CATALYSIS OF ALKALI METAL—POLYNUCLEAR AROMATICS COMPLEXES II

REACTION OF ALKYLBENZENES WITH OLEFINS IN THE PRESENCE OF POTASSIUM

AND POLYNUCLEAR AROMATIC HYDROCARBONS

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The reaction of alkylbenzenes with olefins by metallic potassium in the presence of anthracene as a promoter was reported by Schaap and Pines.[1] On the other hand, Schramm and Langlois studied the alkali metal catalyzed alkylation of toluene with propylene, and cast a doubt upon the activating effect of the promoter, such as anthracene, especially in the case of potassium system.[2]

In a previous communication,[3] we reported the reaction of alkylbenzenes with ethylene by a binary catalyst system of sodium and polynuclear aromatic hydrocarbons (PNA). An interesting relationship between the catalyst activity and the electron affinity (EA) of the PNA component was observed, and an electron donor–acceptor (EDA) complex of the catalyst components was assumed as the active species of the catalyst.

In this report, the potassium catalyzed reaction of cumene with ethylene in the presence of various PNA was investigated from the viewpoint of the EDA complex catalyst. The reaction procedure was the same as that used for the sodium catalyzed ethylations in the previous paper. Since the activity of potassium catalyst is higher than that of sodium, the reactions were carried out at lower temperature (220°C) than in the case of sodium.

The relationship between the relative catalyst activity of potassium-PNA systems and the EA of PNA is shown in Fig. 1. The EA of PNA is indicated by the coefficient ($\mathcal{M}_{n+1}$) of the lowest vacant orbital energy ($E_{LV} = \alpha + \mathcal{M}_{n+1}\beta$). The conversion rate of cumene of a reference run without PNA was 2.0 % in 1 hr. at 220°C under 90 kg/cm^2 of the ethylene pressure. This value was taken as the basis of the relative conversion rate.

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Bip N Ph Pt Ch Py An   Ac

Rel. conv. rate of cumene

10 — Extrapolated to the value
   of benzene used
   as an electron acceptor

5

Experiment without PNA

1

0
-0.8 -0.7 -0.6 -0.5 -0.4 -0.3 -0.2

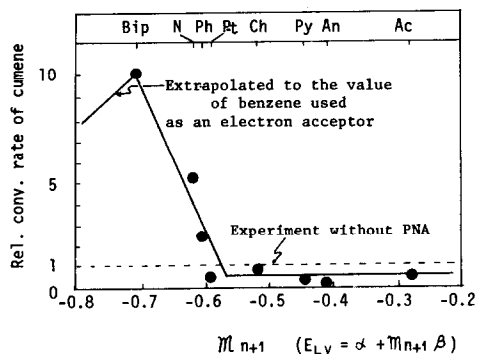m_{n+1} $(E_{LV} = \alpha + m_{n+1}\beta)$

Fig. 1. Correlation of relative conversion rate of cumene vs coefficient
of lowest vacant MO energies of PNA for the potassium 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).

Pyrene, chrysene, and anthracene, which are effective promoters in the sodium catalyzed

ethylation of cumene, are not effective in the potassium catalyzed ethylation. On the other

hand, biphenyl is quite effective in the case of a potassium catalyst. Thus, it is of

interest to note that the nature of PNA at the highest catalyst activity varies in accordance

with the alkali metal species.

In the lithium catalyzed reaction of cumene with ethylene, the PNA component at the

highest catalytic activity was anthracene.[4] The order of ionization potentials (Ip) of the

three alkali metal catalysts agrees to the order of EA values of the corresponding PNA com-

ponents at the highest catalyst activities.

$$I_p : K < Na < Li$$

$$EA : Biphenyl < Pyrene < Anthracene$$

These findings will be reasonably understood by the assumption of the mechanism through the

EDA complex. For the formation of effective EDA complex, the EA value of the suitable elec-

tron acceptor will vary according to the ionization potential of the alkali metal.

REFERENCES

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2) R. M. Schramm and G. E. Langlois, J. Am. Chem. Soc., 82, 4912 (1960).

3) T. Saegusa, T. Waragai and H. Kawaguchi, Tetrahedron Letters, the preceding paper.

4) To be published in Bull. Chem. Soc. Japan.