

Disproportionation and Propylation of Toluene over Electron Donor-Acceptor Complexes of Aromatic Hydrocarbons with Sodium

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The disproportionation and the propylation of toluene over electron donor-acceptor (EDA) complexes of naphthalene, phenanthrene, anthracene, and chrysene with sodium have been investigated. The EDA complexes showed high catalytic activity and selectivity for the reactions. Two types of alkylation, side-chain and nuclear, have been suggested by the reaction products: ethylbenzene and *o*-xylene for the disproportionation reaction and butylbenzenes and cymenes for the propylation reaction. The analogy of catalytic selectivity was observed between the disproportionation and the propylation reactions, depending upon the electron affinity of the acceptor compounds. The catalyst for the side-chain alkylation in the disproportionation reaction also catalyzes the side-chain propylation of toluene.

INTRODUCTION

The disproportionation reaction of toluene to form benzene and xylenes is of great importance in petrochemistry, and a good catalytic process of the reaction is still of interest. Since Kondow *et al.* (1) found that the hydrogen-deuterium equilibration reaction was catalyzed by a tetracyanopyrene-cesium complex, extensive studies on heterogeneous catalysis by electron donor-acceptor (EDA) complexes have been reported (2). The types of reactions mainly investigated so far, however, are limited to hydrogen-deuterium exchange and equilibration and to hydrogenation and double-bond migration reactions.

In the present work, the disproportionation and the propylation of toluene over the EDA complexes of various aromatic hydrocarbons with sodium have been in-

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vestigated in order to obtain further information on heterogeneous catalysis by EDA complexes.

EXPERIMENTAL

Apparatus and materials. A continuous-flow system at atmospheric pressure was used to follow the reaction, helium (99.995%) or nitrogen (99.99%) being used as diluent. The catalysts used, the EDA complexes of naphthalene, phenanthrene, anthracene, and chrysene with sodium, were prepared beforehand in a vacuum system similar to that described previously (3-5) and were then fixed in the flow system.

The reactants, toluene (99.9%) and propylene (99%), were obtained from standard commercial sources, and the purity was checked by gas chromatography.

Procedure. The nitrogen stream with toluene or the helium stream with toluene

and propylene was initially passed through the by-pass, and then introduced into the reactor by changing the flow to start the reactions. The amount of reactant, toluene in the nitrogen stream or toluene and propylene simultaneously admitted into the helium stream, was occasionally measured before entering the reactor. Analytical samples of the products were collected after leaving the reactor.

Analysis. The reaction mixtures were analyzed by gas chromatography. For aromatic hydrocarbons, a 4-m stainless-steel column with a diameter of 3 mm, with a stationary phase of Celite-545 (60–80 mesh) containing 10 parts of Bentone-34 (dimethyldiocta-decylammonium chloride) and 10 parts of DIDP (diisodecylphthalate) with respect to 100 parts of solid support, was used at 100°C, as suggested by Yashima *et al.* (6). For lower aliphatic hydrocarbons, a 2-m copper column with active alumina (60–80 mesh) coated with three parts of liquid paraffins was used at room temperature. The detector used was a Shimadzu FID.

RESULTS

Disproportionation of Toluene

The disproportionation of toluene to form benzene and xylenes over the EDA complexes of various aromatic hydrocarbons with sodium has been investigated. "Xylenes" is used to represent ethylbenzene (EtPh), *o*-, *m*-, and *p*-xylene (*o*-, *m*-, *p*-X).

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

Table 1 shows typical results for the disproportionation of toluene over various EDA complexes. The nitrogen/toluene and W/F, the contact time parameter, were 350 mol/mol and 5 g/mol·hr⁻¹, respectively. The W/F and the conversion of toluene were defined as: W/F = (weight of catalyst, grams)/(feed rate of toluene and nitrogen, moles per hour), and conversion = [1 - (moles of toluene remaining)/(moles of toluene fed)] × 100. The composition of xylenes formed was independent of the conversion of reaction in the range of about 2–20%, suggesting that the EDA complexes have high catalytic selectivity for the disproportionation of toluene. The selectivity of the EDA complexes is seemingly dependent upon the electron affinity of the acceptor compounds (E. A.), the values of which were obtained from Briegleb's paper (7).

Propylation of Toluene

The reaction of toluene with propylene has also been measured over the same kind

TABLE 1
Disproportionation of Toluene over EDA Complexes

Catalyst	Temperature (°C)	Conversion ^a (%)	Xylenes formed (%)				E. A. (eV)
			EtPh	<i>o</i> -X	<i>m</i> -X	<i>p</i> -X	
Naphthalene-Na	90	12	100	—	—	—	-0.25
Phenanthrene-Na	90	8	100	—	—	—	0.01
Anthracene-Na	90	10	38	62	—	—	0.15
Chrysene-Na	135	5	—	100	—	—	0.31

^a Taken at the steady state which usually occurred after 30 min.

TABLE 2
Reaction of Toluene with Propylene over EDA Complexes

Catalyst	Temperature (°C)	Composition of aromatic compounds (%)			
		Toluene unreacted	Benzene + xylenes	Cymenes	Butylben- zenes
Phenanthrene-Na	120	95	1	0	4
	110	96	1	0	3
Anthracene-Na	100	36	13	0	51
	95	40	10	0	50
Chrysene-Na	110	44	0	56	0
	90	67	0	33	0

of EDA complexes as employed in the case of the disproportionation reaction. The reaction did not take place over either of the components of the EDA complexes up to 150°C but proceeded over the EDA complexes of phenanthrene, anthracene, and chrysene with sodium. Over the naphthalene-sodium complex the reaction could not be measured.

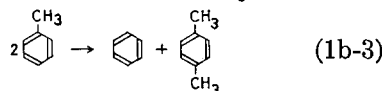
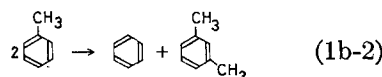
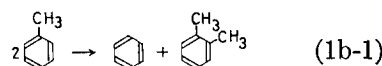
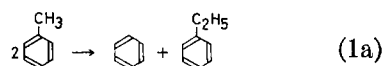
Table 2 shows typical results for the reaction of toluene with propylene over the EDA complexes. The ratios, (helium)/(toluene + propylene), propylene/toluene, and (weight of catalyst)/(feed rate of toluene + propylene + helium), the parameter of contact time, were 30 mol/mol, 20 mol/mol, and 5 g/mol·hr⁻¹, respectively. Either cymene or butylbenzene, other than benzene and xylenes, was selectively formed depending upon the EDA complexes employed. The butylbenzenes given by the anthracene-sodium complex were only tert- and sec-butylbenzene, and the ratio, tert/sec, was about 4. The cymene isomers were not separately measured in the present experiments. No lower aliphatic hydrocarbons other than propylene could be observed in the helium stream. Over the naphthalene-sodium complex the formation of neither benzene nor xylenes was observed in the presence of propylene.

DISCUSSION

Disproportionation of Toluene

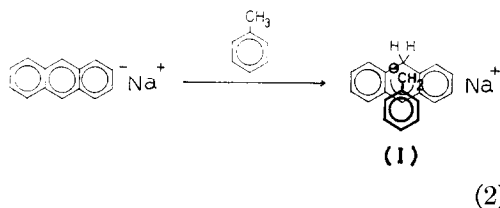
The amounts of the individual xylene isomers are comparable at thermodynamic equilibrium, as reported by Taylor (8), and the mixtures of xylene isomers have generally been obtained by the catalytic disproportionation of toluene (9). It is, therefore, of great interest that the EDA complexes have high catalytic selectivity for the disproportionation reaction.

The reaction can be expressed by the following equations (1a and 1b); ethylbenzene or *o*-xylene is formed by either a side-chain alkylation (1a) or by a nuclear alkylation (1b-1) of methyl group of one toluene molecule.

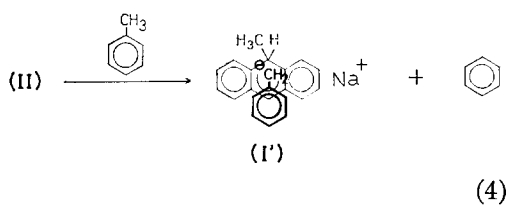
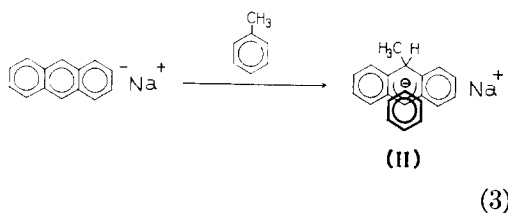


The two types of alkylation are catalyzed differently by the EDA complexes, depending upon the acceptor compounds.

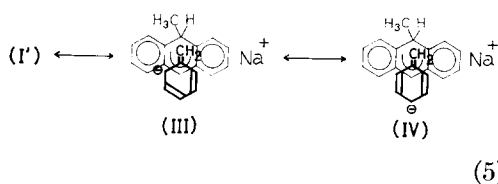
The reaction scheme of disproportionation is tentatively shown, e.g., over the anthracene-sodium complex, as follows:



Toluene is dissociatively adsorbed on the catalyst by the π - π interaction between its benzene ring and the π -conjugated system of the catalyst, giving the hydrogen to the catalyst, perhaps at the 9-position of anthracene, Eq. (2). Another possibility is shown by Eqs. (3) and (4).



First, one toluene molecule is adsorbed on the catalyst, giving the methyl group to the catalyst, Eq. (3). The adsorbed toluene, (II), is an adsorbed benzene in practice. Then another toluene molecule approaching is dissociatively adsorbed on the catalyst as a benzylcarbanion, (I'), displacing benzene adsorbed, Eq. (4); the state (I') is different from (I) at the 9-position of anthracene.

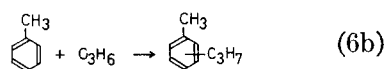
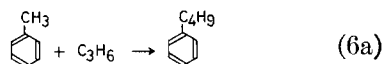


Three canonical forms, (I'), (III), and (IV), of the carbanion can be considered, as shown by Eq. (5), corresponding to three xylene isomers, ethylbenzene, *o*-xylene, and *p*-xylene, respectively. However, it is impossible that the methyl group adsorbed at the 9-position of anthracene attacks the 4-position of the adsorbed benzylcarbanion, (IV), to form *p*-xylene, because of a steric effect. Accordingly, *p*-xylene was not formed in the reaction.

As shown in Table 1, the formation of ethylbenzene and *o*-xylene is correlated with the electron affinity of the acceptor compound of the EDA complexes. The results can be acceptable, considering that the carbanion is differently adsorbed on the EDA complexes in the adsorption-angle and -strength and that the reaction proceeds predominantly through either form (I') or (III), depending upon the EDA complexes.

Propylation of Toluene

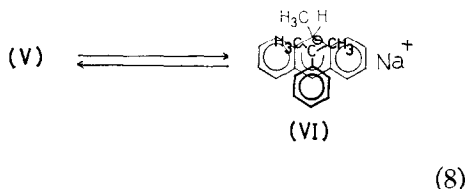
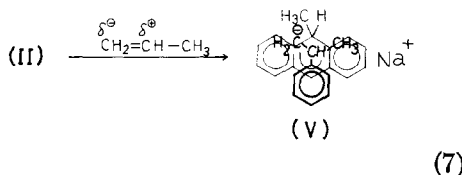
The propylation of toluene can be expressed by the following equations, Eqs. (6a) and (6b); butylbenzenes or cymenes are formed by either a side-chain alkylation (6a) or a nuclear alkylation (6b). The reaction products



depend upon the acceptor of the EDA complexes. Benzene and xylenes are probably formed by the disproportionation of toluene, although the catalytic activity of the EDA complexes for the reaction may be different in the presence of propylene.

The reaction scheme of propylation of toluene, e.g., over the anthracene-sodium

complex, is tentatively shown as follows:



Propylene reacts with the adsorbed benzene, (II), formed as in Eq. (3), to give an adsorbed propylbenzene carbanion, (V) or (VI), corresponding to the isomer, tert- or sec-butylbenzene, respectively. The carbanion (VI) is probably more stable than (V), and the amount of tert-butylbenzene formed was more than that of sec-butylbenzene formed; they were formed from the carbanion and the methyl group at 9-position of anthracene.

Over the chrysene-sodium complex, on the other hand, propylene reacts with the adsorbed benzylcarbanion, (I or I'), to form cymenes. (I or I'), (III), and (IV) yield isobutylbenzene and *o*- and *p*-cymene, respectively.

The variation in selectivity is accordingly attributed to the predominance in the adsorption of intermediates, benzene and benzylcarbanion, depending upon the EDA complexes. The propylation activity may

TABLE 3
Types of Alkylation in Disproportionation and Propylation

Catalyst	Disproportionation	Propylation
Naphthalene-Na	Side-chain	— ^a
Phenanthrene-Na	Side-chain	Side-chain
Anthracene-Na	Side-chain, nuclear	Side-chain
Chrysene-Na	Nuclear	Nuclear

^a Catalytic activity was not observed.

be due to the amount and/or strength of adsorption on the complexes. The information on adsorption at the working state can be obtained by Tamaru's method if an applicable technique for the present reaction system is developed (10).

Comparison of Disproportionation and Propylation

An interesting analogy between disproportionation and propylation has been observed in view of the type of alkylation, as shown in Table 3. The catalyst for the side-chain alkylation in the disproportionation reaction also catalyzes the side-chain propylation of toluene.

Side-chain alkylation in the propylation of toluene, however, is not necessarily the same as in the disproportionation reaction in view of the reaction scheme mentioned above. In the propylation reaction, the reaction intermediates are the adsorbed benzylcarbanion, (I or I'), and the adsorbed benzene, (II), which does not have an important role in the disproportionation reaction; (II) gives toluene in the disproportionation reaction. By side-chain alkylation in the absence of disproportionation, however, isobutylbenzene would be formed from the benzylcarbanion and propylene. Pines *et al.* (11) reported that isobutylbenzene was formed from toluene and propylene in the presence of sodium and anthracene. In their reaction system, the anthracene-sodium complex of catalytic activity may be formed, and propylene could react with the benzylcarbanion to give isobutylbenzene under such severe reaction conditions as 297°C and 90 atm in an autoclave. Accordingly, the reaction intermediate, either benzylcarbanion or benzene, is predominant depending upon the reaction conditions, and tert- and sec-butylbenzene or isobutylbenzene may be formed by side-chain alkylation.

The activity of the EDA complexes for disproportionation apparently increases

with decreasing E. A. (Table 1), but the opposite trend is observed in the presence of propylation (Table 2). This behavior suggests that the adsorption during the reaction in the presence of propylene is different from that in the absence of propylene; the amounts as well as the strength of adsorption on the catalyst are affected by the pressure of propylene during the reaction.

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