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Hydrogenation Pathway of Quinolines over Raney Nickel and Ru/C

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Quinoline, 2-methylquinoline, and 8-methylquinoline were hydrogenated over Raney nickel (R-Ni) under 10 atm hydrogen pressure at about 200 °C and over ruthenium on carbon (Ru/C) under 100 atm hydrogen pressure at 150 °C. All the substrates were commonly hydrogenated into the initial products, 1,2,3,4-tetrahydroquinolines. The initial products were competitively converted over R-Ni to the final products, decahydroquinolines, directly or via 5,6,7,8-tetrahydroquinolines which were mainly formed from the initial products by isomerization. Ru/C promoted exclusively the direct hydrogenation of 1,2,3,4-tetrahydro derivatives to the final products. The hydrogenation and isomerization of 1,2,3,4-tetrahydroquinoline was completely inhibited in the competitive hydrogenation of quinoline and isoquinoline over R-Ni. Such features of these substrates are explained by the strong basicity of 1,2,3,4-tetrahydroisoquinoline. Roles of 1,2,3,4-tetrahydroisoquinoline are much moderate on Ru/C, where the π-coordination may be important. The effects of methyl substituent and different reactivities of quinoline and isoquinoline are discussed in terms of the steric hindrance on adsorption, heats of hydrogenation, basicities, and electronic properties of the related compound, which are calculated according to the MNDO-PM3 method.

Quinoline (**1a**), 2-methylquinoline (**2a**), and 8-methylquinoline (**3a**) are major constituents together with isoquinoline (**4a**) in the basic fraction of coal tar, and their hydrogenated products are proved to be useful in the chemical industry.[1,2] However, the kinetic study on hydrogenation of the quinolines has been scarcely reported.

It has been well-known that the pyridine ring in quinoline nucleus is selectively hydrogenated on conventional metal catalysts such as nickel, platinum, and copper chromite.[3–6] In contrast, its benzene ring is exclusively hydrogenated in an acidic media.[7,8] Conversion of **1a** to its completely hydrogenated decahydroquinoline (**1d**) requires rather severe conditions on nickel catalyst,[9] while ruthenium catalysts readily produce the compound.[10]

The methyl group located at 2- or 8-position of quinoline nucleus which occupies the neighbors of N-atom attracts another interest for study on catalysis because it may affect electronically as well as sterically adsorption on catalyst.[11] The present authors have studied extensively the kinetics and mechanism on the hydrogenation of isoquinoline.[12–15] Although quinoline and isoquinoline have similar basicity, their N-atoms in quinolines and isoquinoline are expected to behave differently in the catalytic reactions according to the location relative to the benzene ring as indicated by the respective similarities of their initial hydrogenated products to aniline and benzylamine. For example, the basicities of their products are very different.[12,16] Hence, their adsorption and reactivities may modify the reaction route of consecutive hydrogenation steps.

In the present study, quinolines (**1a**—**3a**) were hydrogenated over Raney nickel (R-Ni) and ruthenium on carbon (Ru/C) to clarify the reaction pathways. The structural influences of substrates including isoquinoline in previous papers[12–14] on adsorption and activation are also discussed with the aid of semiempirical molecular orbital calculations. The time-dependent product distributions were kinetically analyzed based on the Langmuir–Hinshelwood mechanism for the competitive reactions. An unique isomerization path of 1,2,3,4-tetrahydroisoquinoline (**4b**) to 5,6,7,8-tetrahydro derivative (**4c**) was found kinetically in a previous paper[13] to be essential for the completion of its hydrogenation on R-Ni. It is another major interest of this study to clarify whether such an isomerization of 1,2,3,4-tetrahydroquinolines takes place.

Experimental

Materials. Commercial grade quinolines obtained from coal tar were purified by recrystallization from their sulfates. The details of procedure were described in a previous paper.[12] Their purities were up to 99%, and no sulfur-contaminant was contained. 1,2,3,4-Tetrahydroquinoline (**1b**) was separated from the hydrogenated product of **1a** over copper chromite. R-Ni and Ru/C were purchased from Nikki Chemical Co., Ltd. and Nippon Engelhard Ltd., respectively.

Hydrogenation Procedure and Analytical Method. A starting material (100 g) was hydrogenated over R-Ni and Ru/C in a 200 cm^3-autoclave with stirring under a constant pressure and temperature. The detailed reaction conditions were shown in Table 2. The reaction mixture was sampled and diluted to 5 ml with methanol, and then analyzed by gas chromatography as described previously.[12] The major products: **b**, **c**, and **d** of substrates **1**—**3** were identified by GC-MS. The amounts of decahydroquinolines were the sums of their isomers. The minor products unidentified were less than 6 wt% in all runs.

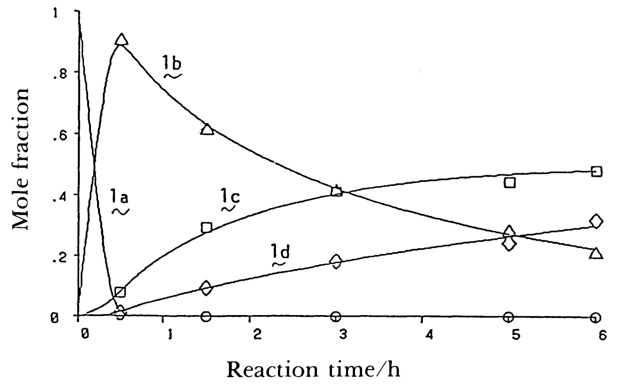
Quantum Chemistry and Basicity. Quantum chemical indices of related compounds were calculated by the MNDO-PM3 (modified neglect of diatomic overlap, parametric method 3).[17] Their geometries were energetically optimized. The pK_a values of some related compounds were determined in aqueous solution as described previously.[12]

Results

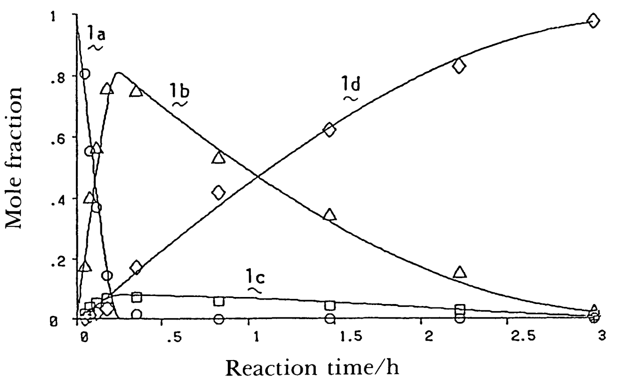
Hydrogenation of Quinolines. Figures 1 and 2 illustrate the time-dependent product distributions in the hydrogenation of substrates **1a** and **2a**. The figure in the reaction of **3a** was omitted because of its good similarity to that of **1a**. Combinations of each substrates and catalysts provided their unique reaction profiles.

In the initial stages of reactions, the quinolines were rapidly hydrogenated almost exclusively into 1,2,3,4-tetrahydro derivatives over both the catalysts regardless of the position of methyl group on either ring. The yields of initial products reached to their maximum values which are 80—90% by the reaction for 0.5—1 h with **1b**, and 60—70% with **2b**, and then decreased gradually with former and rapidly with latter over R-Ni. Different adsorption and reactivity of products are suggested. 5,6,7,8-Tetrahydro derivatives (**ic**) were produced rather gradually in the initial stages but increased their yields steadily even after the starting substrates disappeared. Hence, it is suggested that the products are produced from the initial products (**ib**) through the consecutive isomerization as well as slowly (or less selectively) from the starting substrates. It should be also noted that **1a** disappeared completely within 30 min. In contrast, **2a** decreased by the almost same rates as that of **1a** in first 20 min but then very slowly, indicating some retardation by the products.

The yields of products **ic** again depended very much on the substrates. The yield of **1c** increased slowly to about 40%. In contrast, that of **2c** increased very rapidly to 60% by 1.5 h and then started to decrease very slowly over R-Ni. Compound **3c** showed rather rapid increase to 20% by 1 h and kept the level for 2 h. Isoquinoline showed similar profile to that of quino-

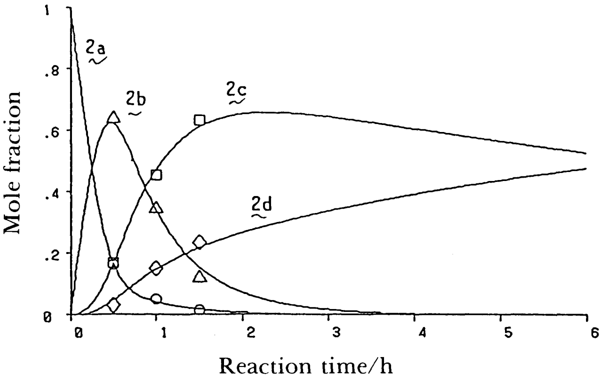


(a) Over R-Ni at 210 °C under 10atm hydrogen pressure.

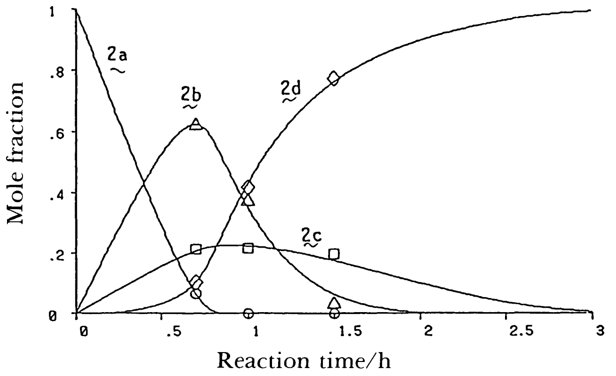


(b) Over Ru/C at 150 °C under 100atm hydrogen pressure.

Fig. 1. Product distributions on the hydrogenation of quinoline. See Table 3 for the chemical names of symbols.



(a) Over R-Ni at 210 °C under 10atm hydrogen pressure.



(b) Over Ru/C at 150 °C under 100atm hydrogen pressure.

Fig. 2. Product distributions on the hydrogenation of 2-methylquinoline. See Table 3 for the chemical names of symbols.

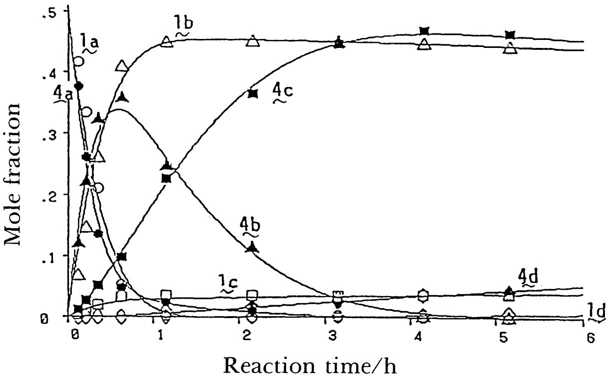
line although the yield increased to 80% by 5 h.[13] Thus, the appearance and disappearance of products **ic** are very sensitive to the structure of substrates although the isomerization of **ib** was commonly observed regardless of the substrates.

The final products in the hydrogenation of quinolines were found first after the reaction of 1 h and gradually increased their yields, which became 25 and 40%, respectively, with **1d** and **2d** after 6 h. The considerable yields of these perhydro products are characteristic to the quinolines on R-Ni because no production was observed for 6 h from isoquinoline as shown previously.[13]

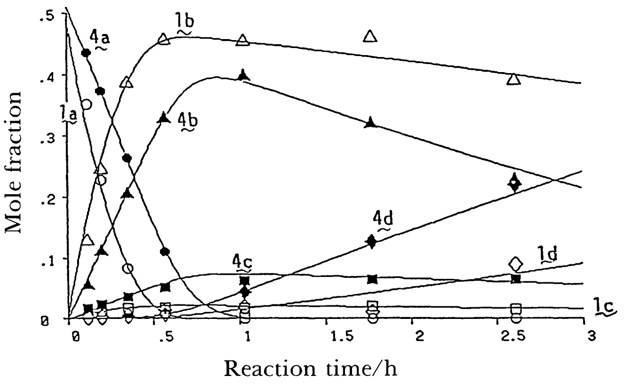
The reaction profiles on Ru/C were different from those over R-Ni although products **ib** were commonly dominant in the initial stage of hydrogenation. The maximum yields of **ib** were high over 80% except for **2b** (60%). Preferential production of **id** and very minor production of **ic** were observed in the reaction of the next stage over Ru/C. Quinolines exhibited almost complete conversions into these final products **id** by 3 h, while the yields of products **ic** stayed very low especially with quinoline during the reaction. The reaction profile of **2a** seems to be similar to that of isoquinoline,[14] although the reaction rate is very large.

Reactivity of 1,2,3,4-Tetrahydroquinoline. Table 1 summarizes the reactivity of 1,2,3,4-tetrahydroquinoline (**1b**) over R-Ni under hydrogen atmosphere in a closed reactor (Run 1′), and under nitrogen atmosphere in an open and a closed reactors (Runs 11 and 12). Under hydrogen pressure, **1b** gave 32% of **1c** and 21% of **1d** after 2 h. Longer reaction time increased both the products, however the increment of **1c** during 2—6 hours was less than the corresponding value of **1d**. Dehydrogenation of **1b** back to **1a** was not observable. Such reaction feature suggests that the hydrogenation of **1b** proceeds simultaneously through the routes of **1b**→**1c**→**1d** and **1b**→**1d**. Under the nitrogen atmosphere, **1b** was converted competitively to the dehydrogenated product **1a** and the isomerized product **1c** in an open reactor. The latter product **1c** was dominant in a closed reactor.

Competitive Reactions of 1a and 4a. Figure 3 illustrates the time-dependent product distributions in the competitive hydrogenation of **1a** and **4a** on R-Ni



(a) Over R-Ni at 215 °C under 15atm hydrogen pressure.



(b) Over Ru/C at 150 °C under 100atm hydrogen pressure.

Fig. 3. Product distributions on the competitive hydrogenation of quinoline and isoquinoline. See Table 3 for the chemical names of symbols.

Table 1. Reaction of 1,2,3,4-Tetrahydroquinoline Over R-Ni (5 wt%)

Run No.	Reaction conditions					Product composition[a)]				
	Temp	Atmosphere			Time	1a	1b	1c	1d	Others
	°C	Gas	atm[b)]	Reactor	h	wt%				
1′	200	H_2	10	Closed	0	0.0	99.0	1.0	0.0	0.0
					2	0.0	45.2	31.7	21.0	2.1
					6	0.0	15.9	40.8	40.2	3.1
11	200	N_2	1	Open	0	0.0	99.0	1.0	0.0	0.0
					2	13.3	70.5	11.3	0.5	4.4
					4	17.7	61.5	13.0	0.8	7.0
12	200	N_2	11	Closed	0	0.0	99.0	1.0	0.0	0.0
					3	3.4	59.7	28.9	2.3	5.7
					6	4.3	42.2	41.6	2.7	9.2

a) **1a**: quinoline, **1b**: 1,2,3,4-tetrahydroquinoline, **1c**: 5,6,7,8-tetrahydroquinoline, **1d**: decahydroquinoline. b) 1 atm= 1.01325×10^5 Pa.

and Ru/C. Over R-Ni **1a** and **4a** decreased at the same rates into **1b** and **4b**. The comparison of the results of single substrates with Fig. 3 indicates that the initial reaction of quinoline was hardly influenced by isoquinoline. It is interesting that **4b** was converted to **4c** while **1b** stayed almost unchanged for 6 h. Strong retardation of the reaction of **1b** by **4b** and also **4c** is suggested.

The profiles were fairly different on Ru/C. The substrate **1a** decreased more rapidly than **4a**, although the rate of **1a** disappearance was reduced by **4a**. Another interesting feature is that the reaction of **1b** principally into **1d** was strongly retarded while that of **4b** into **4d** was slightly retarded. Stronger adsorption of isoquinoline and its derivative is suggested, however they compete for the catalyst with quinoline and its derivatives, the features being different from those in the reactions on R-Ni.

Kinetic Analyses for the Reactions. The following rate equations[13–15] were applicable to reproduce the present experimental results.

$$\frac{dC_1}{dt}=\frac{m[-(k_{12}+k_{13}+k_{14})K_{1/4}C_1+k_{21}K_{2/4}C_2]}{K_{1/4}C_1+K_{2/4}C_2+K_{3/4}C_3+C_4}, \quad (1)$$

$$\frac{dC_2}{dt}=\frac{m[k_{12}K_{1/4}C_1-(k_{21}+k_{23}+k_{24})K_{2/4}C_2]}{K_{1/4}C_1+K_{2/4}C_2+K_{3/4}C_3+C_4}, \quad (2)$$

$$\frac{dC_3}{dt}=\frac{m[k_{13}K_{1/4}C_1+k_{23}K_{2/4}C_2-k_{34}K_{3/4}C_3]}{K_{1/4}C_1+K_{2/4}C_2+K_{3/4}C_3+C_4}, \quad (3)$$

and

$$\frac{dC_4}{dt}=\frac{m[k_{14}K_{1/4}C_1+k_{24}K_{2/4}C_2+k_{34}K_{3/4}C_3]}{K_{1/4}C_1+K_{2/4}C_2+K_{3/4}C_3+C_4}, \quad (4)$$

where C_i is the concentration of species i, t is the reaction time (h), m is the concentration of catalyst (g dm^{-3}), k_{ij} is the apparent rate constant of reaction $i\rightarrow j$ (the constant is a function of hydrogen pressure), and $K_{i/4}$ is the relative equilibrium adsorption constant of i vs. its decahydro derivative (equal to K_i/K_4: K_i is the equilibrium adsorption constant of species i). The set of equations is based on the reaction network illustrated in Fig. 4. The unity that typically appears in the denominator of a Langmuir–Hinshelwood kinetic expression was neglected because the sum of K_iC_i is expected to be much larger than unity.[13–15] In the cases of competitive hydrogenation, the sum of $K_{i/4}C_i$ for both isoquinoline and quinoline was used as the denominator of the rate equations.

The k_{ij} and $K_{i/4}$ for each substrate were determined by a curve fitting procedure[13] to reproduce the time-dependent product distributions. Two assumptions were introduced. The equilibrium adsorption constants of all the decahydro derivatives are same because

Table 2. Rate Constants and Relative Equilibrium Adsorption Constants on Hydrogenation of Quinolines and Isoquinoline

Run No.	Cat. (wt%)[a]	Reaction conditions			Rate constants							Relative equilibrium adsorption constant[c]			
		H_2-Pres.	Temp	Substrate	k_{12}	k_{13}	k_{14}	k_{21}	k_{23}	k_{24}	k_{34}	K_1	K_2	K_3	K_4
		atm	°C		10^{-2} dm^3 (g of cat.)$^{-1}$ h^{-1}										
1	R-Ni(5)	10	210	Quinoline	5.6	0.16	0.00	0.00	0.80	0.22	0.14	1.5	0.2	0.4	1
1′		10	200	—,1,2,3,4-Tetrahydro-	—	—	—	0.00	0.90	0.36	0.20	—	0.2	0.4	1
2		10	200	—,2-Methyl-	4.8	0.00	0.00	2.40	3.80	1.00	0.40	1.5	0.3	0.2	1
3		10	200	—,8-Methyl-	9.0	0.36	0.00	0.00	0.80	0.32	1.35	0.8	0.2	0.2	1
4		15	205	Isoquinoline	4.4	0.15	0.00	0.42	0.48	0.00	0.04	2.0	2.0	0.6	1
5		15	205	Quinoline[b]	5.0	0.32	0.00	0.00	0.03	0.01	0.03	1.5	0.2	0.4	1
				Isoquinoline	5.1	0.34	0.00	0.40	0.62	0.02	0.03	2.0	2.0	0.6	1
6	Ru/C(2)	100	150	Quinoline	21.0	2.0	2.0	0.0	0.3	3.1	0.9	100	5	20	1
6′		10	150	—,1,2,3,4-Tetrahydro-	—	—	—	0.0	0.03	0.3	0.1	—	5	20	1
7		100	150	—,2-Methyl-	5.8	1.6	0.0	0.0	2.1	16.5	1.1	150	5	20	1
8		100	150	—,8-Methyl-	45.0	0.5	2.0	0.0	0.15	3.3	2.0	50	5	20	1
9		100	150	Isoquinoline	5.5	0.8	0.0	0.0	0.2	2.05	0.35	150	20	60	1
10		100	150	Quinoline[b]	20.0	0.9	0.0	0.0	0.0	1.05	0.4	100	5	20	1
				Isoquinoline	4.5	0.8	0.0	0.0	0.1	0.85	0.3	150	20	60	1

a) Weight % vs. substrate. b) Competitive hydrogenation (1/1 ratio). c) Equivalent to K_i/K_4.

of little difference in the geometric and electronic properties of N-atoms in **1d**—**4d** as described later. The rate constants k_{12} of quinoline and isoquinoline are same in both cases of single and competitive reactions. These assumptions allow to compare the reactivity and strength of adsorption with all substrates and their products using calculated constants. Table 2 lists the sets of plausible values in all the runs together with the results of isoquinoline. The simulated product distributions using the above equations with the optimized constants are illustrated as solid lines in Figs. 1 to 3. The calculated results are in good agreement with experimental data (plots). Hydrogenation of 1,2,3,4-tetrahydro quinoline and isoquinoline was kinetically analyzed in similar manners. The same constants of $K_{i/4}$ in the hydrogenation of their mother substrates reproduced the results. Hence, their constants appear unique. However, the values of constants K_{ij} and $K_{i/4}$ of methylquinolines may not be unique because some other sets of constants also reproduced well the product distributions.

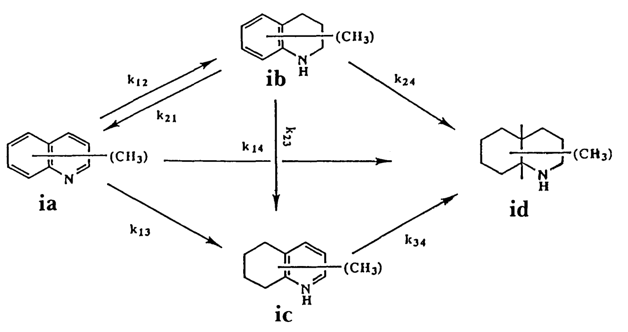


Fig. 4. Simplified reaction network for kinetic analysis.

Quantum Chemical Properties of Substrates. Some quantum chemical indices of related compounds were calculated by several semiempirical MO methods containing the original MNDO[18] and AM1.[19] Only the MNDO-PM 3 could explain the lower basicity of 1,2,3,4-tetrahydroquinoline than that of 1,2,3,4-tetrahydroisoquinoline on the basis of N-electron densities.

Figure 5 illustrates the optimized molecular structures of related compounds using ORTEP routine.[20] The lone-pair electrons of N-atoms in all the molecules direct to lower side (around the symbol N). The molecular shapes illustrated in the figure suggest the magnitude of steric hindrance on adsorption of such substrates over a catalyst surface. When a substrate adsorbs through its lone-pair electrons of N-atoms vertically toward the catalyst surface, the steric hindrance by a methyl group appears to be large in 8-methylquinoline and its 5,6,7,8-tetrahydroquinoline. The similar but smaller hindrance may exist in 2-methylquinoline and its 5,6,7,8-tetrahydro derivative.

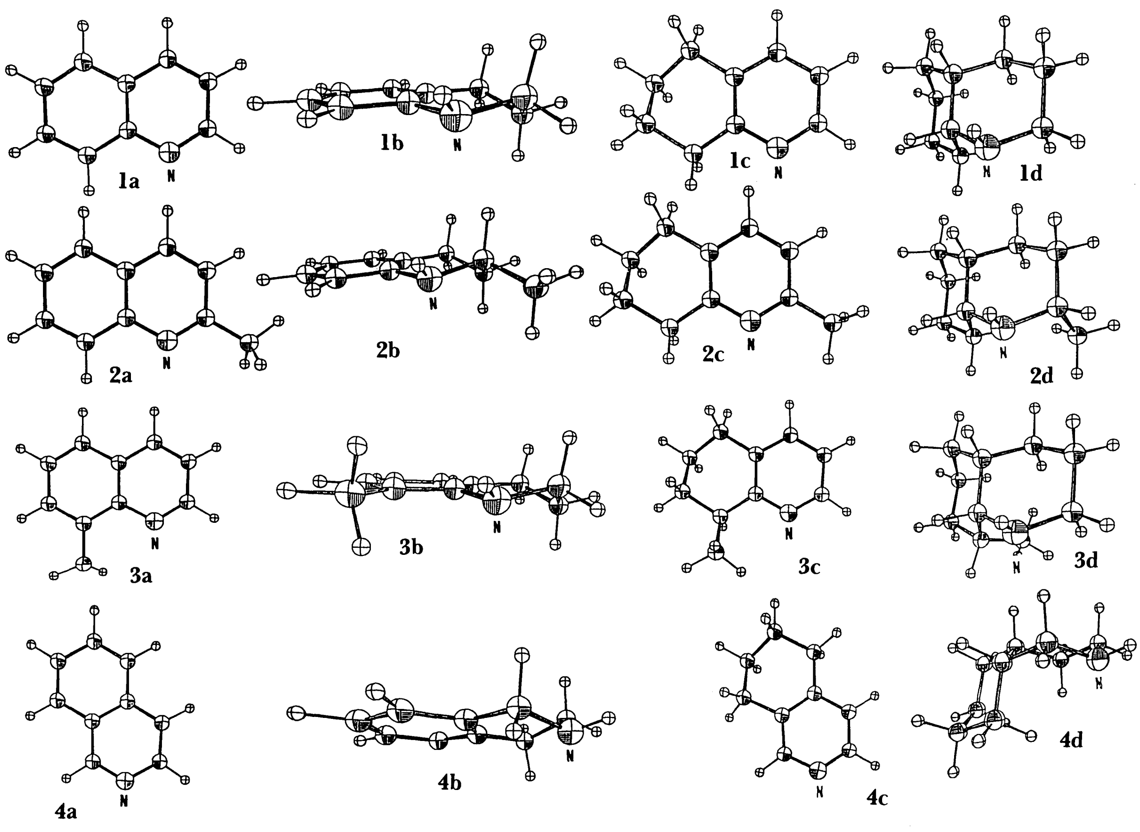
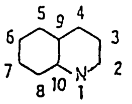
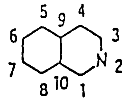


Fig. 5. Structure models of related compounds. See Table 3 for the chemical names of symbols.

Table 3. The pK_a Values[a] and Quantum Chemical Indices[b] of Related Compounds

Compound (Symbol)	pK_a	H_f	Elec. density of N-atom		HOMO				LUMO			
					Energy	Elec. density (atom #)[d]			Energy	Elec. density (atom #)[d]		
		kJ mol^{-1}	Total	π[c]	eV	N	C(py)[e]	C(bz)[f]	eV	N	C(py)[e]	C(bz)[f]
Quinoline (**1a**)	4.92	199.2	5.059	1.080	−9.24	0.240	0.247(4)	0.449(8)	−0.65	0.316	0.422(4)	0.319(5)
—,1,2,3,4-Tetrahydro- (**1b**)	4.90	57.2	4.964		−8.42	0.668		0.326(6)	0.45	0.009		0.639(9)
—,5,6,7,8-Tetrahydro- (**1c**)	6.60	45.2	5.077	1.092	−9.54	0.003	0.522(9)		0.07	0.038	0.653(10)	
—,Decahydro- (**1d**)	10.90	−128.0	5.057		−9.29	1.250						
2-Methylquinoline (**2a**)	5.70	161.5	5.062	1.096	−9.14	0.278	0.278(1)	0.426(8)	−0.61	0.317	0.417(4)	0.315(5)
—,1,2,3,4-Tetrahydro- (**2b**)		32.2	4.963		−8.38	0.680		0.322(6)	0.46	0.009		0.636(9)
—,5,6,7,8-Tetrahydro- (**2c**)		7.1	5.073	1.101	−9.33	0.006	0.547(9)		0.08	0.037	0.603(2)	
—,Decahydro- (**2d**)		−148.1	5.053		−9.31	1.264						
8-Methylquinoline (**3a**)	4.80	165.3	5.060	1.080	−9.03	0.185	0.193(4)	0.461(8)	−0.63	0.308	0.414(4)	0.318(8)
—,1,2,3,4-Tetrahydro- (**3b**)		24.3	4.967		−8.30	0.686		0.317(6)	0.47	0.000		0.532(5)
—,5,6,7,8-Tetrahydro- (**3c**)		29.3	5.072	1.088	−9.55	0.001	0.532(9)		0.07	0.017	0.617(10)	
—,Decahydro- (**3d**)		−139.3	5.055		−9.21	1.182						
Isoquinoline (**4a**)	5.50	197.5	5.080	1.083	−9.18	0.067	0.439(4)	0.371(5)	−0.68	0.138	0.375(1)	0.349(8)
—,1,2,3,4-Tetrahydro- (**4b**)	9.55	76.6	5.055		−9.13	0.718		0.235(10)	0.39	0.000		0.556(6)
—,5,6,7,8-Tetrahydro- (**4c**)	6.65	43.9	5.081	1.085	−9.69	0.074	0.486(3)		0.07	0.324	0.530(3)	
—,Decahydro- (**4d**)	10.95	−117.6	5.058		−9.13	1.306						
Pyridine (py)	5.20	127.2	5.080	1.079	−10.10	0.000	0.515(3)		−0.01	0.000	0.529(2)	
Aniline (al)	4.70	90.0	4.962		−8.73	0.782						

a) The pK_a values were determined by potentiometry at 20 °C in water. b) Calculated by MNDO-PM3 method. c) 2p orbital directed orthogonal to aromatic ring.

d) Numbering of atoms are as follows:  ,  . e) Highest value in pyridine ring. f) Highest value in benzene ring.

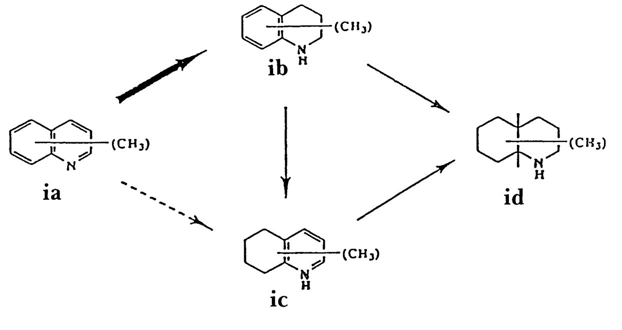
The substrates having a piperidine ring (1,2,3,4-tetrahydro and decahydro derivatives of both quinoline and isoquinoline) appear almost free from the hindrance in spite of a methyl group at the 2- or 8-possition.

Table 3 lists the heats of formation (H_f), electron densities of N-atoms, and the pK_a values of related compound. The H_f values are the indices for thermodynamic stabilities of substrates, and the latter two properties closely relate to the adsorption features of substrates. It should be noted that **3b** is less stable than **3c**, according to their H_f values.[21)]

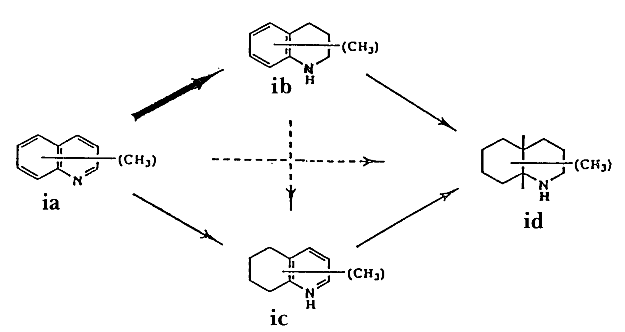
Table 3 also lists some quantum-chemical indices in the frontier orbitals of related compounds. The atoms having the highest LUMO's electron densities which indicate the most reactive position of hydrogenation[22,23)] are found in the pyridine ring in all the unhydrogenated compounds (at C_4 in quinolines and C_1 in isoquinoline).

Discussion

The present study revealed that the quinoline and its methylated derivatives are hydrogenated stepwise to perhydro derivatives and that the pathways and their rates are dependent upon the structure of substrate and catalyst. Hydrogenation pathways on both catalysts are illustrated in Fig. 6. Several points of discussion in terms of the reactivities of substrates are included in the pathways.



(a) over R-Ni.



(b) over Ru/C .

Fig. 6. Dominant reaction routes on the hydrogenation of quinolines. (a) Over R-Ni. (b) Over Ru/C. ➔; major, —>; medium, ---->; minor.

Some contrast features were found between quinoline and isoquinoline. Quinoline exhibited higher reactivity and selectivity in the first step of the hydrogenation into **1b** over R-Ni, reflecting its higher rate constants, although its adsorption constant was smaller than that of isoquinoline. The heats of hydrogenation, H_f(**ia**)—H_f(**ib**), and frontier electron densities of substrates may explain their reactivities. The heat of hydrogenation of quinoline is higher than that of isoquinoline. Electron densities of the N-atom and the highest C-atom in LUMO of quinoline are also higher than the corresponding values of isoquinoline. The difference of reactivity between pyridine and benzene rings in quinoline is definitely larger than that in isoquinoline according to their highest electron densities of LUMO.

Secondly, the reactivity of 1,2,3,4-tetrahydroquinoline (**1b**) for isomerization into **1c** is lower than that of 1,2,3,4-tetrahydroisoquinoline (**4b**), reflecting smaller adsorption constant. The difference reflects also their heats of isomerization, H_f(**ib**)—H_f(**ic**), suggesting structural similarity of the intermediates to the products. In contrast, the reactivity of **1b** for direct hydrogenation into its decahydrogenated derivative is higher than that of **4b**, reflecting its larger rate constant. The self-poisoning effect of **1b** on the hydrogenation of its benzene ring seems to be weak because of its low basicity (smaller adsorption constant) whereas the strongly basic **4b** showed strong poisoning.[13)] Strong adsorption of **4b** and **4c** is also indicated definitely in the competitive hydrogenation of quinoline and isoquinoline over R-Ni, where the hydrogenation of **1b** hardly took place. The stronger adsorption of **4b** and **4c** may also cause the induced deactivation[24—26)] of catalysis.

Finally, the reactivity of 5,6,7,8-tetrahydroquinoline (**1c**) into perhydro derivative is higher than that of 5,6,7,8-tetrahydroisoquinoline (**4c**) reflecting the rate constants. The reason appears that the π-electrons in **4c** are less reactive than those in **1c** as shown by the energy levels of HOMO or the frontier electron densities (both the HOMO and LUMO) of the most reactive positions.

Methyl group plays important roles in the present hydrogenation. The group at 2-position slightly decreased the rate of the first step in the hydrogenation on R-Ni, while the group at 8-position showed no influence. Such difference reflects again the heat of hydrogenation shown in Table 3. In a marked contrast, the group enhanced the successive reactions of **2b**. The roles of the group may be explained by the steric hindrance and the thermodynamic stabilities of the substrates and products: smaller difference between **2a** and **2b**, and larger difference between **2b** and **2c** in the heat of formation than the corresponding values of quinoline. Enhanced hydrogenation of its benzene ring in **2b** is also due to the steric effect. The benzene ring in **2a** can be adsorbed more close to the catalyst surface than those in **1b**. Small hindrance of methyl group at 8-position is noted in all steps of **3a**. First step occurs in the N-ring without methyl group. The hydrogenation of N-ring in the last step is rather enchanced. Some release of steric hindrance may be expected by the nonplanar structure of the products.[27)]

Ru/C exhibited two major differences in the hydrogenation from that over R-Ni. First of all, higher reactivities of quinoline and 8-methylquinoline than those of 2-methylquinoline and isoquinoline, reflecting the rate constants, are more marked. Such reactivities of substrates on Ru/C are also related to their heat of hydrogenation. Larger difference in the reactivities on the catalyst may reflect the different forms on adsorption on Ru/C from those on R-Ni which should define the stability of intermediates. Such a trend is observable in the values of equilibrium adsorption constants. Second characteristic of Ru/C catalyst is the rapid formation of perhydro derivatives, which are produced directly from 1,2,3,4-tetrahydro derivatives before their isomerization. Affinity of Ru to benzene ring in tetrahydro derivatives may be the reason. The formation of perhydro derivatives, **id**, starts soon after the disappearance of the starting substance. The strongest adsorption of the starting substrates, reflecting the largest adsorption constants, is due to the largest number of π-electrons to interact with the catalyst. Accordingly the retardation of **4b** against the hydrogenation of **1b** in the competitive reaction is much minor over Ru/C. The results indicate that the π-coordination instead of basicity of the substrate is the major factor influencing the reactivity over the catalyst.

5,6,7,8-Tetrahydro derivative is found at a relatively high yield only with 2-methylquinoline over Ru/C. The hydrogenation of benzene ring in **2a** may be allowed because of the steric hindrance of the methyl group at 2-position.

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