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Studies of the Electric Discharge of Organic Compounds. II. The Decomposition of *o*-, *m*-, and *p*-Xylenes in 10-MHz and 2450-MHz Discharges

KO TAKI

The Institute of Physical and Chemical Research, Yamato-machi, Saitama

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As has previously been shown1) toluene gives benzene and ethylbenzene as the principal products in high-frequency electric discharges. The series of xylene isomers were chosen as the higher methyl-substituted benzene homologues in order to get further information on high-frequency electric discharges. Radical and electron scavengers were also used as additives in order to examine the reaction processes. The electric discharge assembly and the procedure of handling of the product were essentially the same as in previous studies. Product analyses were carried out by gas chromatography. The xylenes (Wako Pure Chemical Industries, Ltd.) were purified by repeated distillation or by recrystallization.

TABLE 1. THE RELATIVE YIELDS OF THE PRODUCTS BASED ON *p*-XYLENE CONSUMED

Residence time *p*-Xylene %	10-MHz discharge 0.15 sec 7.5% in He	2450-MHz discharge 0.009 sec 7.5% in He
Benzene	—	0.03
Toluene	1.00	1.00
2, 5-Dihydro-1,4-xylene	0.37	0.06
o-Xylene	—	0.03
4-Ethyltoluene	0.5	0.94
Styrene	0.05	0.05
1,2,4-Trimethylbenzene	0.13	0.03
Phenylacetylene		0.11 5-Unidentified products
Methane	—	0.1
Ethane	0.19	0.14
Ethylene	—	0.02
Propane	—	0.01
Acetylene	—	0.04
Methylacetylene	0.04	0.06
Allene	0.02	0.01
Isobutane	0.01	0.11
1, 3-Butadiene	0.02	0.02 3-Unidentified products
Polymer	17.7	0.41

Results and Discussion

The major products from *p*-xylene decomposition were benzene, toluene, 2,5-dihydroxylene,[*1] and ethyltoluene. These products are similar to those from the toluene decomposition. The relative yields of these products are listed in Tables 1, 2, and 3.

TABLE 2. THE RELATIVE YIELDS OF THE PRODUCTS BASED ON *m*-XYLENE CONSUMED

Residence time *m*-Xylene %	10-MHz discharge 0.12 sec 9.5% in He	2450-MHz discharge 0.008 sec 9.2% in He
Benzene	0.05	0.1
Toluene	1.00	1.00
3-Ethyltoluene	0.6	0.7
Styrene	0.07	0.04
1, 2, 4-Trimethylbenzene	—	0.03
Phenylacetylene	—	0.04
Ethane	0.17	0.05
Polymer	14.6	1.8

TABLE 3. THE RELATIVE YIELDS OF THE PRODUCTS BASED ON *o*-XYLENE CONSUMED

Residence time *o*-Xylene %	10-MHz discharge 0.18 sec 3.1% in He	2450-MHz discharge 0.01 sec 3.5% in He
Benzene	0.2	0.1
Toluene	1.00	1.00
2-Ethyltoluene	1.8	1.0
Ethane	0.5	2.0
Polymer	12.6	2.3

The effects of the scavengers may be summarized as follows: the formations of ethyltoluene, toluene, and ethane are not affected by N_2O in the 10-MHz discharge, but the yields of toluene and ethyltoluene are inhibited to about half in the 2450-MHz discharge. On the other hand, while O_2 inhibits the

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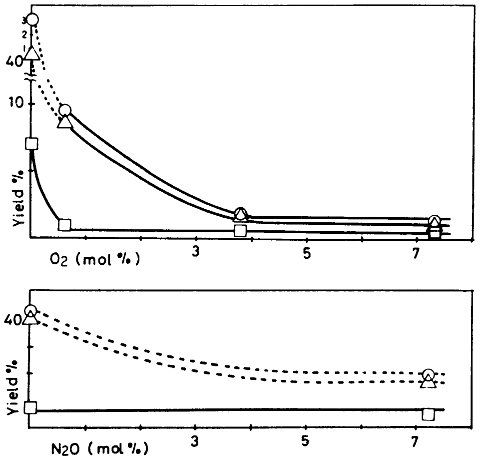
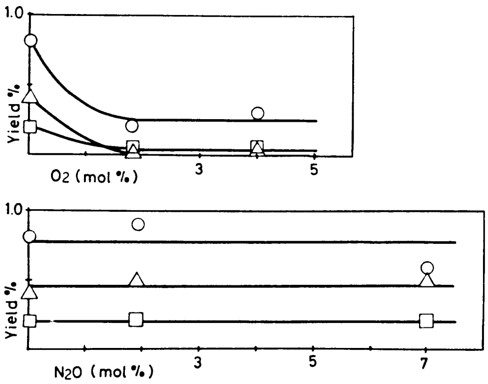
1) K. Taki, This Bulletin, **43**, 1574 (1970).

[*1] 2,5-Dihydroxylene was identified by comparison with an authentic sample prepared by the reduction of *p*-xylene in a liquid ammonia solution in the presence of sodium and water.



○ Toluene, △ Ethyltoluene, □ Ethane

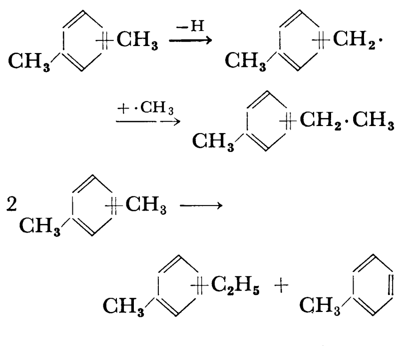
Fig. 1 2450-MHz discharge of *p*-xylene.



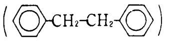
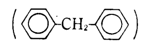
○ Toluene, △ Ethyltoluene, □ Ethane

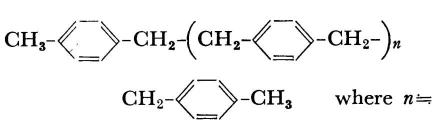
Fig. 2. 10-MHz discharge of *p*-xylene.

yield of products in both the discharges, as is shown in Figs. 1 and 2. From the above results, both the radical and ionic (not radical) processes may be considered to be present in the 2450-MHz discharge and the radical process is predominant in the formation of products in the 10-MHz discharge as well as in the toluene decomposition.[*2] In the 2450-MHz discharge, however, the inhibition of the product yields by O_2 is relatively higher in *p*-xylene than in toluene and the inhibition of the product by N_2O is smaller in *p*-xylene than in toluene. The difference in the effects of the scavengers between *p*-xylene and toluene may be considered to be the effects of the substituted methyl group. The ionic process is not more important than that of toluene decomposition. The process may be described as follows:

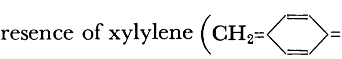


The High-boiling Fraction, Oligomer from *p*-Xylene. The IR spectra of the polymers from *p*-xylene showed the presence of an aliphatic methylene group at 2910 cm^{-1} and 2850 cm^{-1}, and a methyl group at 2950 cm^{-1} and 2875 cm^{-1}. The presence of the methylene group was also confirmed by another band at 1445 cm^{-1} (methylene skeleton vibration), and that of the *C*-methyl group, by a weak band at 1380 cm^{-1}. The presence of an aromatic ring was confirmed by the characteristic vibrations at 1510 cm^{-1} and 1605 cm^{-1}. In the 600—900 cm^{-1} region, the strong band at 815 cm^{-1} showed clearly the presence of *p*-substitution of the benzene ring. The band of double-bond stretching (1640 cm^{-1}) was not observed.

The NMR spectra of the polymers were determined in carbon tetrachloride, using tetramethylsilane (at τ value 10.0) as an internal standard. The chemical shifts were measured relative to the standard. The spectra involve three single bands, at τ 3.03, 7.15, and 7.67, having area ratios of 4.0 : 1.3 : 3.0 in both the 2450-MHz and 10-MHz discharge polymers. These protons are, respectively, those of *p*-substituted benzene, *p*-substituted methylene, and *p*-substituted methyl with IR data. From the area ratio of the protons, the number of *p*-substituted methylene  can be said to be small. However, it can not be monomethylene  because the chemical shift of the proton of monomethylene is measured at τ 6.15. From these results, the structure of oligomer may be represented as:



where $n \fallingdotseq 0$.

The presence of xylylene  and its dimers could not be confirmed in these discharge reactions. The fraction of oligomers among the products was larger in the 10-MHz discharge than in the 2450-MHz, while the total conversion of *p*-xylene was higher in the 2450-MHz than in the 10-MHz discharge. The fraction of oligomer production may be considered to depend on the time of

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[*2] The photolysis of *o*-xylene gives ethyltoluene as the major product.[2]

2) H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 2369 (1967).

residence in the discharge zone.[*3]

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[*3] Mr. K. Hiraoka[3)] discussed the structure of the polymer obtained in the high-frequency electric discharge at the 20th and 21st Annual Meetings of The Chemical Society of Japan in 1967 and 1968.

3) K. Hiraoka, H. Kamada, and S. Hanai, *Nippon Kagaku Zasshi*, **90**, 1239 (1969).