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Studies of the Electric Discharge of Organic Compounds. I. The Decomposition of Toluene in 10-MHz and 2450-MHz Discharges

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Extensive studies of the reactive species have been carried out with regard to the decomposition of inorganic and organic compounds in an electric discharge.[1-10]

In the present investigation, high-frequency electric discharges were used as the source for the formation of reactive species, and toluene was chosen as a representative substrate. Some comparisons of the reaction of toluene in a glow discharge produced by 10-MHz and by 2450-MHz fields will also be reported. The radical scavengers (such as NO, O_2, and C_2H_4) and the electron scavengers (such as N_2O) were used in both the discharges in order to ex-

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amine the reaction mechanism. The mechanism is compared with that of the reactions by other energy sources (radiolysis,[11–15] photolysis,[16,17] and pyrolysis[18–20]). Also the formation of some reaction intermediates is discussed.

Experimental

All the runs were carried out in a flow system using helium as the carried gas. The 10-MHz electric discharge was carried out in Pyrex tubing (1.3 cm od.) around which two 2.5-cm aluminum foil bands (3 cm apart) were fitted; the 10-MHz power of a few watts was generated by a hand-made Toshiba 2B29 valve generator. Microwave (2450-MHz) discharge was also carried out in Pyrex tubing (1.3 cm od.) using a cavity (2×1.4 cm); microwaves were fed into the cavity by means of a Raytheon PGM-10 magnetron (2450 MHz, 85 W). The experimental arrangement is shown in Fig. 1. All the products were analysed gas-chromatographically.

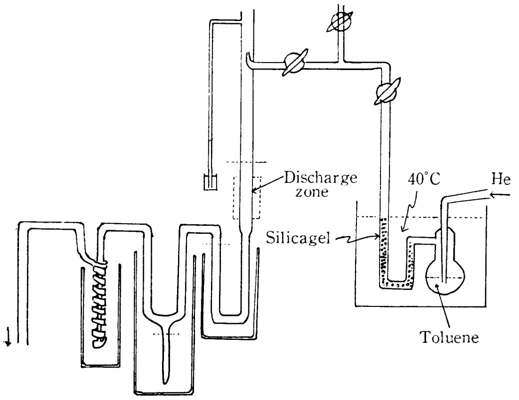
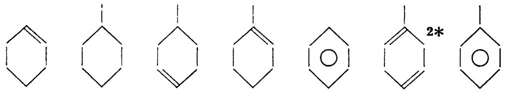


Fig. 1

Results and Discussion

The relative product yields are shown in Table 1. The eluting order[*1] of C_6 and C_7 compounds in gas chromatography using a polyethylene glycol column is as follows:



1-Methylcyclohexene and 4-methylcyclohexene, which are obtained in comparatively large yields, are the reduction products from toluene in the

Table 1. Relative product yields based on toluene consumed

	10-MHz discharge Toluene 6.7% in He (residence time 0.35 sec)	2450-MHz discharge Toluene 8.5% in He (residence time 0.008 sec)
Hydrogen	—	—
Methane	0.2	0.2
Ethane	1.0	0.7
Ethylene Acetylene	0.3	0.4
Methylacetylene Allene	0.2	1.0
Benzene	1.0	1.0
2,5-Dihydrotoluene	0.005	0.9
Ethylbenzene	0.8	1.5
Styrene	0.2	0.3
Phenylacetylene	—	0.7
Bibenzyl	0.04	0.09
Diphenylmethane	—	0.005
Polymer	9.6	1.5

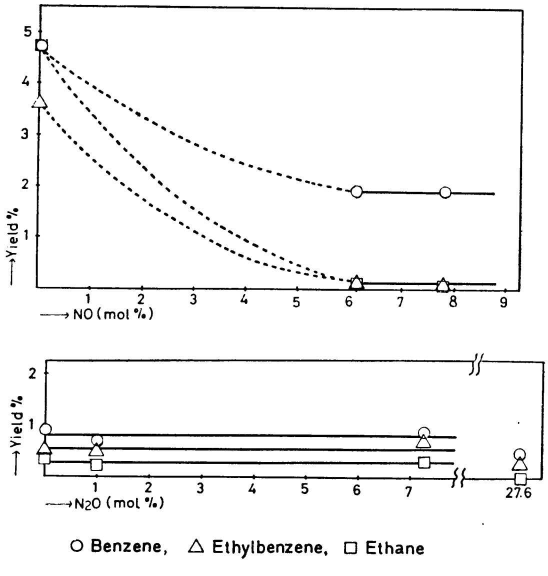


Fig. 2. 10-MHz discharge of toluene.

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19) A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 1142 (1954).

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[*1] Professor M. Amagasa (Faculty of Engineering, Tohoku University) has been studying the reduction of toluene and related compounds. He kindly communicated the results of his gas-chromatographical analysis to Professor Murahashi.

[*2] 2,5-Dihydrotoluene was identified by comparison with an authentic sample prepared by the reduction of toluene.[21]

21) M. Amagasa, T. Yamaguchi and M. Tanaka, Brit. 1033760; *Chem. Abstr.*, **65**, 7075h (1966).

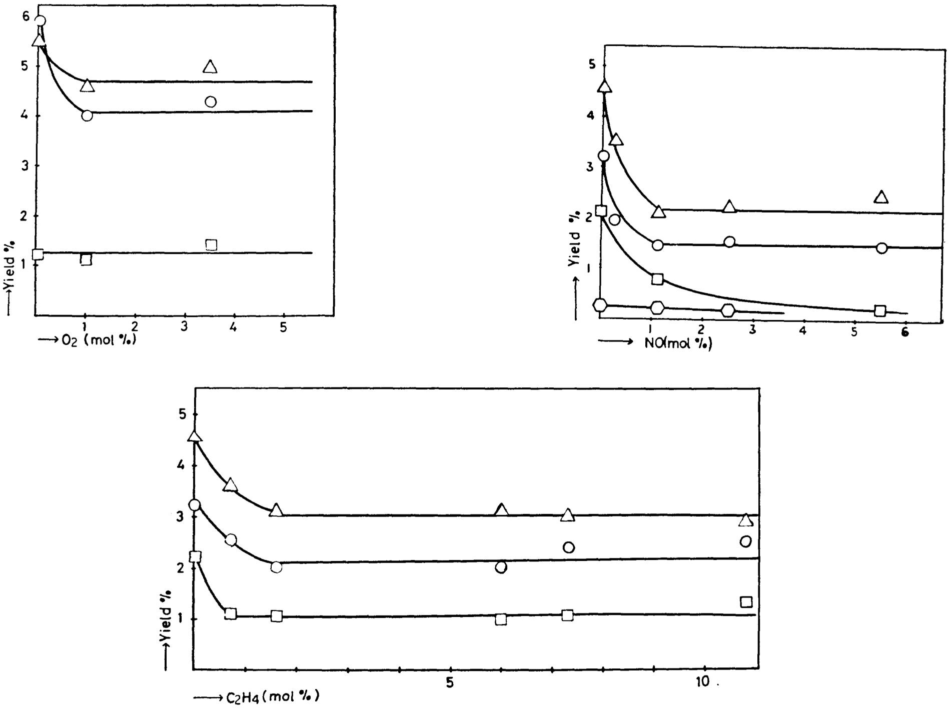

Fig. 3. 2450-MHz discharge of toluene.

△ Ethylbenzene, ○ Benzene, □ Ethane ⬡ 2,5-Dihydrotoluene

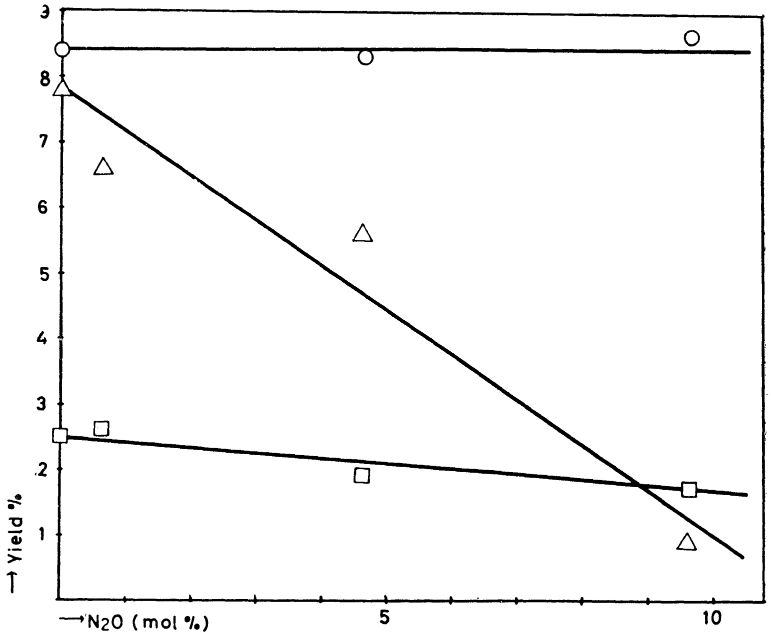

Fig. 4. 2450-MHz discharge of toluene.

△ Ethylbenzene, ○ Benzene, □ Ethane

electric discharge. Concerning the products, no difference in the reaction between 10 and 2450 MHz was found. Benzene and ethylbenzene were the main products in both the discharges. However, the variation in the product yields (based on the toluene consumed) with the concentration of the scavenger showed much difference between the 10- and 2450-MHz discharges, as is shown in Figs. 2, 3, and 4.

The Formation of Ethylbenzene. The main products are benzene and ethylbenzene. This experimental finding indicates that, in these discharges, phenyl radical are produced as well as benzyl radicals. Benzyl radicals have been reported to be commonly produced in the photolysis,[17] pyrolysis, and radiolysis of toluene. In the radiolysis[14] of liquid toluene, however, ethylbenzene is not the principal product. Cher[22] has found ethylbenzene, in the photolysis of gaseous toluene, to be a major non-gaseous product. Schüler and Stockburger[17] have also reported the formation of benzene and the benzyl radical in the discharge reaction of toluene and have pointed out, that in the electric discharge, the dissociation into H atoms is not a single process.

Effect of Scavenger. The fact that a small percentage of nitric oxide strongly inhibits the formation of ethylbenzene in the 10-MHz discharge, while nitrous oxide does not greatly inhibit it, suggests that the radical process is predominant in the reaction. On the other hand, in the 2450-MHz discharge about half of the ethylbenzene yield disappears in the presence of such radical scavengers as nitric oxide and ethylene. Moreover, the yield of ethylbenzene is also inhibited greatly in the presence of nitrous oxide. These experimental facts suggest that not only the radical but the ionic (not radical) process must be considered in the 2450-MHz discharge. This ionic process was also assumed by Streitwieser and Ward in the microwave discharge. However, these differences between the two discharge types are not yet clear.

Other Products. Benzaldehyde was found when nitric oxide and oxygen were used as scavengers in the 10-MHz discharge. One possible process of benzaldehyde formation may be shown as follows:

$$C_6H_5\text{-}CH_2\cdot + NO \rightarrow (C_6H_5\text{-}CH_2\text{-}NO) \rightarrow C_6H_5\text{-}COH + NH$$

In the 2450-MHz discharge, benzaldehyde was not detected in the presence of nitric oxide.

A small amount of nitrosobenzene was found in both the discharges; it may be produced by the reaction of the phenyl radical with nitric oxide. Phenylpropylene and phenylcyclopropane were not detected in these discharges when ethylene was used as a scavenger. Therefore, the formation of the benzal diradical[23] (C_6H_5-CH) was not confirmed. By using maleic anhydride, the formation of fulvene derivatives was not confirmed, either.

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