Catalytic Activity of the Electron Donor–Acceptor Complex of Polynaphthoquinone with Potassium

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Summary High catalytic activities of the electron donor–acceptor complex of polynaphthoquinone with potassium are reported for H_2–D_2 exchange, the synthesis of ammonia, hydrogen exchange of propene with deuterium, hydrogenation of propene, and isomerization of butene.

A CHELATE complex of poly-naphthoquinone[1] with $FeCl_3$ was prepared from a mixture of the components in ethyl alcohol by gradually evaporating the solvent at room temperature followed by treatment at 350° for 12 h under vacuum. The electron donor-acceptor (e.d.a.) catalysts were prepared by the addition of potassium vapour to the metal-free polynaphthoquinone and to the polynaphthoquinone containing $FeCl_3$ followed by heating at 350° under vacuum. The BET surface areas of the catalysts thus obtained was about 120 $m^2\ g^{-1}$.

Table 1. *Hydrogen exchange of propylene with deuterium over* (Q–$FeCl_3$–K)

$[\mathrm{H}^2]$-Propylene (%)	[a] $CHD{=}CH{-}CH_3$ (%)	$CH_2{=}CH{-}CH_2D$ (%)	$CH_2{=}CD{-}CH_3$ (%)
7·2	32	67·6	0·4
15·2	35	64·6	0·4

[a] monodeuteriated propylene per total propylene.

Isomerization of *cis*-but-2-ene into *trans*-but-2-ene and but-1-ene over the e.d.a. complexes proceeded rapidly in the range −8° to 50°. Isomerization over polynaphthoquinone was negligible under similar conditions.

Hydrogen exchange between propene and deuterium was studied in the range from room temperature to 200°. The results, shown in Table 1, show that the intermediate of the reaction over both the e.d.a. complex of potassium with the Fe-free polynaphthoquinone (Q–K) and that of potassium with the polynaphthoquinone containing $FeCl_3$-(Q–$FeCl_3$–K) is of the isopropyl type.

The hydrogenation of propene by hydrogen was studied in the range 100° to 200°. The rate of the propane formation is expressed by the equation, $d(\text{propane})/dt = k_p(\text{propene})(H_2)^{1/2}$. The Fe containing complex (E_a = 4·7 kcal mol^{-1}) was more active than the Fe-free complex (E_a = 11·3 kcal mol^{-1}). The rate of the hydrogen exchange of propene with deuterium was markedly faster than that of the hydrogenation of propene.

H_2–D_2 exchange proceeded rapidly over both (Q–K) and (Q–$FeCl_3$–K) at room temperature and was observed even at −78°. H_2–D_2 exchange was not affected by the addition of $FeCl_3$ to the e.d.a. complex. The results are given in Table 2.

As shown in Table 2, catalytic formation of ammonia was observed over (Q–K), while both the exchange reaction of hydrogen and the synthesis of ammonia did not occur over polynaphthoquinone itself. However, with (Q–$FeCl_3$–K) NH_3 formation was accelerated by a factor of 13.

Table 2.

	Ammonia synthesis at 300° (21 *h*)				H_2–D_2 *exchange reaction at* 23° (10 *min*)			
	Partial Pressures (cmHg)				Partial Pressures (cmHg)			Activation Energies
Catalyst	N_2	H_2	Conv. %	$cm^3\ g^{-1}$	H_2	D_2	Conv. %	(kcal/mol^{-1})
Q–K	15	45	1·4	1·8	20	15	52	6·0
Q–$FeCl_3$–K	15	45	18·4	24·4	20	15	53	5·9
Q–$FeCl_3$	15	45	0	0	20	15	0	—

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[1] Y. Iwasawa, M. Soma, T. Onishi, and K. Tamaru, *J.C.S. Faraday I*, **1972**, 1617.