Transfer Hydrogenation and Transfer Hydrogenolysis. 14. Cleavage of Carbon–Halogen Bond by the Hydrogen Transfer from Organic Compounds Catalyzed by Noble Metal Salts

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It is shown that in the presence of Pd(II) salts the carbon–halogen bond of aryl halides is cleavaged to give the corresponding aryl compounds and hydrogen halides by hydrogen transfer from organic compounds. Secondary cyclic amines have excellent hydrogen-donating ability, and the ability decreases in the order indoline > tetrahydroquinoline > pyrrolidine > *N*-methylpyrrolidine > 3-pyrroline > piperidine > 2,5-dihydrofuran. The addition of bases, such as potassium hydroxide, sodium acetate, sodium carbonate, cyclohexylamine, and *n*-propylamine, promoted the hydrogenolysis. The addition of potassium halides, hydrogen halides, and triphenylphosphine retarded the reaction. Several alcohols were examined as a solvent, and methanol was found to be an excellent one. When chlorobenzene, indoline, and palladium chloride were heated in methanol, the initial rate of the formation of benzene was independent of the concentration of chlorobenzene and can be expressed as $r = k[\text{indoline}][PdCl_2]$.

There are few studies about the catalytic hydrogenolysis of the carbon–halogen bond by hydrogen transfer from organic compounds. In heterogeneous systems, cyclohexene, limonene, and *p*-menthene have been reported to donate hydrogen to halides in the presence of palladium carbon.[1] For homogeneous systems, polychloroalkyl compounds have been reported to be hydrogenolyzed with alcohols in the presence of $RuCl_2(PPh_3)_3$.[2] In this case, aryl halides were not hydrogenolyzed.[2] Further, it has been reported that in some reactions of aryl halides in the presence of palladium[3] or nickel compounds[4] the corresponding aromatic hydrocarbons were detected, but in these reactions the sources of hydrogen were not identified. So far as we know, no systematic studies of the transfer hydrogenolysis seem to have yet been reported.

In the course of the transfer hydrogenation of olefins, we found that aryl halides were hydrogenolyzed to the corresponding aryl compounds and this study was undertaken to examine the transfer hydrogenolysis of aryl halides in detail.

Results and Discussion

Catalytic Activity. The catalytic activity of several transition metal salts and phosphine complexes was investigated. In the reaction system in which chlorobenzene (0.5 M), indoline (0.5 M), and a catalyst (0.056 M) in methanol were heated at 140 °C for 4 h, the activity decreased in the order $PdCl_2$ (76%), $(NH_4)_2PdCl_4$ (75%), $RhCl_3{\cdot}3H_2O$ (59%), $PdBr_2$ (50%), $IrCl_3$ (32%), K_2PtCl_4 (12%), $RuCl_3{\cdot}nH_2O$ (3%), K_2PtCl_6 (3%). Here, the percentages shown in the parentheses are the yield of benzene. Phosphine complexes, such as $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, $RuCl_2(PPh_3)_3$, $RuH_2(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $PtCl_2(PPh_3)_2$ hardly catalyzed the hydrogenolysis, and $ReCl_5$, $FeCl_2{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$, and $CoCl_2{\cdot}6H_2O$ showed no catalytic activity under these reaction conditions. The reason why the catalytic activity of $PdBr_2$ was lower than that of $PdCl_2$ may be that the retarding effect of HBr, which was formed in the generation of Pd(0) species, was larger than that of HCl, as described later.

When a reaction mixture was cooled after hydrogenolysis, a black precipitate was obtained in all the reaction systems in which noble metal salts were used as a catalyst and a metallic mirror was found in some reaction systems. The reactions are inferred to proceed homogeneously, because the precipitates and mirrors collected hardly catalyzed the hydrogenolysis. All the transfer hydrogenolyses described hereafter were carried out using $PdCl_2$ as a catalyst.

Hydrogen-Donating Ability of Some Organic Compounds. The hydrogen-donating ability of several organic compounds to chlorobenzene was examined. When a methanol solution of $PdCl_2$ (0.056 M), chlorobenzene (0.5 M), and a hydrogen donor (0.5 M) was heated at 140 °C for 4 h, the hydrogen-donating ability of several organic compounds decreased in the order indoline (76%), tetrahydroquinoline (42%), pyrrolidine (28%), *N*-methylpyrrolidine (25%), 3-pyrroline (24%), piperidine (16%), 2,5-dihydrofuran (7%), *N*-methylpiperidine (4%). Here, the percentages shown in the parentheses are the yield of benzene. The high hydrogen-donating power of these amines may be attributable at least partly to the basic nature of the compounds. Methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, 2-butanol, cyclohexanol, cyclohexylamine, morpholine, tri-*n*-propylamine, dioxane, tetrahydrofuran, tetralin, indan, and formic acid had no hydrogen-donating ability. Except for amines, only 2,5-dihydrofuran showed a weak hydrogen-donating ability. The addition of bases promoted the reaction as described later, and it was thought that the removal of the free HX formed was the important step of the hydrogenolysis of halides. When sodium carbonate (0.25 M) was added to the reaction systems in which tetralin or 2-propanol was used as a hydrogen donor, the hydrogenolysis proceeded to give 16% or 3% yield of benzene, respectively. However, in the case of 2,5-dihydrofuran the addition of sodium carbonate hardly affected the yield of benzene.

When chlorobenzene (0.5 M), indoline (0.5 M), and $PdCl_2$ (0.056 M) were heated in methanol at 140 °C for 4 h, benzene (0.38 M) and indole (0.44 M) were confirmed and some substrate (0.12 M) and hydrogen donor (0.05 M) survived. This result is summarized as follows. (1) The amount of indole was equal to that which is needed to form benzene and to reduce Pd(II) to Pd(0) species within experimental error. (2) The total amount of benzene formed and the surviving chlorobenzene was equal to the amount of the charged chlorobenzene. (3) The total amount of the surviving donor and indole equaled the amount of the charged donor within experimental error. This result shows that the following reactions proceeded without remarkable side reactions.

$$\text{Pd(II)} + \text{indoline} \rightarrow \text{Pd(0)} + \text{indole} + 2H^+$$

$$\text{PhCl} + \text{indoline} \rightarrow \text{PhH} + \text{HCl} + \text{indole}$$

In this study, indoline was used as a hydrogen donor.

Table I. Transfer Hydrogenolysis of Halides[a]

Registry no.	Substrate	Product, % yield
108-90-7	Chlorobenzene	Benzene, 76
591-50-4	Iodobenzene	Benzene, 53
100-44-7	Benzyl chloride	Toluene, 45
108-86-1	Bromobenzene	Benzene, 39
104-92-7	*p*-Bromoanisole	Anisole, 38
104-83-6	*p*-Chlorobenzyl chloride	Toluene, 14; benzyl chloride, 24
622-24-2	β-Phenethyl chloride	Ethylbenzene, 37
106-41-2	*p*-Bromophenol	Phenol, 34
106-43-4	*p*-Chlorotoluene	Toluene, 34
672-65-1	α-Phenethyl chloride	Toluene, 32
106-48-9	*p*-Chlorophenol	Phenol, 28
106-39-8	*p*-Chlorobromobenzene	Chlorobenzene, 26
106-46-7	*p*-Dichlorobenzene	Benzene, 18; chlorobenzene, 2
106-37-6	*p*-Dibromobenzene	Bromobenzene, 20
90-11-9	α-Bromonaphthalene	Naphthalene, 20
541-73-1	*m*-Dichlorobenzene	Benzene, 12; chlorobenzene, 3
95-50-1	*o*-Dichlorobenzene	Benzene, 10; chlorobenzene, 2
104-88-1	*p*-Chlorobenzaldehyde	Chlorobenzene, 6
98-56-6	*p*-Chloro benzotrifluoride	Benzotrifluoride, 4
106-47-8	*p*-Chloroaniline	Aniline, trace
99-91-2	*p*-Chloroacetophenone	Acetophenone, trace
111-85-3	*n*-Octyl chloride	*n*-Octane, trace
	Chlorobenzene[b]	Benzene, 74
	Bromobenzene[b]	Benzene, 40
	Iodobenzene[b]	Benzene, 46

[a] The substrate (0.5 M), indoline (0.5 M), and $PdCl_2$ (0.056 M) were heated in methanol at 140 °C for 4 h. [b] The substrate (0.5 M), indoline (0.5 M), $PdCl_2$ (0.056 M), and cyclohexylamine (0.25 M) were heated in methanol at 140 °C for 1 h.

Table II. Effect of Additives[a]

Additive	Yield of benzene, %
None	27
Potassium hydroxide	64
Sodium acetate	61
Sodium carbonate	56
n-Propylamine	54
Cyclohexylamine	53
N,N-Dimethylcyclohexylamine	48
Sodium bicarbonate	46
Morpholine	45
Tri-*n*-propylamine	33
Water	31
Acetonitrile	30
Potassium chloride	24
Acetic anhydride	22
Pyridine	19
Potassium bromide	14
Hydrochloric acid	5
Dimethyl sulfoxide	5
Hydrobromic acid	2
Potassium iodide	trace
Hydriodic acid	trace
Triphenylphosphine	0

[a] Chlorobenzene (0.5 M), indoline (0.5 M), $PdCl_2$ (0.056 M), and the additive (0.25 M) were heated in methanol at 80 °C for 1 h.

Transfer Hydrogenolysis of Halides. In the presence of $PdCl_2$, aryl halides were hydrogenolyzed to give the corresponding aryl compounds and hydrogen halides (Table I). The susceptibility of substituted halobenzenes to hydrogenolysis was influenced by the kind of substituents, but there seems to be no clear relation between the susceptibility and the electronic nature of the substituents. The yield of products increased in the order for p-X-C_6H_4Cl, X = $COCH_3 < NH_2 < CF_3 < Cl < OH < CH_3 < H$, and for p-Y-C_6H_4Br, Y = $Br < Cl < OH < OCH_3 < H$. It has been reported that oxidative addition of aryl halides with electron-withdrawing substituents to Pd(0) species occurs faster than that of those with electron-donating substituents.[5] In our reaction system, the electronic nature of the substituents is considered to influence the following steps: (1) the oxidative addition of the halobenzenes; (2) the reductive elimination of the products; and (3) the coordination and the dehydrogenation of the hydrogen donor. Moreover, it is also possible that the substrates coordinate through the substituent group. The yield of products may be affected by the total results of these effects and this is the reason why the substituent effect is complicated. In the case of *p*-chlorobenzaldehyde, decarbonylation occurred to form chlorobenzene, and the chlorobenzene formed did not undergo hydrogenolysis. *p*-Chlorobromobenzene was selectively hydrogenolyzed to chlorobenzene and chlorobenzene formed did not undertake further reduction. The affinity of C–Br bond to palladium species seems to be larger than that of C–Cl bond. The reactivity of benzyl chloride was lower than that of chlorobenzene. The reactivity of chloro compounds decreased in the order $PhCl > PhCH_2Cl > PhCH_2CH_2Cl > PhCHClCH_3$. The reactivity of α-phenethyl chloride, which has a benzyl-substituted chloride, is inferior to that of β-phenethyl chloride. Aliphatic halides were hardly hydrogenolyzed.

As to halobenzenes, PhX, the yield of benzene decreased in the order X = Cl > I > Br. Fluorobenzene did not react under these reaction conditions. The ease of oxidative addition of PhX to palladium complex has been reported to be in the order X = Cl < Br < I.[5] The hydrogen halides formed poison the catalytic species and deactivate indoline by salt formation. The amine hydrochloride may be sufficiently acidic to deactivate the catalytic species.[6] The poisoning effect of the hydrogen halides is presumed to increase in the order HCl < HBr < HI, because the retarding effect caused by the addition of HX and KX increased in that order, that is, HCl < HBr < HI and KCl < KBr < KI, as described later. Therefore, the yield of benzene is inferred to be realized by the balance between the ease of the oxidative addition of PhX to the palladium species and the poisoning power of HX formed.

Unless otherwise noted, all the experiments discussed in the following sections were carried out using chlorobenzene as a hydrogen acceptor.

Effect of Additives. The effect of several additives on the reaction system was examined at 80 °C (Table II) and varies with their concentration. Under conditions given in Table II, the effectiveness of the additives was in the order potassium hydroxide > sodium acetate > sodium carbonate > *n*-propylamine > cyclohexylamine > *N,N*-dimethylcyclohexylamine > sodium bicarbonate > morpholine. This result indicates that the addition of bases promotes the hydrogenolysis. The role of base is the removal of hydrogen halides formed, which is the poison of the catalytic species and the hydrogen donor, indoline, by salt formation.

$$Pd^0 + HCl \rightarrow HPdCl$$

$$HPdCl + base \rightarrow Pd^0 + base\cdot HCl$$

$$indoline\cdot HCl + base \rightarrow indoline + base\cdot HCl$$

When amines, such as *n*-propylamine, cyclohexylamine,

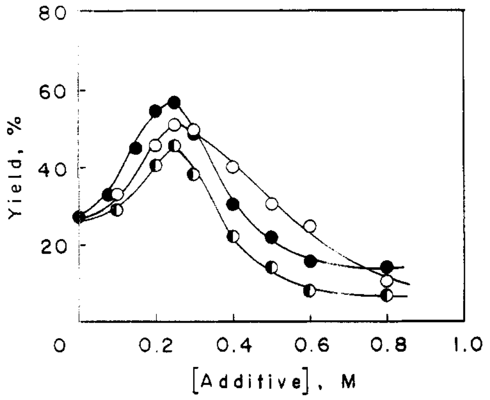

Figure 1. Dependence of the yield of benzene on the concentration of additives. Chlorobenzene (0.5 M), indoline (0.5 M), $PdCl_2$ (0.056 M), and the additive were heated in methanol at 80 °C for 1 h: ○ cyclohexylamine; ◐ *N*,*N*-dimethylcyclohexylamine; ● *n*-propylamine.

Table III. Effect of Reaction Solvents[a]

Solvent	Yield of benzene, %
Methanol	76
Cyclohexanol[b]	68
N,*N*-Dimethylacetamide	45
2-Propanol	42
Ethanol	40
1-Propanol	37
2-Butanol	32
N,*N*-Dimethylformamide	20
1-Butanol	12

[a] Chlorobenzene (0.5 M), indoline (0.5 M), and $PdCl_2$ (0.056 M) were heated in the designated solvent at 140 °C for 4 h. [b] Cyclohexene, 0.22 M, was obtained as the dehydration product of cyclohexanol.

and *N*,*N*-dimethylcyclohexylamine, were added to the reaction system, the yield of benzene showed the maximum values in the concentration range 0.2–0.3 M; that is, the concentration of the additives is 3.5–5.4 times as high as that of the catalyst (Figure 1). The yield of benzene rapidly decreased when more than 0.4 M of the amines were added. This shows that at higher concentration amines themselves coordinate on the catalyst to depress the hydrogenolysis. The promoting power of *N*,*N*-dimethylcyclohexylamine was lower than that of *n*-propylamine and cyclohexylamine, and the effective range of the concentration of the first is narrower than that of the latter two.

The addition of water hardly affected the hydrogenolysis. The addition of hydrochloric acid, hydrobromic acid, and hydriodic acid retarded the reaction in the order HCl < HBr < HI. The addition of potassium halides also gave the same result; that is, the retarding effect on the reaction increased in the order KCl < KBr < KI. The inference based on this result has been mentioned in the previous sections. The poisoning effect of triphenylphosphine, dimethyl sulfoxide, pyridine, and acetic anhydride was also confirmed.

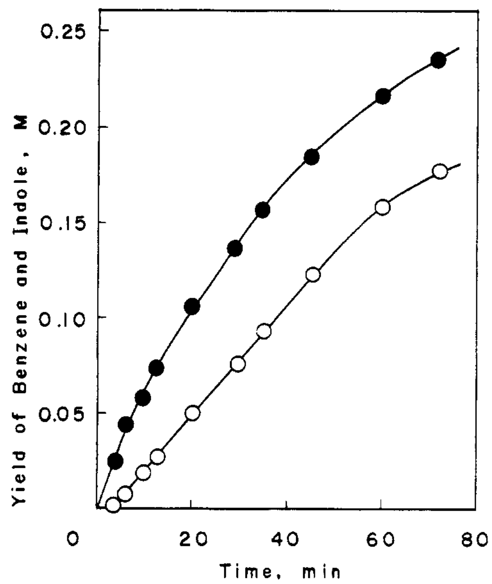

Figure 2. Dependence of yield on reaction time. Chlorobenzene (0.5 M), indoline (0.5 M), and $PdCl_2$ (0.056 M) were heated in methanol at 70 °C: ○ benzene; ● indole.

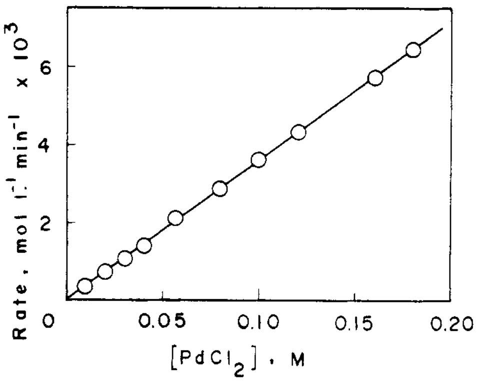

Figure 3. Dependence of the rate of hydrogenolysis of chlorobenzene on catalyst concentration. Chlorobenzene (0.5 M), indoline (0.5 M), and the catalyst were heated in methanol at 70 °C.

Reaction Solvents. Several alcohols and amides were examined as solvents (Table III). When the reaction was carried out in alcohols, the yield of benzene decreased in the order methanol > cyclohexanol > 2-propanol > ethanol > 1-propanol > 2-butanol > 1-butanol. This result suggests that long chain or normal alcohols are less suitable solvents. In *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide, a metallic mirror was formed as the reaction proceeded. When the hydrogenolysis was carried out in aromatic hydrocarbons, such as toluene and cumene, a Friedel–Crafts reaction occurred as a side reaction. So, these solvents were not suitable for the transfer hydrogenolysis of aryl halides. In this study, methanol was used as a solvent.

The Measurement of Initial Rate. Chlorobenzene (0.5 M), indoline (0.5 M), and $PdCl_2$ (0.056 M) were heated in methanol at 70 °C, and the dependence of the yield of benzene and indole on the reaction time is shown in Figure 2. Hydrogenolysis of chlorobenzene hardly occurred until the yield of indole became about 0.02 M. This suggests that the first step of this reaction is the activation of $PdCl_2$, that is, the reduction of Pd(II) to Pd(0) species. After the yield of indole became more than 0.03 M, that of benzene increased linearly with time until it reached 0.13 M. After 15 min, the amount of indole equaled the total amount of benzene formed and the catalyst. This result also suggests that indoline reduced the Pd(II) species to the Pd(0) species. The yield of benzene deviated from the linear relationship in more than 0.13 M yield, and this deviation is caused by the deactivation effect of the hydrogen chloride formed and by the consumption of the reactants. The reaction rate of the hydrogenolysis of chlorobenzene was derived from the gradient of the linear part.

The initial rate of the hydrogenolysis was found to be proportional to the concentration of the catalyst, and the extrapolation of the line to lower concentration passes through the origin as shown in Figure 3. The reaction rate has a linear relationship with the concentration of indoline over the range

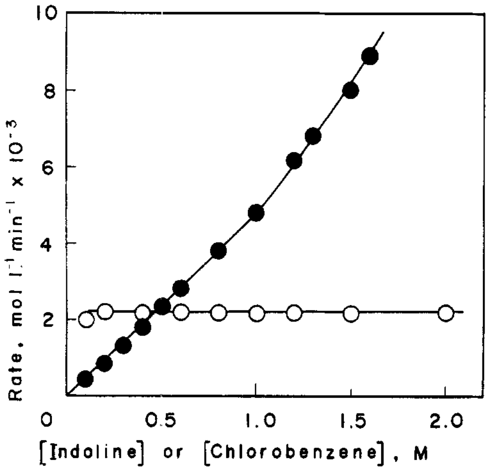

Figure 4. Dependence of the rate of hydrogenolysis of chlorobenzene on the concentration of indoline (0.5 M chlorobenzene), ●, and the halides (0.5 M indoline), ○, in methanol at 70 °C with 0.056 M $PdCl_2$.

of 0–1.0 M. However, in higher concentration more than 1.0 M the linearity no longer held and the rate deviated upwards (Figure 4). In higher concentration more than 1.0 M, the volume of indoline occupies more than 10% volume of the total solution, and the deviation seems to be caused by the solvent effect of indoline to stabilize palladium active species.

The reaction rate was independent of the concentration of chlorobenzene in the range examined (Figure 4). As the concentration of chlorobenzene was increased, the induction period became longer.

Reaction Temperature. The hydrogenolysis of chlorobenzene proceeded even at 60 °C, but that of bromobenzene and iodobenzene hardly occurred below 100 °C with or without added base. The rate of the hydrogenolysis of chlorobenzene was measured at 60, 70, 80, 90, 100, and 110 °C, and those of bromobenzene and iodobenzene were done at 110, 120, 130, and 140 °C. In all cases, the plots of log (rate) vs. $1/T$ showed good linear relationship, indicating uncomplicated reaction kinetics. From the plots, activation energies of 14.5, 14.4, and 13.5 kcal mol^{-1} are obtained for chlorobenzene, bromobenzene, and iodobenzene, respectively.

Discussion of Kinetics

As can be seen from Figure 1 and the result of quantitative relation, the first step of this transfer hydrogenolysis was the reduction of $PdCl_2$ to form the Pd(0) species (Scheme I).

Scheme I

$$PdCl_2 \overset{\text{indoline}}{\rightleftharpoons} PdCl_2(\text{indoline}) \rightarrow Pd^0 + 2HCl + \text{indole}$$

Since the initial rate of the hydrogenolysis was derived from the linear part of time vs. conversion curve, the kinetic discussion in this paper concerns the process after the activation of $PdCl_2$. It has been reported that aryl halides oxidatively add to the Pd(0) species.[5-7] Based on this inference, the results described earlier, and the comparison with the mechanism of transfer hydrogenation of olefins,[8] the following two catalytic cycles are reasonably considered as the mechanism of the transfer hydrogenolysis of chlorobenzene (Schemes II and III).

Scheme II

$$Pd^0 \overset{PhCl,\ K_1}{\rightleftharpoons} Pd(Ph)(Cl) \xrightarrow{\text{indoline},\ k_2} Pd^0 + HCl + PhH + \text{indole}$$

Scheme III

$$Pd^0 \xrightarrow[-\text{indole}]{\text{indoline},\ k_3} PdH_2 \xrightarrow{PhCl,\ k_4} Pd^0 + HCl + PhH$$

From Scheme II, the rate is expressed as

$$R = \frac{k_2K_1[PhCl][\text{indoline}][PdCl_2]}{1 + K_1[PhCl]} \qquad (1)$$

where K_1 is an equilibrium constant and k_2 is a rate constant, respectively. Since the rate was independent of the concentration of chlorobenzene, the following relation should be satisfied in the numerator of eq 1; $1 \ll K_1[PhCl]$, that is, $[Pd^0] \ll [Pd(Ph)(Cl)]$. Biphenyl was not obtained in the hydrogenolysis of chlorobenzene, and the concentration of the phenyl palladium species was negligible in the reaction system. It has been also reported that the rate of the oxidative addition of chlorobenzene to the Pd(0) species was relatively slow.[5] Therefore, Scheme II is unreasonable for the catalytic cycle of the hydrogenolysis of chlorobenzene.

From Scheme III, the rate expression becomes as follows

$$R = k_3[\text{indoline}][PdCl_2] \qquad (2)$$

where k_3 is a rate constant. In order to derive this equation, it is assumed that the indole formed was not hydrogenated. This assumption was not so unreasonable because the indole is an aromatized product and the addition of indole to the reaction system did not reduce the reaction rate. Equation 2 is found to accommodate all of the other experimental observations described earlier. (1) The dependence of the rate on the concentration of the catalyst should be linear and this agrees with the result as shown in Figure 3. From this figure, 7.6×10^{-2} mol^{-1} L min^{-1} was obtained as the value of k_3. (2) The rate should be proportional to the concentration of indoline, and this is in agreement with the result in Figure 4. From this figure, the same value, 7.6×10^{-2} mol^{-1} L min^{-1}, was obtained as the value of k_3. (3) The rate is independent of the concentration of chlorobenzene, and this agrees with the result shown in Figure 4. As the value of k_3, 7.6×10^{-2} mol^{-1} L min^{-1} was obtained. Then, the overall rate expression at 70 °C is formulated as follows.

$$R = 0.076[PdCl_2][\text{indoline}] \qquad (3)$$

The oxidative addition of chlorobenzene may not be the rate-determining step, because the coordinating power of chlorobenzene was not so large and the rate of the hydrogenolysis was independent of the concentration of chlorobenzene. As hydrogenolysis proceeded, hydrogen halide accumulated to deactivate the catalytic species. When bases were added to the reaction system, the induction period became shorter, but the initial rate of the hydrogenolysis was scarcely changed. The addition of bases promotes the activation of $PdCl_2$ to Pd(0) species in the initial reaction stage, and did not affect the rate-determining step. The rate-determining step of the transfer hydrogenolysis of chlorobenzene seems to be the dehydrogenation of the hydrogen donor, that is, the formation of the palladium dihydride species. There is no evidence to decide whether the hydrogenolysis proceeds via the Pd(IV) species, $H_2Pd(Ph)(Cl)$, or the Pd(II) species with four-center transition state.

When chlorobenzene (0.5 M), bromobenzene (0.5 M), indoline (0.5 M), and $PdCl_2$ (0.056 M) were heated at 70 °C in methanol for 1 h, neither benzene nor indole was obtained. In the case of chlorobenzene and iodobenzene, the same result was confirmed. These results show that bromobenzene and iodobenzene act as poisons at 70 °C. The reaction mechanism of the hydrogenolysis of bromobenzene and iodobenzene may be different from that of chlorobenzene.

Experimental Section

Materials. Palladium chloride, ammonium palladous chloride, rhodium trichloride, palladium bromide, iridium trichloride, platinum(II) potassium chloride, ruthenium trichloride, and platinum(IV) potassium chloride were purchased and used without purification. Alcohols and amines were purified by distillation. Aryl halides were purified by distillation or recrystallization.

An Example of Transfer Hydrogenolysis. Chlorobenzene (28 mg, 0.25 mmol), indoline (30 mg, 0.25 mmol), and $PdCl_2$ (5 mg, 0.028 mmol) were put into a Pyrex tube which had been sealed at one end, and the total volume of the solution was made 0.5 mL by the addition of methanol as a solvent. The tube was cooled with liquid nitrogen and sealed under vacuum. The sealed tube was heated for 4 h in a polyethylene glycol bath kept at 140 ± 1 °C. The reaction mixture was submitted to GLC analysis, which was performed at 90 °C using 2 m × 6 mm stainless steel column packed with 15% of Silicone DC-11 on Diasolid L and 30 μL of *n*-heptane as an internal standard. The amount of indoline and indole was measured by the use of a 2 m × 6 mm stainless steel column packed with 10% diethylene glycol succinate on Diasolid L and dibenzyl ether as an internal standard.

Other transfer hydrogenolyses were carried out in a similar way.

An Example of Kinetic Runs. Ten samples, prepared by the method described above, were heated at 70 ± 1 °C for 3, 6, 10, 15, 20, 30, 37, 45, 60, and 75 min. The reaction mixtures were submitted to GLC analysis.

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Anodic Oxidation of Cyclohexene in the Presence of Cyanide Ion

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The electrochemical oxidation of cyclohexene in methanol solution of sodium cyanide results in isocyanation as well as cyanation and methoxylation. The current efficiency of isocyanide increases outstandingly with increasing electrode potential. Current–potential data suggest adsorption of a product of the electrolysis on the electrode. The current efficiencies of products are dependent on the cyclohexene concentration, whereas the product distribution is found to be independent of the relative concentration of both electroactive species, i.e., CN^- and C_6H_{10}, on the electrode which changes with changing bulk concentration of cyclohexene. These observations indicate that a primary electron transfer from cyclohexene adsorbed while expelling an electrolysis product adsorbed is a key step to derive organic products.

Cyanation of olefins or dienes has been thus far unsuccessful. We previously reported on the products obtained from the electrochemical reaction of methanol solution of cyclohexene in the presence of mercuric cyanide and proposed simultaneous operation of both the substrate oxidation reaction and the ion discharge reaction to account for low yields of cyanated products.[1] Recently, however, several types of experimental evidence in favor of direct anodic oxidation of the substrate have been presented.[2–9]

Anodic oxidation of cyclohexene has received a great deal of recent attention.[10–23] Much of the interest in this compound has been due to the fact that it serves as an easily studied model for both addition and allylic substitution reactions to olefins. The present paper describes a careful study of the products of cyclohexene oxidation in the presence of cyanide. Some mechanistic experiments will also be reported and the formation of isocyanide will be discussed.

Results

Products. The electrolyses were conducted in methanol solution of sodium cyanide using a two-compartment cell under a nitrogen atmosphere in the potential region 1.9–2.7 V vs. SCE at platinum electrode. The products formed were identified as such from comparisons with the authentic samples prepared by other routes, and determined by VPC. Isolation of the various products was performed using preparative VPC techniques. Besides 3-methoxycyclohexene (**1**) and dimethoxymethylcyclopentane (**2**), 3-isocyanocyclohexene (**3**), 2-cyclohexene-1-carbonitrile (**4**), isocyanocyclohexane (**5**), cyclohexanecarbonitrile (**6**), and *trans*-2-methoxycyclohexanecarbonitrile (**7**) were found together with bis-2-cyclohexen-1-yl (**8**) and unidentified minor components. Traces of methoxycyclohexane and *trans*-1,2-dimethoxycyclohexane were also noted.

Current–Potential Data. Figure 1 presents current–potential curves for oxidation of sodium cyanide in methanol and for the same solution with added cyclohexene. As can be seen in Figure 1, a methanolic solution of sodium cyanide is discharged at about 1.5 V,[4] whereas the addition of cyclohexene results in a remarkable decreasing of the current in the region of 1.6–1.9 V. Under experimental conditions cyclohexene begins to be oxidized at about 2.0 V ($E_{1/2}$ = 1.89, 2.05, and 2.16 V vs. Ag,Ag^+,[10,17,24] 2.14 and 2.35 V vs. SCE[16,20]).

Cyclic voltammograms were taken at a platinum electrode in a solution of 0.1 M tetraethylammonium fluoroborate within the range of 1.0–2.2 V vs. SCE at 0.1 V/s. The background current is not affected by added sodium cyanide (concentration $\sim 10^{-2}$ M). With cyclohexene added (concentration $\sim 10^{-2}$ M) the current decreases instantaneously at essentially the same potential and the curve of current vs. potential falls below that for the system without the substrate. The trend does not change even when the order of addition of the substrate and the cyanide is inverted. This suggests that a product of the electrolysis would be adsorbed on the anode, thus decreasing the area available for the normal electrochemical reaction.

Influence of the Concentration. Table I summarizes the results of controlled potential electrolyses performed with