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Catalytic Hydrogen Transfer Reactions between Hydroaromatics and Nitrobenzene over Polynaphthoquinone

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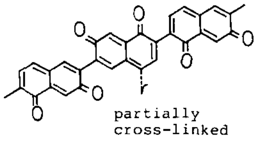
The catalytic hydrogen transfer reactions between hydroaromatics and nitrobenzene over polynaphthoquinone catalyst were found to proceed with 98–100% selectivities in the temperature range 300–330°C in conjunction with the redox cycle of surface quinone and hydroquinone groups. The quinones/hydroquinones ratios during reactions were 52/48%–56/44%, depending upon the nature of the hydroaromatics. The characteristic reaction mechanism was clarified on the basis of the well-defined reaction sites of polynaphthoquinone with a nearly uniform (89.2%) property in activity.

INTRODUCTION

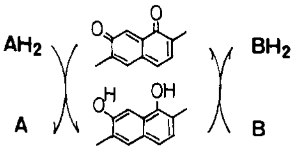
Polynaphthoquinone (*1–6*) has been demonstrated to be a typical heterogeneous molecular catalyst with well-defined reaction sites and to have the following characteristic structure (shown below) and properties: (i) a unique quinone structure conjugated with a long π-electron system without breaking of the C=C conjugated chain by quinoid bonds, (ii) a low frequency of the C=O stretching (1600 cm^{-1}) which makes quinone groups more reactive, (iii) minimum hindrance in the structural change between quinones and hydroquinones, (iv) thermal stability up to 450°C in N_2 or 390°C in air, and (v) insolubility in water and organic solvents. Polynaphthoquinone (Q) has been found to function as an active and selective catalyst for dehydrogenations of many substrates (AH_2) in a relatively low temperature range (*1–4*). The reaction mechanism is expressed by the following two stoichiometric steps by way of formation of hydroquinone groups (QH_2) (*2–4*):



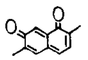
$$AH_2 + Q \rightleftharpoons A + QH_2 \qquad (1)$$

$$QH_2 + \tfrac{1}{2}O_2 \rightleftharpoons Q + H_2O \qquad (2)$$

When suitable hydrogen acceptors (B) are employed instead of oxygen, the catalytic hydrogen transfer between AH_2 and B was found to proceed as shown in Scheme 1 (*6*).



SCHEME 1. Catalytic hydrogen transfer process.

where  stands for a structure unit of polynaphthoquinone. The reaction rate may depend upon the hydrogen pulling ability of quinone groups as well as the reducing power of hydroquinones. The reduction of B to BH_2 would be affected by the nature of trapped hydrogen atoms (hydroquinones) which should have a different property from dihydrogen, the hydrogen atoms dissociated on metals, metal oxides, etc., and the hydrogen of a N–H bond.

Thus the study on the catalytic hydrogen transfer reactions between hydroaromatics and nitrobenzene to form simultaneously the dehydrogenated product and aniline on the polynaphthoquinone was undertaken to

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examine the characteristic reactivities of quinones and hydroquinones as active sites and the behavior of trapped hydrogen atoms, and to determine the reaction mechanism.

EXPERIMENTAL

Polynaphthoquinone was synthesized by oxidation of 1,7-naphthalenediol with nitric acid in a procedure similar, but with slight modifications, to that described in the previous paper (*1*). 1,7-Naphthalenediol, 1 g in 50 ml ethanol, was added in small portions for 15 min to 200 ml of aqueous 25% nitric acid in a water bath (10–20°C) by stirring vigorously in air and stirring was continued for another 15 min. It was diluted to 600 ml with distilled water before filtration. The deep brown precipitate obtained was repeatedly washed with distilled water until the pH of the filtrate became 7, followed by drying at 120°C. The dark brown powder was arranged to the size of 60–80 mesh. At this stage the polymer was slightly soluble in organic solvents such as THF, pyridine, DMF, etc. and showed the C=O stretching frequency of quinone groups at 1650 cm^{-1}. This polymer was heated to 200°C for 8 hr in air and then washed again with water and decanted twice. The black-colored polymer was stepwisely heated at intervals of 50°C up to 350°C at which it was kept for 3 hr. The final, thermostable and insoluble polynaphthoquinone which consists of the tight aggregation of plate-like microcrystals (*4*), had the C=O frequency at 1600 cm^{-1}. The polynaphthoquinone catalyst was further treated at 340°C in a flow of helium prior to experimental runs. The $FeCl_3$-containing polynaphthoquinone was obtained by mixing the polynaphthoquinone and an ethanol solution of known amounts of $FeCl_3$ and by gradually evaporating the solvent.

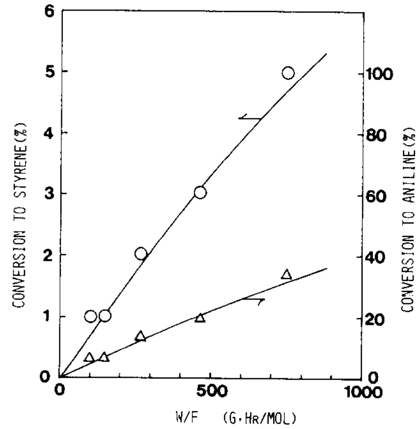


FIG. 1. Conversion vs *W/F* plots in the hydrogen transfer reactions between ethylbenzene and nitrobenzene at 315°C; ethylbenzene/nitrobenzene = 19.8/1 (molar ratio).

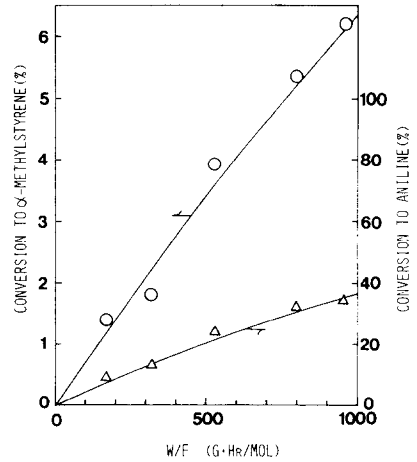


FIG. 2. Conversion vs *W/F* plots in the hydrogen transfers between cumene and nitrobenzene at 315°C; cumene/nitrobenzene = 17.6/1 (molar ratio).

Hydroaromatics like ethylbenzene, cumene, *n*-propylbenzene, and nitrobenzene of chemically pure grade were purified by single distillation. Nitrosobenzene commercially obtained was used without further purification.

The reactions were carried out in a fixed-bed flow reactor using 1 g of catalyst; the carrier gas was helium. The reaction products were quantitatively analyzed by gas chromatography using a 50-cm column of PEG 1500/Celite 545 at 97°C.

RESULTS

When the mixture of hydroaromatics (0.09–0.1 atm) and nitrobenzene (0.0052 atm) was passed through the

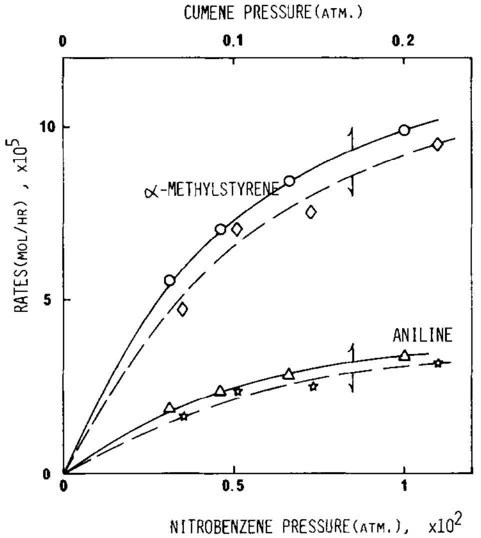


FIG. 3. Dependencies of rates of α-methylstyrene and aniline formations upon the partial pressures of cumene and nitrobenzene, in the cumene–nitrobenzene reaction at 315°C.

polynaphthoquinone (1 g) in a flow of helium, the hydrogen transfer reactions between them were found to proceed in the temperature range 285–330°C. Figures 1 and 2 depict hydrogen transfer reactions in ethylbenzene–nitrobenzene and cumene–nitrobenzene systems at 315°C, where two products, styrene–aniline and α-methylstyrene–aniline, respectively, were simultaneously produced in a stoichiometric ratio of 3 : 1. The amount of aniline formed below 300°C was less than the stoichiometric amount which is probably due to stronger adsorption of aniline at lower temperatures. The TPD analysis curve (6°C/min, 40 ml He/min) exhibited maximum desorption peaks at 190–210°C for aromatic hydrocarbons and at 245°C for aniline. Therefore the desorption of reaction products is not rate controlling in the reaction under the present conditions.

The rates of hydrogen transfer reactions depended upon the partial pressures of both reactants. Figure 3 is a typical result in the cumene–nitrobenzene system at 315°C.

No inhibition effects of the added styrene or aniline on the reaction rate between ethylbenzene and nitrobenzene were observed in Fig. 4.

The activation energies are given in Fig. 5 and Table 1. For three different hydroaromatics similar values (14.0–14.8 kcal/mol) were found, suggesting similar reaction patterns. The oxidation of ethylbenzene to styrene by oxygen had the activation energy of 10.6 kcal/mole (*3*). The hydrogen transfer process from hydroquinone groups to nitrobenzene described hereinafter also contributes to the activation energy of the overall reaction. Hydrogen transfers on polynaphthoquinone steadily took place and hence the formations of both dehydrogenated and hydrogenated products manifested the same activation energies.

Again Table 1 shows selective hydrogen transfer processes. The dehydrogenations of ethylbenzene and cumene, respectively, to styrene and α-methylstyrene proceeded with 100% selectivity. By-products by cracking, etc. were not observed. *n*-Propylbenzene was converted to β-methylstyrene as well as allylstyrene. The main product was always β-methylstyrene (91.9% to 310°C, 88.5% at 330°C). The selectivity toward the dehydrogenation (β-methyl- and allylstyrene) was 100%. The hydrogenation

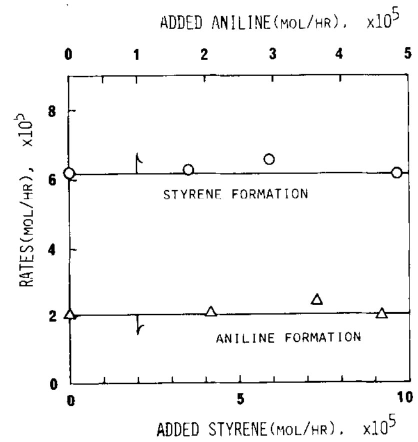


FIG. 4. Effects of added styrene and aniline on the rates of the hydrogen transfer between ethylbenzene and nitrobenzene at 315°C; ethylbenzene supplied: 2.03 mmol/hr; nitrobenzene supplied: 0.101 mmol/hr; total space velocity: 441 ml/hr · g-cat.

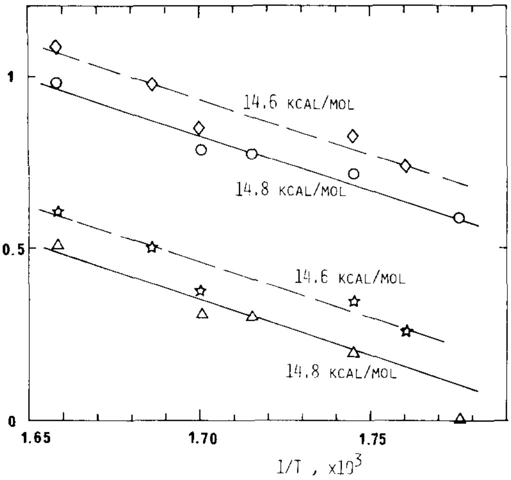


FIG. 5. Activation energies; the formations of styrene (○) and aniline (△) in the ethylbenzene–nitrobenzene system and of α-methylstyrene (◇) and aniline (☆) in the cumene–nitrobenzene reaction.

of nitrobenzene to form aniline had a slightly lower selectivity (98–99%) although side reaction products were not detected by gas chromatography.

When cumene alone was admitted onto the polynaphthoquinone in an atmospheric pressure of helium, α-methylstyrene was produced accompanied with the formation of hydroquinones. However, α-methylstyrene formation rapidly decreased to zero as shown in Fig. 6. After the dehydrogenation of cumene stopped, aniline was produced by introducing nitrobenzene instead of cumene. Its formation also decreased with time and eventually approached zero. Figure 6 reveals that the hydroquinones in the polynaphthoquinone have a reducing power, accordingly hydrogen atoms of cumene were transferred to nitrobenzene by two successive steps through the catalyst surface. A similar result was also observed in the ethylbenzene–nitrobenzene system.

In Fig. 7 rates of the hydrogen transfer from hydroquinones to nitrobenzene were plotted against the number of hydroquinone groups in polynaphthoquinone which was

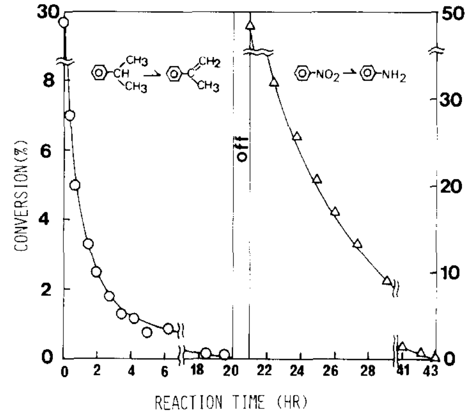


FIG. 6. Plots of conversions against reaction time in flow of cumene (1.78 mmol/hr) or nitrobenzene (0.101 mmol/hr) alone: catalyst: 1 g; carrier gas: helium; reaction temperature: 300°C.

TABLE 1

Catalytic Hydrogen Transfer Reactions on Polynaphthoquinone (1 g)

Reactants[a]	Products	Conv. %	Rate ($\times 10^5$) (mol/hr)	Selec. (%)	T (°C)	Total space velocity (ml/g · hr)	E_A (kcal/mol)
Cumene	α-Methylstyrene	6.9	12.2	100	330	436	14.6 ± 1.0
Nitrobenzene	Aniline	40.0	4.0	98			
Cumene	α-Methylstyrene	4.3	8.3	100	315	436	—
Nitrosobenzene	Aniline	100	4.13	99			
n-Propylbenzene	β-Methylstyrene	4.8	8.15	100	330	442	14.0 ± 1.0
Nitrobenzene	Aniline	28.3	2.7	99			
Ethylbenzene	Styrene	4.8	9.7	100	330	441	14.8 ± 1.0
Nitrobenzene	Aniline	31.7	3.2	99			

[a] Ratios to hydroaromatics:nitrobenzene (4 vol (liquid)%), nitrosobenzene (2.12 mol%); partial pressures of hydroaromatics: 0.0086–0.11 atm.

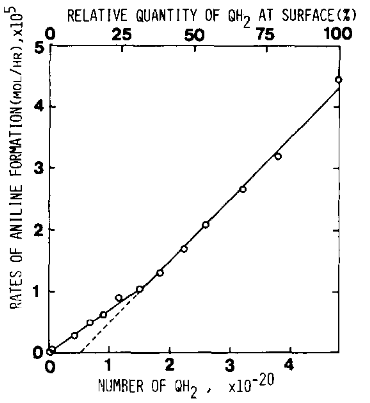


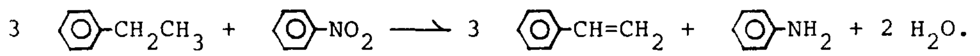
FIG. 7. Relation between the number of hydroquinone groups (QH_2) and the rates of aniline formation in the hydrogen transfer from QH_2 to nitrobenzene at 300°C.

calculated from Fig. 6, in order to examine the reactivity of individual hydroquinone (also quinone) groups. The rate linearly decreased as the number of hydroquinones decreased, followed by a decrease with another gentle slope; the break in the line was observed.

The effects of the addition of $FeCl_3$ (2 mol%) in the catalyst on the reaction rates are given in Table 2. The $FeCl_3$-containing polynaphthoquinone accelerated the hydrogen transfer reactions by a factor of about 2 versus the metal-free polynaphthoquinone.

DISCUSSION

It was found in Fig. 1 and Table 1 that hydrogen transfer reactions between hydroaromatics and nitrobenzene over polynaphthoquinone catalytically proceeded in the temperature range 300–330°C. Thus the admission of a mixture of ethylbenzene and nitrobenzene onto the polynaphthoquinone gave two products simultaneously, styrene and aniline, in a ratio of 3 : 1 by the following equation:



It has been demonstrated in previous papers that various dehydrogenations of formic acid (*1*), alcohols (*2, 5*), ethylbenzene (*3*), hydrosulfide (*4*), etc. (*1, 3*) obeyed a two-stage redox mechanism as expressed by the Eqs. (1) and (2). When the surface quinones were saturated with hydrogen atoms forming hydroquinone groups, the reaction in Eq. (1) stopped. The quantity of surface hydroquinones formed in Scheme 1 was determined by the uptake of oxygen (Eq. (2)) in a separate experimental run to be one-eighth of whole quinone groups of catalyst which is in agreement with the number of effective quinone groups at the surface found in previous papers (*1, 3, 4*). The total amount of aniline formed in Fig. 6 reveals that all of the hydrogen atoms of the hydroquinones were transferred to nitrobenzene, while hydroquinones are oxidized

TABLE 2

Catalytic Hydrogen Transfers on the $FeCl_3$-Containing Polynaphthoquinone at 330°C

Reactants[a]	Products	Conv. %	Rate (r) ($\times 10^5$) (mol/hr)	Selec. (%)	Total space velocity (ml/g · hr)	$r(Q - FeCl_3)$ / $r(Q)$
Cumene	α-Methylstyrene	15.2	27.1	100	436	2.2
Nitrobenzene	Aniline	76.0	7.7	85		1.9
Ethylbenzene	Styrene	9.7	19.6	100	441	2.0
Nitrobenzene	Aniline	60.9	6.15	94		1.9

[a] Under same conditions as Table 1.

to quinones again. Consequently, a catalytic cycle for hydrogen transfers is made up on the polynaphthoquinone.

The rate of aniline formation vs the number of hydroquinones plots in Fig. 7 displayed a break in the slope. It was found from the extrapolation of the slope that the polynaphthoquinone has 89.2% uniformity in activity. The rest (10.8%) has less activity; the former sites showed a turnover number of 0.061 molecules/hr/site, while the latter was 0.042 molecules/hr/site. Thus there are two types of active quinone sites with slightly different activities. The polynaphthoquinone was synthesized by simple synthetic procedures. It may be surprising that the polynaphthoquinone catalyst showed nearly uniform property in hydrogen transfer reactions.

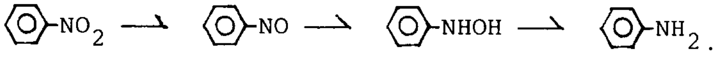
The catalytic hydrogen transfer reactions between hydroaromatics (AH_2) and nitrobenzene (NB) over polynaphthoquinone (Q) may be expressed as follows:

$$AH_2 + Q \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A + QH_2 \tag{3}$$

$$QH_2 + NB \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Q + NS + H_2O \tag{4}$$

$$2QH_2 + NS \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} 2Q + AN + H_2O \tag{5}$$

where QH_2, A, NS, and AN represent the hydroquinone groups, the dehydrogenated product (styrene etc.), nitrosobenzene, and aniline, respectively. The reduction of nitrobenzene to aniline has been said to proceed by the successive steps (*7*),



When nitrosobenzene was employed as a hydrogen acceptor, nitrosobenzene was rapidly reduced to aniline under similar conditions; the conversion was 100% as given in Table 1. Therefore the rate of the NS reduction is much higher than that of the NB reduction and the reduction step of phenylhydroxylamine need not be taken into consideration in reaction kinetics.

$$r_3 = d(A)/dt = k_3(AH_2)(Q) - k_{-3}(A)(QH_2) \tag{6}$$

$$r_5 = d(AN)/dt = k_5(QH_2)^2(NS) - k_{-5}(Q)^2(AN)(H_2O) \tag{7}$$

$k_{-5}(Q)^2(AN)(H_2O)$ is negligible for the mixture of AN and H_2O was not converted to NS or NB on Q; r_5 is reduced to $k_5(QH_2)^2(NS)$. In a steady state,

$$d(NS)/dt = k_4(QH_2)(NB) - k_{-4}(Q)(NS)(H_2O) - k_5(QH_2)^2(NS) = 0. \tag{8}$$

From $r_3 = 3r_5$ and Eq. (8),

$$(3k_4(NB) + k_{-3}(A))(QH_2) = (k_3(AH_2) + 3k_{-4}(NS)(H_2O))(Q). \tag{9}$$

Combining Eq. (6) and (9), and the relation, $(Q) + (QH_2) = (Q)_0$,

$$r_3 = \frac{(3k_3k_4(AH_2)(NB) - 3k_{-3}k_{-4}(A)(NS)(H_2O)(Q)_0}{k_3(AH_2) + k_{-3}(A) + 3k_4(NB) + 3k_{-4}(NS)(H_2O)}.$$

Nitrobenzene (NB) acts as a much stronger hydrogen acceptor to hydroquinones than styrene or α-methylstyrene (A). This and the relatively low conversion of AH_2 to A give $k_{-3}(A) \ll 3k_4(NB)$, $k_3(AH_2)$, $k_3(AH_2) + 3k_4(NB)$. Since the concentration of NS is nearly constant and close to zero during the reaction, $3k_{-4}(NS)(H_2O)$ can be neglected. Similarly, $k_{-3}k_{-4}(A)(NS)(H_2O)$ is far smaller than $k_3k_4(AH_2)(NB)$.

Accordingly,

$$r = r_3 = 3r_5 = \frac{3k_3k_4(\mathrm{AH_2})(\mathrm{NB})(\mathrm{Q})_0}{k_3(\mathrm{AH_2}) + 3k_4(\mathrm{NB})}. \quad (11)$$

Neither (A) nor (AN) is contained in the denominator of Eq. (11). Indeed styrene (A) and aniline (AN) did not give any inhibition effects on the rate of the catalytic hydrogen transfer reaction as shown in Fig. 4.

Modifying Eq. (11) and using 1 g of polynaphthoquinone $(\mathrm{Q})_0$.

$$1/r = 1/k_3(\mathrm{AH_2}) + \tfrac{1}{3}k_4(\mathrm{NB}). \quad (12)$$

$1/r$ was plotted against $1/(\mathrm{AH_2})$ and 1 (NB) in Fig. 8a for the ethylbenzene–nitrobenzene system and in Fig. 8b for the cumene–nitrobenzene system, where linear correlations were found. From the figures the rate constants, k_3 and k_4, were determined to be, respectively, 6.49×10^{-2} and 4.85×10^{-1} $\mathrm{hr^{-1}\ g^{-1}}$ for the ethylbenzene–nitrobenzene reaction, and 8.0×10^{-2} and 4.85×10^{-1} $\mathrm{hr^{-1}\ g^{-1}}$ in the cumene–nitrobenzene system.

The ratio of the concentrations of hydroquinones and quinones, $(\mathrm{QH_2})_s/(\mathrm{Q})_s$, in a steady state of reaction is equivalent to $k_3(\mathrm{AH_2})_s/k_4(\mathrm{NB})_s$. Using the values of k_3 and k_4, $(\mathrm{QH_2})_s/(\mathrm{Q})_s$ during the reaction at 315°C was determined to be 52/48% and 56/44% in the ethylbenzene–nitrobenzene and cumene–nitrobenzene reactions, respectively.

Equation (13) is obtained by integration of Eq. (12).

$$\frac{W}{F} = \frac{1}{(\mathrm{AH_2})_0}\left(\frac{1}{k_3}\ln\frac{1}{1-x} + \frac{1}{k_4}\ln\frac{3C}{3C-x}\right) \quad (13)$$

where x and C represent the conversion ($\times 10^2\%$) and the ratio, $(\mathrm{NB})_0/(\mathrm{AH_2})_0$, respectively. Using the known amounts of $(\mathrm{NB})_0$ and $(\mathrm{AH_2})_0$, and the rate constants, k_3 and k_4, W/F could be calculated against x. The solid lines in Figs. 1 and 2 are the calculated curves from Eq. (13). The experimental values (○ and △) showed good agreement with the calculated lines.

It is consequently concluded that the catalytic hydrogen transfer reactions between hydroaromatics and nitrobenzene over polynaphthoquinone proceeded by successive hydrogen transfer processes in conjunction with the redox quinone–hydroquinone cycle. The individual hydrogen transfer steps consist of the stoichiometric intermolecular reactions between organic compounds and surface functional groups. No evolution of dihydrogen was observed in the course of reactions. Thus almost all of the hydrogen atoms of $\mathrm{AH_2}$ were catalytically transferred to nitrobenzene with good selectivities. One of the important considerations for the choice of catalyst is the selectivity. The good catalysts for dehydrogenations seem to act as effective hydrogen transfer catalysts; other examples are $\mathrm{ZrO_2}$ (*8*), MgO (*9*), hydroxyapatite (*10*), In (*11*), etc., for the hydrogen transfer from alco-

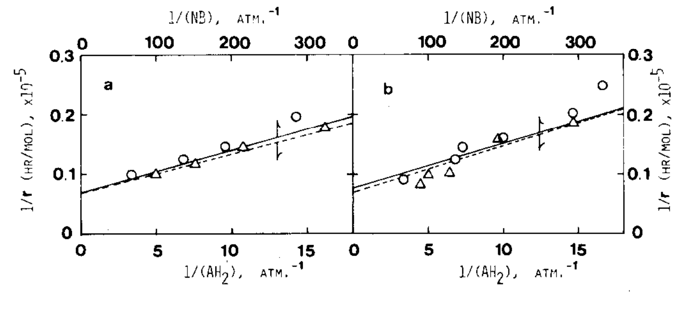


FIG. 8. $1/r$ vs $1/(\mathrm{AH_2})$ or $1/(\mathrm{NB})$ plots; (a) $\mathrm{AH_2}$: cumene; (b) $\mathrm{AH_2}$: ethylbenzene; reaction temperature: 315°C.

hols to ketones. The reaction pattern on polynaphthoquinone is applicable to many sets of hydrogen donors and acceptors. For example, when water and iodine were chosen, the hydrogen transfer from water to iodine took place to form HI in the presence of SO_2 which worked as a chemical trapping agent of oxygen (*12*).

The addition of $FeCl_3$ in the catalyst promoted the rate of hydrogen transfer as given in Table 2. The acceleration mechanism of added $FeCl_3$ is not clear, but Lewis acids like $FeCl_3$ coordinate to the quinone groups in the polynaphthoquinone as described in previous papers (*1*, *5*). Its effect may be due to the electronically combined action of $FeCl_3$ and the quinones.

Aromatic nitro-compounds can be generally reduced under slight H_2 pressure (for large exothermisty) with Rh, Pd, Pt, or Cu on inorganic or polymer supports, or with Raney Ni (*13*). The polynaphthoquinone never activated dihydrogen, so nitrobenzene is not reduced by dihydrogen. Only the hydrogen atoms (hydroquinones) trapped at the active quinone sites which were formed by dehydrogenation of AH_2 were available for reducing nitrobenzene. The behavior of a catalyst in hydrogen transfers depends upon the property of the bond between the abstracted hydrogen and the active site, for example, the O–H bond in hydroquinone. Dihydrogen is simultaneously evolved in the dehydrogenations over metal oxides like ZnO (*14*), Ni-molybdate (*15*), etc. (*8–11*), while over Bi-molybdate water is produced for an easy removal of lattice oxygens (*16*). The hydrogenation of nitrobenzene with H_2 is first-order with respect to H_2 pressure and zero-order with respect to nitrobenzene (*13a*, *b*). The rate of hydrogen transfer reactions between AH_2 and nitrobenzene on the polynaphthoquinone depended upon the pressures of both AH_2 and nitrobenzene as shown in Fig. 3 and in Eq. (12). The polynaphthoquinone is clarified to have a different nature from other metal or metal oxide catalysts as understood from the reaction mechanism. The polynaphthoquinone with well-defined active sites constitutes a convenient sample to investigate the origin of catalysis as well as reaction kinetics.

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