert-Butylphenols (o,m,p=4,3,3)

[a] rf power: 20-30 W; O_2 flow rate: 5-9 mmol/min; substrate flow rate: 1-2 mmol/min.
[b] total moles of oxidation products per moles of reacted substrates.

without oxygen, was completely suppressed when oxygen was fed sufficiently. The hydroxylation of aromatic ring was so general that naphthalene gave naphthols as major volatile products with somewhat lower yields than that of phenol from benzene. The isomeric ratio of naphthols(1-/2-) was approximately 1.7.

The oxidation of alkyl side-chains competed with aromatic hydroxylation in the reactions of monoalkylbenzenes(Table 1). Thus, benzaldehyde and benzyl alcohol were obtained as well as phenol and three isomeric cresols in the oxidation of toluene. Secondary or tertiary alkylbenzene yielded acetophenone as another major product. The oxidation of alkyl groups took place on the α-carbon atoms exclusively. This was seen even in the case of tert-butylbenzene having no α-hydrogen. In addition, with the increase in size of the alkyl groups, the oxidation of side-chains got favorable. These results suggest that benzyl radicals are the most likely precursors of the side-chain oxidation products. As for the aromatic hydroxylation of alkylbenzenes, it should be noted that ipso substitution to phenol was preferred to hydrogen substitution to alkylphenols. The positional selectivities of alkylphenols were lower than those found in the reactions with $O(^3P)$.[3] Further investigation is in progress to elucidate the mechanism and explore unique reactions.

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References

1) For example, see Y.H.So and L.L.Miller,J.Am.Chem.Soc.,103, 4204(1981).
2) M.Tezuka and L.L.Miller, ibid.,100,4201(1978).
3) E.Grovenstein,Jr. and A.J.Mosher, ibid.,92,3810(1970).

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