670 © *1993 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,66, 670—672(1993)* [Vol.66, No.2

Relative Reactivities of Some Polycyclic Aromatic Hydrocarbons in Catalytic Hydrogenation over Raney Nickel

Masahiro MINABE,* Shuuichi URUSHIBARA, Fumihiko MISHINA, Takao KIMURA, and Motohiro TSUBOTA
Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321

(Received September 11, 1992)

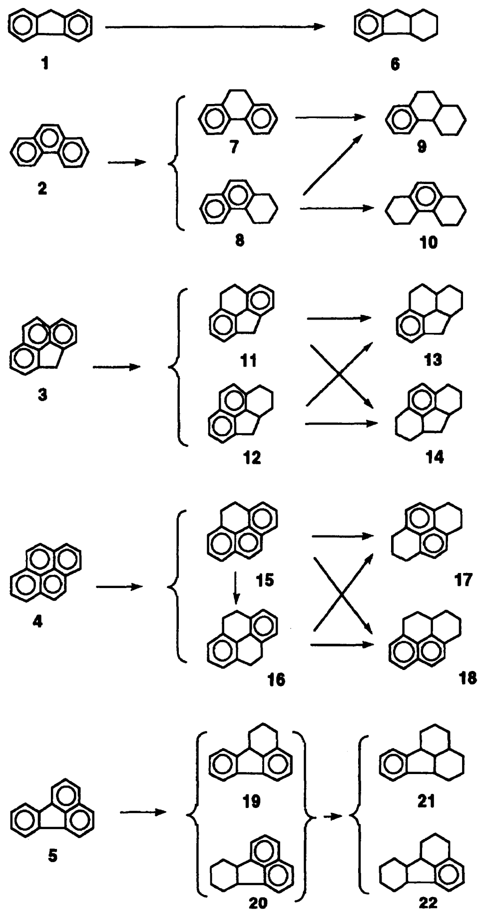
Synopsis. Catalytic hydrogenation of 9*H*-fluorene (**1**), phenanthrene (**2**), 4*H*-cyclopenta[*def*]phenanthrene (**3**), pyrene (**4**), and fluoranthene (**5**) was carried out over Raney nickel (W-7) at 323 K under 608 kPa of hydrogen. The order of the reaction rate was $\mathbf{5}>\mathbf{4}>\mathbf{3}>\mathbf{2}>\mathbf{1}$. The adsorption equilibrium constant of the substrates decreased in the order $\mathbf{4}\geq\mathbf{5}\gg\mathbf{2}>\mathbf{3}\gg\mathbf{1}$.

The catalytic hydrogenation of polycyclic aromatic hydrocarbons (PAHs) has been extensively investigated from both stereochemical and mechanistic standpoints.[1)] The hydrogenated products were studied both as synthetic intermediates and as hydrogen-donor solvents for coal liquefaction. However, the relative reactivities of PHAs toward hydrogenation have been scarcely reported,[2)] in spite of the fact that the catalytic hydrogenations of PAHs have been studied in detail.[2—5)]

The present paper deals with the relative reactivities of 9*H*-fluorene (**1**),[2)] phenanthrene (**2**),[3)] 4*H*-cyclopenta[*def*]phenanthrene (**3**),[4)] pyrene (**4**)[2,5)] and fluoranthene (**5**)[2)] in catalytic hydrogenation over Raney nickel (W-7) under mild conditions. These compounds are of interest because hydrogenation may be influenced by the following three factors: (a) the number of six-membered aromatic ring, (b) the presence versus absence of the methylene group, and (c) the presence versus absence of a strained five-membered ring. In this paper, the results obtained by both individual and competitive reactions are considered concerning both the reaction rate and the adsorption ability of each substrate (Scheme 1).

Results and Discussion

The hydrogenation of **1**—**5** was carried out over Raney nickel (W-7) in ethanol at 323 K under 608 kPa of hydrogen. The composition of the reaction mixture was measured using GLPC by comparing their retention times with an authentic specimen. The reaction rate (*R*) of each substrate during the initial stage was roughly estimated from the time-conversion relation of each individual reaction, as is summarized in Table 1. The order of the rate was $\mathbf{5}>\mathbf{4}>\mathbf{3}>\mathbf{2}>\mathbf{1}$. Further, the selectivity of the reaction products during the initial stage was determined using the same method as reported previously.[5)]



Scheme 1.

Table 1. Rate (*R*) and Selectivities in Individual Hydrogenation of **1**—**5**

Substrate	$R/\mathrm{mol\,s^{-1}\,g\text{-}cat^{-1}}$	Selectivities/(mol %)
1	$5.6_7\times10^{-7}$	**6**(100)
2	$1.1_3\times10^{-6}$	**7**(81), **8**(18), **9**(1)
3	$2.6_0\times10^{-6}$	**11**(84), **12**(1), **13**(9), **14**(6)
4	$2.7_2\times10^{-6}$	**15**(35), **16**(5), **17**(48), **18**(12)
5	$5.0_6\times10^{-6}$	**19**(93), **20**(2), **21**(2), **22**(3)

The hydrogenation reaction of **1** gave exclusively *cis*-2,3,4,4a,9,9a-hexahydro-1*H*-fluorene (**6**).[6)] The reaction of **2** afforded 9,10-dihydro- (**7**), 1,2,3,4-tetrahydro- (**8**), and 1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**9**). The formation of 1,2,3,4,5,6,7,8-octahydrophenanthrene (**10**) with a decrease of **7** and **8** was observed after the disappearance of **2**. The reaction of **3** yielded 8,9-dihydro- (**11**), 1,2,3,3a-tetrahydro- (**12**), *cis,cis*-1,2,3,3a,8,9,9a,9b-octahydro- (**13**),[4)] and *cis*-1,2,3,3a,4a,5,6,7-octahydro-4*H*-cyclopenta[*def*]phenanthrene (**14**).[4)] These hydrogenated products were identified by ^{1}H and

^{13}C NMR analysis.

The hydrogenation of **11** gave **13** (selectivity 73%) and **14** (27%) under similar conditions; the reaction rate was 2.1×10^{-7} mol s^{-1}g-cat^{-1}. The selectivity of **14** increased with decreasing hydrogen pressure. The formation of **14** from **11** indicates that catalytic interconversion takes place under these conditions, similar to the case of hydropyrenes.[5)]

The hydrogenation reaction of **4** afforded 4,5-dihydro- (**15**), 4,5,9,10-tetrahydro- (**16**), 1,2,3,6,7,8-hexahydro- (**17**), and 1,2,3,3a,4,5-hexahydropyrene (**18**) with similar selectivities to the case in a previous report.[5)] The reaction of **5** yielded 1,2,3,10b-tetrahydro- (**19**), 6b,7,8,9,10,10a-hexahydro- (**20**), 1,2,3,3a,4,5,6,6a,10b,10c-decahydro-(**21**), and 1,2,3,6b,7,8,9,10,10a,10b-decahydrofluoranthene (**22**).[2)]

In a competitive reaction, a mixture of any two substrates among **1**—**5** was reacted under conditions similar to the case of each individual reaction. The apparent reaction rate (R') of substrates **1** and **3**—**5** in the presence of **2** during the competitive reaction is summarized in Table 2, with the apparent reaction rate (R'_2) of the coexistent **2** in the reaction. The order of the rate was **4**$\geq$**5**>**2**>**3**>**1**; this order accords with the rate that is calculated based on the other sets of the experiment.

The reaction rate (R') of a substrate during a competitive reaction in a molar ratio of 1 : 1 should be twice the rate (R) of the individual reaction, if the coexistent substrate has no relation to the heterogeneous catalytic reaction.[7)] On the other hand, R' should be smaller than R, if the reaction of the substrate is inhibited by the coexistent substrate. For example, in a combination of **1** and **2**, the hydrogenation of **2** is little influenced by the coexistence of **1**, because the individual reaction rate of **2** (R_2) is 1.1 and the competitive reaction rate of **2** (R'_2) is 2.1. In other words, the reaction of **1** is retarded by the presence of **2** at a magnitude of about 88% (or $1-0.14/(0.57\times2)$).

Under the assumption that the molecular size is nearly the same among **1**—**5**, the ratio of the adsorption equilibrium constant (K) of a substrate to that (K_2) of **2** is expressed as

$$K/K_2=(R'/R'_2)/(R/R_2)$$

according to the literature.[8)] The order of the ratio of the adsorption equilibrium constant (Table 2) is **4**$\geq$**5**$\gg$**2**>**3**$\gg$**1**.

The reaction of **1** is slowest among the PAHs examined here, and is retarded by all of the PAHs. The presence of **1** scarcely influences the hydrogenation of other PAHs; it is due to the low adsorption ability on the catalyst. The rate (R) of **2** is smaller than that of **3**. In the competitive reaction, **2** retards the reaction of **1**, **3**, and **5**; on the other hand, the hydrogenation of **2** is decreased by the presence of **4** or **5**. The reaction of **3** is retarded in the presence of **2**, **4**, or **5**, which is also due to the low adsorption ability on the catalyst. The reaction of **4** is controlled only by **5**; on the other hand, the presence of **4** influences the reaction of the other PAHs, indicating that the adsorption ability of **4** is strongest among the PAHs. The rate (R) of **5** is the largest among the PAHs and is controlled by **4**, being due to the high adsorption ability, as in the case of **4**.

The adsorption ability of PAHs over a catalyst depends on the ability for π-coordination of the substrate with the catalyst, forming the π-adsorption state. The strong adsorption, or large K/K_2 value of a substrate, is first controlled by the high π-donor ability. The PAHs examined here are divided into three classes according to the number of π-electrons: **1** (12π), **2** and **3** (14π), and **4** and **5** (16π). This classification is in accord with the K/K_2 value, as well as with the total energy (indicated in the literature[9)]), which is the sum of the electronic and nuclear energies carried by all of the electrons and nuclei in a PAH, using the MNDO (modified neglect of diatomic overlap) method.

An exception of the above-mentioned explanation is the relation between **2** and **3**; the adsorption equilibrium constant K of **3** is smaller than that of **2**, compared with their total energies. This is temporarily due to the effect of the methylene group of **3**. The extremely low K of **1** is caused by a similar reason to the case of **3**. The calculated LUMO energy[9)] of **1**, **2**, and **3** is reflected by the effect of the methylene group, in addition to the effect of the π-electrons. The methylene group of **1** and **3** inhibits adsorption on the catalyst surface with regard to both the acidic property (pK_a is 22.7 for **1** and 22.6 for **3**[10)]) and to the non-planarity. It is not presently clear which of the two factors mainly affects the adsorption; however, the non-planarity factor may be a major reason, as in the case between substituted quinoline and isoquinoline.[11)]

The last point concerning these findings involves the fact that the rate (R) of **5** is larger than that of **4** in an individual reaction, similar to the cases of **4** and **5** in hydrogenation over supported noble metals.[2)] The same trend is recognized between **3** and **2**. This is due to the chemical reactivity of the substrate adsorbed over the catalyst. The addition of hydrogen to the strained five-membered ring causes an extension of the carbon-carbon bonds, thus decreasing the strain of the molecule; this accelerates the reaction.

Experimental

All of the melting points are uncorrected. The distribution of products was examined by GLPC with a Shimadzu GC-6AFP gaschromatograph equipped with a column (3 mm ID, 1 m) containing Dexsil 300 GC (5%) or SP-1000 (5%) on Chromosorb WAW (80—100 mesh) under a nitrogen atmosphere (50 ml min^{-1}). The chromatogram obtained using an FID detector was calculated with a Hitachi D-2500 integrator. The sensitivities of all the substrates and products were assumed to be equal.

The ^{1}H and ^{13}C NMR spectra of CDCl$_3$ (0.7 ml) solutions

Table 2. Kinetic Data for Hydrogenation of **1**—**5**

	1	**2**	**3**	**4**	**5**
R (10^6 mol s^{-1} g-cat^{-1})	0.57	1.1_3	2.6_0	2.7_2	5.0_6
R' (10^6 mol s^{-1} g-cat^{-1})	0.14	(2.2_6)	1.9_1	3.7_9	3.7_7
R'_2 (10^6 mol s^{-1} g-cat^{-1})	2.1_1	(2.2_6)	1.1_7	0.74	0.40
K/K_2	0.13	(1)	0.71	2.1_3	2.1_1
Total energy $^{a)}$ (eV)	−1803	−1930	−2058	−2186	−2185
LUMO energy $^{a)}$ (eV)	−0.369	−0.480	−0.454	−0.878	−0.939

a) Cited from Ref. 9.

were recorded with a Varian VXR-300. The sample used was 1—3 mg for ^{1}H NMR and 20—30 mg for ^{13}C NMR.

The Raney nickel catalyst (W-7) used was prepared with a Ni–Al alloy (50 : 50) 1 h prior to use according to a general procedure. The amount of catalyst was the weight of the alloy, which differed (31.3—500 mg) according to the reactivity of the substrate.

Individual Hydrogenation. General Procedure. The substrate (1.0 mmol) was dissolved in EtOH (20 ml) in a glass reactor (Taiatsu Scientific Glass TEM-V100) at 55°C; a R-Ni catalyst was added to the solution with EtOH (10 ml). Upon the substitution of air with hydrogen (4 times), the mixture was stirred (800 rpm) mechanically at 50±1°C (323±1 K) under a hydrogen pressure of 5 kg cm^{-2} (608 kPa). A small amount (ca. 0.1 ml) of the mixture was taken out, filtered, and submitted to GLPC after 1/3, 2/3, 1, 1.5, 2 h, and then additionally every 1 h.

After the reaction the mixture was filtered; the filtrate was evaporated to dryness, and the residue was then chromatographed on a silica-gel column using hexane (or hexane–benzene) as an eluent to yield each of the hydrogenated products.

Competitive Reaction. A mixture of two substrates (0.5 mmol of each substrate) was treated in a way similar to the case of an individual reaction.

Retention Time (min) and Spectral Data. In the reaction of **1** (8.6), **6** (1.7) was confirmed with SP-1000 column at 175°C. ^{1}H NMR of **6**: δ=1.16—1.62 (6H, m, H_1, H_2, H_3), 1.70—1.92 (2H, m, H_4), 2.36—2.48 (1H, m, H_{9a}), 2.58 (1H, dd, J=15.1, 4.5 Hz, H_9), 2.84 (1H, dd, J=15.1, 6.9 Hz, H_9), 3.08 (1H, q, J=5.7 Hz, H_{4a}), 7.06—7.18 (3H, m, H_6, H_7, H_8), and 7.22 (1H, d, J=6.4 Hz, H_5); ^{13}C NMR δ=22.4 (C_2), 23.7 (C_3), 27.1 (C_4), 27.8 (C_1), 37.4 (C_9), 39.7 (C_{9a}), 43.9 (C_{4a}), 122.8, 125.7, 125.8 (C_6, C_7, or C_8), 143.8, and 146.9 (C_{4a} or C_{8a}).

In the reaction of **2** (7.8), **7** (4.8), **8** (6.8), **9** (1.2), and **10** (5.2) were confirmed with Dexsil at 160°C. In the reaction of **3** (7.6), **11** (6.2), **12** (6.0), **13** (2.7), and **14** (3.3) were confirmed with Dexsil at 175°C.

13: Mp 63—65°C; ^{1}H NMR δ=0.60—0.76 (1H, m, H_3), 0.94 (1H, dq, J=12.7, 2.7 Hz, H_1), 1.11—1.27 (1H, m, H_2), 1.36—1.56 (3H, m, H_1, H_2, H_3), 1.81—1.97 (2H, m, H_9), 2.04—2.14 (1H, m, H_{9a}), 2.37 (1H, d, J=15.1 Hz, H_4), 2.42—2.52 (1H, m, H_{3a}), 2.57—2.76 (2H, m, H_8), 2.98 (1H, dd, J=15.1, 5.6 Hz, H_4), 3.04 (1H, t, J=5.6 Hz, H_{9b}), 6.88 (1H, d, J=6.2 Hz, H_7), and 7.02—7.08 (2H, m, H_5, H_6) ; ^{13}C NMR δ=22.6 (C_8), 24.8 (C_2), 24.9 (C_1), 27.2 (C_3), 28.4 (C_9), 32.2 (C_{9a}), 38.8 (C_4), 40.8 (C_{3a}), 44.0 (C_{9b}), 122.2 (C_5), 124.6 (C_7), 126.0 (C_6), 133.8 (C_{7b}), 141.2, and 142.8 (C_{4a} or C_{7a}).

14 : Mp 53—55°C; ^{1}H NMR δ=1.00—1.14 (2H, m, H_3, H_5), 1.15 (1H, q, J=11.2 Hz, H_4), 1.66—1.83 (2H, m, H_2, H_6), 1.98—2.14 (4H, m, H_2, H_3, H_5, H_6), 2.45 (1H, dt, J=11.2, 5.6 Hz, H_4), 2.50—2.65 (2H, m, H_1, H_7), 2.74—2.84 (2H, m, H_1, H_7), 2.85—2.98 (2H, m, H_{3a}, H_{4a}), and 6.86 (2H, s, H_8, H_9); ^{13}C NMR δ=23.8 (C_2, C_6), 25.9 (C_1, C_7), 29.0 (C_3, C_5), 41.3 (C_{3a}, C_{4a}), 44.3 (C_4), 125.8 (C_8, C_9), 131.0 (C_{7b}, C_{9b}), and 144.1 (C_{7a}, C_{9a}).

In the reaction of **4** (9.5), **15** (7.2), **16** (4.6), **17** (6.3), and **18** (5.8) were confirmed with Dexsil at 190°C. In the reaction of **5** (7.8), **19** (4.7), **20** (3.6), **21** (2.7), and **22** (2.7) were confirmed with Dexsil at 190°C. **21** (28.0) and **22** (30.0) were distinguished from each other with SP-1000 at 135°C.

The work described here was supported in part by a Grant-in-Aid for Scientific Research No. 02640381 from the Ministry of Education, Science and Culture.

References

1) J. S. Yu, B. C. Ankianiec, M. T. Nguyen, and I. P. Rothwell, *J. Am. Chem. Soc.*, **114**, 1927 (1992).

2) K. Sakanishi, M. Ohira, I. Mochida, H. Okazaki, and M. Soeda, *Bull. Chem. Soc. Jpn.*, **62**, 3994 (1989).

3) J. R. Durland and H. Adkins, *J. Am. Chem. Soc.*, **60**, 1501 (1938).

4) M. Minabe, Y. Yamamoto, M. Yoshida, K. Nakada, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **57**, 725 (1984). The structures of **13** and **14** have wrongly been suggested to be diastereomeric 1,2,3,3a,4a,5,6,7-octahydro derivatives, that is, *trans*-3a-*cis*-9a and *cis*-3a-*cis*-9a, respectively, based on their mass spectral analyses.

5) M. Minabe and K. Nakada, *Bull. Chem. Soc. Jpn.*, **58**, 1962 (1985).

6) M. Minabe and K. Suzuki, *J. Org. Chem.*, **40**, 1298 (1975).

7) During the reviewing process of the manuscript, reviewer pointed out the necessity of clear interpretation with regard to partial pressure of hydrogen in the competitive reaction. The effect of the partial pressure is now in study.

8) T. Chihara and K. Tanaka, *J. Catal.*, **80**, 97 (1983).

9) R. A. Hites and W. J. Simonsick, Jr., "Calculated Molecular Properties of Polycyclic Aromatic Hydrocarbons," Elsevier, New York (1987), pp. 16, 24, 30, 44, 45.

10) J. Hine, "Structural Effects on Equilibria in Organic Chemistry," Wiley, New York (1975), p. 174.

11) H. Okazaki, K. Onishi, M. Soeda, Y. Ikefuji, R. Tamura, and I. Mochida, *Bull. Chem. Soc. Jpn.*, **63**, 3167 (1990).