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CATALYSIS OF ALKALI METAL-POLYNUCLEAR AROMATICS COMPLEXES I

REACTION OF ALKYLBENZENES WITH ETHYLENE IN THE PRESENCE OF SODIUM AND POLYNUCLEAR AROMATIC HYDROCARBONS

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The alkali metal catalyzed reaction of alkylbenzenes with olefins has attracted much attention[1-6] in the past several years. Some polynuclear aromatic hydrocarbons (PNA) such as anthracene have been used as a promoter.[1] The mechanism of the function of these promoters, however, has not been revealed.

In the present studies, the side-chain ethylation of alkylbenzenes with ethylene in the presence of sodium metal and PNA was examined. On the assumption of an electron donor-acceptor (EDA) complex between the two catalyst components, the correlation between the catalyst activity and the electron affinity (EA) of the PNA component was investigated. The following PNAs were used as electron acceptors in the binary system: Biphenyl (Bip); Naphthalene (N); Phenanthrene (Ph); *p*-terphenyl (P-t); Chrysene (Ch); Pyrene (Py); Anthracene (An); Acenaphthylene (Ac).

The relative values of EA of these PNA were expressed by the coefficient (m_{n+1}) of the lowest vacant orbital energy ($E_{LV} = \alpha + m_{n+1}\beta$) which was calculated by the Hückel MO method. This coefficient has been shown to be in a good linear correlation with the half wave reduction potential of polarography.[7]

The reactions were carried out in a 50 ml stainless steel pressure tube without stirring or shaking. In this tube, 30 mg atoms of sodium, 3 mmoles of PNA and 20 ml of alkylbenzene were placed and ethylene was compressed up to 60 atm. at room temperature. Then the tube was closed and heated at 255°C for 30 minutes to 3 hrs. After cooling, unreacted ethylene

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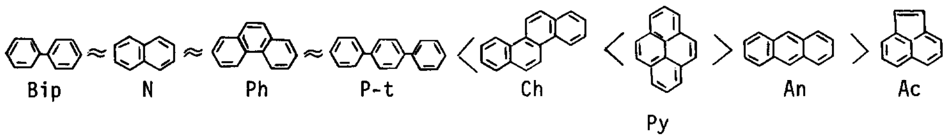
was purged and the reaction products were analyzed by gas chromatography. The activity of the catalyst system was indicated by the relative conversion rate of alkylbenzenes in the early reaction period.

The observed relation between the catalyst activity and the EA of PNA in the case of ethylation of cumene is shown in Fig. 1. The conversion percent of cumene in a reference run without PNA was 1.0 % in 1 hr. at 255°C, which was taken as the basis of relative conversion rate. The activities of PNA in the sodium complex catalyst systems were as follows.



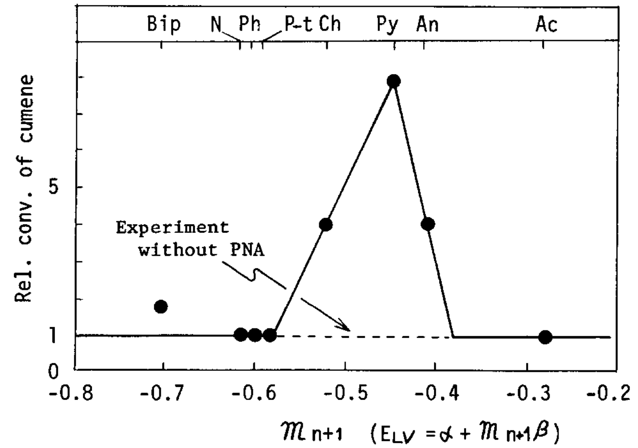


Fig. 1. Relation of relative conversion rate of cumene vs coefficient of lowest vacant MO energies of PNA in the sodium catalyzed reaction of cumene with ethylene. PNA : Biphenyl (Bip), Naphthalene (N), Phenanthrene (Ph), *p*-terphenyl (P-t), Chrysene (Ch), Pyrene (Py), Anthracene (An), Acenaphthylene (Ac).

It is interesting to note that the activity of the binary system of sodium and PNA changes regularly according to the EA of the PNA component. The combination of sodium and pyrene gave the highest catalyst activity. In the ethylations of toluene and ethylbenzene with sodium, a similar dependency of catalyst activity upon the m_{n+1} of PNA was observed (Table I).

TABLE I. Side-chain Ethylation of Alkylbenzenes
by Na-polynuclear Aromatics

Electron Acceptors (PNA)		Relative Conversion		
	$-m_{n+1}$ *	Toluene	Ethylbenzene	Cumene
Biphenyl	0.705	1.0	1.0	1.8
Naphthalene	0.618	1.0	1.0	1.0
Phenanthrene	0.605	1.0	1.4	1.0
p-Terphenyl	0.593	1.0	1.5	1.0
Chrysene	0.520	3.4	3.1	4.0
Pyrene	0.445	9.7	5.1	8.0
Anthracene	0.414	6.9	3.5	4.0
Acenaphthylene	0.285	1.6	2.3	0.8

* Coefficient of lowest vacant orbital energy ($E_{LV} = \alpha + m_{n+1}\beta$)

These results may be taken to assume the formation of an EDA complex, to which the catalyst activity is ascribed.

Similar relationship between the catalyst activity of EDA complex and the EA of acceptor has been observed by Tamaru et al.[8)] in the isomerization of butene. The butene isomerization was assumed to proceed via the chemisorption of butene followed by the dissociation of hydrogen. In addition, similar result was also reported in the H_2-D_2 exchange reaction over the EDA complex.[9)] Consequently, the dissociation of benzylic hydrogen of alkylbenzene by the EDA complex of the sodium-PNA system may reasonablv be assumed to be an essential step in the ethylation of alkylbenzene.

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