# Disproportionation of Toluene over Electron Donor–Acceptor Complexes of Aromatic Hydrocarbons with Sodium

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*Summary* The disproportionation of toluene takes place over electron donor–acceptor complexes of naphthalene, phenanthrene, anthracene, and chrysene with sodium; ethylbenzene and *o*-xylene alone are selectively formed.

THE disproportionation reaction of toluene to form benzene and xylenes over the electron donor–acceptor (EDA) complexes of various aromatic hydrocarbons with sodium has been investigated. 'Xylenes' is used to represent ethylbenzene, *o*-, *m*-, and *p*-xylene (*o*-, *m*-, *p*-X)

A continuous flow system at atmospheric pressure was used to follow the reaction, nitrogen being used as diluent. The EDA complexes, the catalysts, were prepared in a vacuum system similar to that described previously.[1] The reaction mixtures were analysed by g.c., under conditions similar to those used by Yashima *et al.*[2]

The Table shows typical results for the disproportionation of toluene over various EDA complexes and over $SiO_2$–$Al_2O_3$. The $N_2$/toluene and the W/F, the contact time parameter, were 350 (mol/mol) and 5 (g/mol $h^{-1}$), respectively. The W/F and the conversion of toluene were defined as: W/F = (weight of catalyst, g)/(feed rate of toluene and nitrogen, mol $h^{-1}$), and conversion = 1 − (mol of toluene remaining)/(mol of toluene fed) × 100.

Table. *Disproportionation of toluene over EDA complexes and* $SiO_2$–$Al_2O_3$

| Catalyst | Temp. (°C) | Conv.[a] (%) | EtPh | Xylenes formed (%) | | | Electron affinity of acceptor [b] (eV) |
|---|---|---|---|---|---|---|---|
| | | | | *o*-X | *m*-X | *p*-X | |
| $SiO_2$–$Al_2O_3$ | 500 | 2 | 10 | 20 | 42 | 28 | — |
| Naphthalene–Na | 90 | 12 | 100 | — | — | — | −0·25 |
| Phenanthrene–Na | 100 | 10 | 100 | — | — | — | 0·01 |
| Anthracene-Na | 100 | 12 | 38 | 62 | — | — | 0·15 |
| Chrysene–Na | 135 | 5 | — | 100 | — | — | 0·31 |

[a] Taken at the steady state which usually occurred after 30 min. [b] See G. Briegleb, *Angew. Chem.* 1964, **76**, 326.

The reaction did not take place over either of the components of the EDA complexes up to 150°, but proceeded over the EDA complexes even at 20°. Silica–alumina did not show catalytic activity under the same experimental conditions, although activity was shown above 350°. The EDA complexes are therefore much more active and selective catalysts than silica–alumina for the disproportionation of toluene to form benzene and xylenes.

The selectivity of the EDA complexes is dependent on the electron affinity of the acceptor compounds; either ethylbenzene or *o*-xylene was selectively formed. Ethylbenzene or *o*-xylene may be formed by either a side-chain alkylation or by a nuclear alkylation of the methyl group of one toluene molecule. The two types of alkylation may be differently catalysed by the EDA complexes, depending upon the electron affinity of the acceptor compounds.

We thank Prof. N. Hara for supplying us with $SiO_2$–$Al_2O_3$ catalyst.

(*Received, 7th May* 1973; *Com.* 641.)

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[1] S. Tsuchiya, V. Ponec, and W. M. H. Sachtler, *J. Catalysis*, **1971**, **22**, 280.

[2] T. Yashima, H. Ahmad, K. Yamazaki, M. Katsuta, and N. Hara, *J. Catalysis*, **1970**, **16**, 273.