Bull. Chem. Soc. Jpn., 59, 2969—2971 (1986)

The Enantioselective Hydrogenation of Methyl Levulinate on the Interactive and Noninteractive Sites of Nickel Surfaces with Preadsorbed Asymmetric Compounds

Michio Yokozeki, Kazuo Shimokoshi, and Eizo Miyazaki*
Department of Chemistry, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152

(Received February 2, 1986)

The gaseous hydrogenation of methyl levulinate on the Ni surface modified with the optically active tartaric, malic and lactic acids was studied. It was found that γ-valerolactone is formed on an unmodified surface, while optically active methyl 4-hydroxypentanoate [MHP] and γ-valelolactone [VL] are formed consecutively on modified surfaces. Using these results and the temperature dependency of the reaction rates, along with previous theoretical results [*J. Phys. Chem.*, **89**, 2397 (1985)], it was concluded that, on an Ni surface modified with preadsorbed optically active acids, there are two different and independently operative sites, i.e., noninteractive (nonselective) and interactive (selective) sites which give the enantioselectivity. Further, the fractions of the noninteractive sites in the total amount of active sites were estimated to be about 18 and 13% for TA- and MA-modified surfaces respectively. A similar character of the active sites was found for the enantioselective hydrogenation of methyl acetoacetate [MAA] to methyl 3-hydroxybutyrate [MHB] on TA-modified Ni, where the fraction of noninteractive sites was evaluated to be about 15%.

It is known that such transition metal catalysts as Ni, when an optically active molecule such as tartaric acid is preadsorbed on their catalyst surfaces, become enantioselective for the hydrogenation of methyl acetoacetate.[1–3] Two different mechanisms for this selectivite reaction have been proposed as important processes on the surface:[3,5,6] (1) The complex formation with the substrate and modifiers,[4,5] and (2) the control of the orientations of the reactants by rather strong interaction between reactants and modifiers. In the previous theoretical studies based on the molecular orbital calculations with the MNDO method,[7] it was predicted that the hydrogen-bond-like interactions between reactants and preadsorbed hydroxy acids can control the form of the reactants on the surface.

On the other hand, as has been reported by Harada et al. in their study of liquid phase reactions,[8] the enantioselectivity of these systems is dependent upon the nature of the surface sites on which the reaction occurs; i.e., the high enantioselectivity is expected only from the reactions on the appropriately modified surface sites. In fact, the low-pressure gaseous hydrogenation of methyl acetoacetate (MAA) on the modified Ni surface provided an optical yield of, at most about 50%.[3] Therefore, in order to clarify the enantio-face-differentiating activity of the catalysts, it is desirable to obtain detailed knowledge of the processes occurring on both modified and unmodified surface-active sites. Harada et al. have clarified, using KBr as the site selective preadsorber in the modifier solution, that the Raney-Ni surface has two kinds of sites, i.e., effective and noneffective sites for the enantioselectivity.[8]

In the present work we investigated the hydrogenation of methyl levulinate (ML) on a nickel catalyst with and without the modification of optically active hydroxy acids, and found that the products formed on modified surfaces were different from those on an unmodified nickel surface. Using this reactant, we could obtain an insight into the processes on the modified surface. Further, this information on the surface sites of the modified Ni could be made use of in giving reasonable interpretations to the enantioselective hydrogenation of MAA in the gas phase, because the hydrogenation of MAA produced only methyl 3-hydroxybutylate (MHB) on both surfaces of Ni.

In the present paper, first we will describe the results of the enantioselective hydrogenation of methyl levulinate on nickel surfaces modified with various optically active hydroxy acids, and then the results obtained by applying a similar method to the analyses of the enantioselective hydrogenation of MAA to MHB.

Experimental

The apparatus used for the preparation of the catalysts and the reaction was the same as that reported previously.[3a] The modifiers used were (*R*,*R*)-tartaric acid (TA), (*S*)-malic acid (MA), (*S*)-3-hydroxybutyric acid (HBA), and (*S*)-lactic acid (LA). The modification was made by introducing 0.1 mol l^{-1} solutions of hydroxy acids at room temperature into a reaction cell which contained the nickel previously reduced by hydrogen. The pH of the modifier solutions was controlled at 5.0 by the use of sodium hydroxide. After 1.5 h of contact, the catalyst was washed by deaired methanol in a storage area attached to the cell. These processes were performed in the vacuum system.

Hydrogen of 2.66×10^4 Pa was circulated through the liquid ML (or MAA) storage, and a gaseous mixture of H_2 and the reactants was introduced into the reaction cell. The partial pressure of the ML vapour was 90 Pa. The reaction rates of hydrogenation were monitored by the change in the total pressure. The products were collected by means of liquid-nitrogen trap and analyzed by the use of a gas chromatograph (Yanagimoto G2800-F) using a 200 cm glass column packed with polyethylene glycol 20M (20%) on Celite 545 at 110 C. The optical rotation of the products was measured by means of a Yanagimoto OR-50 polarimeter.

Two different products, methyl 4-hydroxypentanoate (MHP) and γ-valerolactone (VL), were obtained by the hydrogenation of ML on TA-modified Ni. The optical yield

Table 1. Rates of the Product Formation, Ratioes of MHP in the Products and the Relative Rates [%r=(100−%MHP)R_1/R_2] of Nonselective Sites on Unmodified, TA-, and MA-modified Ni

Reaction temperature	Unmodified Ni		TA-modified Ni			MA-modified Ni		
	Rate(R_1)	MHP	Rate(R_2)	MHP	r[a]	Rate(R_2)	MHP	r[a]
K	$\times 10^{-11}$	%	$\times 10^{-11}$	%	%	$\times 10^{-11}$	%	%
323	4.8	<0.5	2.8	68	18.6	1.7	64	12.7
333	6.6	<0.5	3.6	67	18.0	2.4	63	13.4
343	9.9	<0.5	4.7	62	18.0	3.3	61	13.0
353	13.0	<0.5	6.0	58	18.9	4.2	57	13.5

a) % fraction of nonselective sites [=(100−%MHP)R_1/R_2].

Table 2. Optical Rotation of the Products Befoere and After Conversion and the Enantioselectivities [ES (%e.e.)]

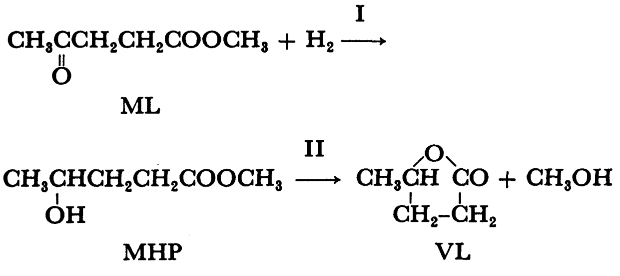
Reaction temperature	Before conversion			After conversion		
		MHP	VL		VL	ES[b]
K	$[\alpha]$[a]	%	%	$[\alpha]$[a]	%	%
322	−0.16	14.0	4.0	+0.22	12.3	5.1
343	−0.24	18.3	7.5	+0.36	21.8	4.7

a) Optical rotation. b) Enantioselectivity (% enantio excess).

of the products was calculated based on the value of $[\alpha]_D^{22}=-35.1$ (neat) for (S)-γ-valerolactone.[9] In the present experiments, in order to obtain the optical rotation accurately, the mixture was heated with Amberlyt 15 to convert all the MHP to VL. The enantioselectivities, ES, were defined as the percentage of enantiomer excess in the products.

Results and Discussion

In the hydrogenation of ML on TA-modified Ni catalysts at 323 to 353 K, two kinds of products, methyl 4-hydroxypentanoate (MHP) and γ-valerolactone (VL), were obtained, whereas on an unmodified Ni surface nearly 100% of the ML was converted to VL. The following consecutive mechanism, consisting of two steps, I and II, has been reported for this reaction on the surface.[10]



$$CH_3COCH_2CH_2COOCH_3 + H_2 \xrightarrow{I} CH_3CH(OH)CH_2CH_2COOCH_3 \xrightarrow{II} VL + CH_3OH$$

The ratio of MHP to the total products (VL+MHP) was about 60—70% in the former case, it decreased gradually with the increase in the reaction temperature. The hydrogenation character on Ni modified with other hydroxy acids, such as MA, LA, and HBA, was similar to that on TA-modified Ni; the ratios of MHP at 323 K were 69 (TA), 64 (ML), 62 (LA), and 60% (HBA). However, the enantioselectivity observed on ML modified Ni was less than that on TA-modified Ni, and on LA- and HBA-modified Ni the enantioselectivities were too low to be detected. The observed reaction rates at various temperatures on the unmodified (R_1) and modified (R_2) catalysts and also the % MHP in the products on Ni modified with TA and MA are compared in Table 1.

Unfortunately, the quantity of MHP in the gas-phase-reaction products was not large enough to measure the rotation of MHP and VL separately, and the optical rotation of MHP has not been reported. The optical rotations of the products were, therefore, measured before and after all the MHP, obtained initially, had been converted thermally into VL. Table 2 lists the optical rotations, the proportions, and the optical yield of the products. As may be seen in the table, the optical rotation was opposite in direction for the samples before and after the conversion. Since the rotating directions of VL and MHP in the same configuration are opposite to the reported value, $[\alpha]_D^{24}=+10.5$, for the related acid [(S)-4-pentanoxiacid] of MHP, the observed change indicates that (R)-MHP was formed on the modified surface and converted to (R)-VL by thermal treatment. The effect of the preadsorbed optically active hydroxy acids on the enantioselectivity is, therefore, apparent, even though their optical yields are not very high.

Figure 1 shows the variations in the rates of the product formation on the unmodified and TA- or MA-modified Ni surfaces with the reaction temperature. It may be seen that the apparent activation energy (33 kcal† mol^{-1}) obtained for VL formation on the unmodified Ni was very close to those on the TA- and MA-modified Ni, i.e., 33 and 31 kcal mol^{-1} respectively, while the energies for MHP on the two

---

† 1 cal=4.184 J.

Table 3. Rates, Enantioselectivities and *r* Values for MAA Hydrogenation to MHB on TA-modified Ni

Reaction temperature	Unmodified Ni	TA-modified Ni		
	Rate	Rate	ES	*r*
K	$\times10^{-11}$	$\times10^{-11}$	%	%
323	23.5	6.6	45.0	15
333	38.0	10.1	43.2	15
343	60.0	14.4	39.1	15
353	90.0	19.0	38.0	13

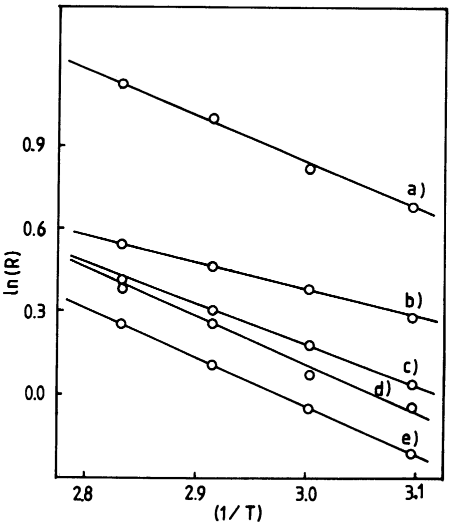


Fig. 1. The variation of the rate of the product formation as a function of reciprocal reaction temperature.
R: The rate of the formation ($\times10^{-11}$ molecules $s^{-1}\,cm^{-2}$).
a) VL formation on unmodified Ni, b) MHP on TA-modified Ni, c) MHP on TA-modified Ni, d) VL on TA-modified Ni, and e) VL on MA-modified Ni.

surfaces modified with TA (18 kcal mol^{-1}) and MA (28 kcal mol^{-1}) were quite different. These results, therefore, strongly suggest that the nature of the reaction for the formation of VL is similar on both unmodified and modified surfaces. Further, in order to estimate the fraction of the surface sites for VL formation in the total amount of active sites for the hydrogenation, the value $\%r=(100-\%\mathrm{MHP})R_1/R_2$ was calculated at each temperature. The values, shown in Table 1, were found to be independent of the reaction temperature, but dependent on the modifiers used, i.e., about 18 and 13% for TA- and MA-modified surfaces respectively.

These results suggest that MHP and VL are formed on different surface sites. On the nickel surfaces modified with the preadsorbed hydroxy acids, there might be two different and independently operative sites, (a) the "interactive" (selective) and (b) "noninteractive" (nonselective) sites. In the hydrogenation of ML on the interactive sites, the reaction may cease at Step I to form MHP, while the reaction proceeds further to Step II on such noninteractive sites as the bare nickel surfaces.

On the other hand, Table 3 summarizes the rates and enantioselectivities obtained for the hydrogenation of methyl acetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB) on TA-modified Ni. It can reasonably be assumed that, in the enantioselective hydrogenation of MAA on modified nickel surfaces, the reaction proceeds on the interactive sites, where the reactants are controlled by neighboring preadsorbed hydroxy acid molecules to form an optically active product preferentially.[7] Therefore, the fraction of the noninteractive sites of a modified surface can be estimated in a manner similar to that described above; i.e., by dividing the rate of the nonstereospecific reaction on TA-modified catalyst by that on the corresponding unmodified catalyst at each temperature. The calculated results are listed in Table 3. The values (%*r*), as expected, were found to hold almost constant (15%) throughout the reaction temperatures.

In conclusion, Ni surfaces modified with optically active acids are divided into interactive and noninteractive parts. The fraction of the noninteractive sites in the total amount of active sites is in the range of 10 to 20%, depending on the modifiers used. These sites seem to exist independently; thereby, it may be suggested that one can suppress the reaction rate on noninteractive sites using some appropriate reagents which cover the noninteractive sites preferentially.

References

1) Y. Izumi, *Angew. Chem. Int. Ed.*, **10**, 871 (1971).

2) Y. Izumi, *Adv. in Catal.* **32**, 250 (1983).

3) a) I. Yasumori, M. Yokozeki, and Y. Inoue, *Faraday Discus. Chem. Soc.*, **72**, 385 (1981); b) Y. Nitta, T. Imanaka, and S. Teranishi, *J. Catal.*, **80**, 31 (1983).

4) E. I. Klabunovskii, A. A. Vadenyapin, E. I. Karpeiskaya, V. A. Pavlov, and N. D. Zelinskii, *Proc. Int. Congr. Catal.*, **7**, 1980, 390.

5) A. Hoek and W. M. H. Sachtler, *J. Catal.*, **58**, 2376 (1979).

6) A. Tai, T. Harada, Y. Hiraki, and S. Murakami, *Bull. Chem. Soc. Jpn.*, **56**, 1414 (1983).

7) M. Yokozeki, K. Shimokoshi, and E. Miyazaki, *J. Phys. Chem.*, **89**, 2397 (1985).

8) T. Harada, M. Yamamoto, S. Onaka, M. Imaida, H. Ozaki, A. Tai, and Y. Izumi, *Bull. Chem. Soc. Jpn.*, **54**, 2232 (1981).

9) H. Minato, *Chem. Pharm. Bull.*, **9**, 625 (1961).

10) R. W. Thomas, H. A. Schuette, and M. A. Cowley, *J. Am. Chem. Soc.*, **53**, 3861 (1931).