August, 1972]   BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2551—2554 (1972)   2551

Asymmetric Hydrogenation of C=O Double Bond with Modified Raney Nickel Catalyst. XXIII

Toshio Ninomiya*

Division of Organic Chemistry, Institute for Protein Research, Osaka University, Kita-ku, Osaka

(Received January 26, 1972)

The ultraviolet spectra of acetylacetone and methyl acetoacetate adsorbed on evaporated nickel film modified with amino or hydroxy acid were measured. The spectroscopic data suggested that the adsorbed species of acetylacetone was affected by the modifying pH, that the interaction between acetylacetone and the hydroxy acid was different from that between acetylacetone and the amino acid, and also that methyl acetoacetate, similar to acetylacetone, chemisorbed with a pseudo aromatic ring on the nickel surface. Consequently, the above results strongly support the theory that in the asymmetic hydrogenation, the substrate, acetylacetone or methyl acetoacetate, approaches the catalyst surface in a form like a pseudo aromatic ring, that it is asymmetrically controlled by the modifying reagent adsorbed on the catalyst surface, and, further, that the ease of the adsorption of the substrate onto the catalyst determines the rate of asymmetric hydrogenation.

In the course of the investigation of asymmetric hydrogenation with modified Raney nickel catalysts, many kinds of ketones have been used as the substrate for the asymmetric hydrogenation; β-ketoester and β-diketone have been demonstrated to be the most suitable substrates.[1] However, the approach mechanism of the substrate to the catalyst surface has not been made clear. The clarification of the approach-mechanism of the substrate to the catalyst surface would give important information for solving the mechanism of the asymmetric hydrogenation.

The present work is intended to make clear the approach-mechanism of the acetylacetone (Hacac) and methyl acetoacetate (MAA) substrates to the catalyst surface.

In a previous short communication[2] the absorption spectra of Hacac adsorbed on evaporated nickel film modified with D-tartaric acid have been reported. The present paper will report, in detail, on the adsorption state of the substrate, Hacac or MAA, onto evaporated nickel film modified with optically-active amino or hydroxy acid.

The experimental procedure developed by Kishi *et al.*[3] was improved. The adsorption spectra of Hacac adsorbed on the nickel film modified at various modifying pH values suggested that the adsorbed species of Hacac on the nickel film can be changed by changing the modifying pH and that Hacac can be adsorbed with ease on the nickel surface with an increase in the modifying pH.

Moreover, from the fact that, at the same modifying pH the absorption spectra of Hacac on the nickel film modified with tartaric acid were different from those of Hacac on the nickel film modified with glutamic acid, it was concluded that the substrate, in approaching the nickel surface, is affected characteristically by the asymmetric control of the modifying reagent adsorbed on the nickel surface and that the asymmetric control mechanism by hydroxy acid for the substrate was different from that by amino acid because of the difference in the chemical interaction between the hydroxy group and the amino group with the substrate.

As for MAA, which is similar to Hacac, it was made clear that MAA chemisorbs like a chelate with a pseudo aromatic ring on the nickel surface, and the ease of the adsorption of MAA on the evaporated nickel film modified with an optically-active compound was parallel with the asymmetric hydrogenation rate of MAA in the presence of a catalyst modified by the corresponding modifying reagent.

Experimental

The experimental apparatus developed by Kishi[3] was improved and used; *cf.* Fig. 1. The evaporation conditions of nickel onto the quartz windows was the same as the conditions reported by Kishi.[3] After the nickel had been evaporated onto the quartz windows, the break-off seal (G) was broken by means of the glass-coated magnet (H) and a 2% modifying aqueous solution (I), which had been degassed, was gently introduced into the quartz cell. At 0°C for 30 min, the nickel surface was modified by the modifying aqueous solution. Then, the modifying aqueous solution was transported into I, the modified nickel film was washed twice with water, and the water was evaporated from the ultraviolet cell. The substrate, acetylacetone or methyl acetoacetate, was introduced into the cell, and then the ultraviolet spectra were recorded on a Hitachi EPS-2 spectrophotometer equipped with a liquid nitrogen trap.

The GR-grade acetylacetone was obtained from Nakarai Pure Chemicals, while the methyl acetoacetate was obtained from The Nippon Synthetic Chemical Co., Ltd., both were distilled several times under a vacuum. The purity of the nickel wire is 99.5%.

Results and Discussion

1) Adsorption of Acetylacetone (Hacac). Figure 2 illustrates the absorption spectra of Hacac adsorbed on the evaporated nickel film modified with D-tartaric acid at pH 2.0, 5.0, and 9.0. As is illustrated in Fig. 2, in the modification at pH 2.0 a weak band was observed around 280 mμ after a 30-min exposure

---

* Present address: Dai Nippon Toryo, Co., Ltd., 38 Nishinoshimonocho, Konohana-ku, Osaka.

[1] Y. Izumi, M. Imaida, T. Harada, T. Tanabe, S. Yajima, and T. Ninomiya, This Bulletin, **42**, 241 (1969); T. Tanabe, *ibid.*, to be published.

[2] T. Ninomiya, K. Kishi, and S. Ikeda, *ibid.*, **43**, 2270 (1970).

[3] K. Kishi, S. Ikeda, and K. Hirota, *J. Phys. Chem.*, **71**, 4384 (1967).

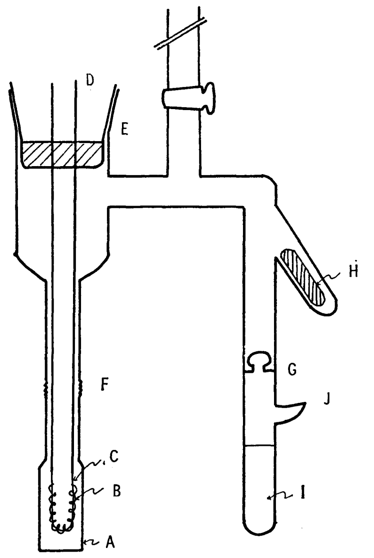

Fig. 1. Dirgram of the ultraviolet cell.
A: quartz cell
B: nickel metal wire
C: tungsten filament
D: heavy tungsten leads
E: taper joint
F: graded seal
G: break-off seal
H: glass-coated magnet
I: tartaric acid solution
J: fused seal

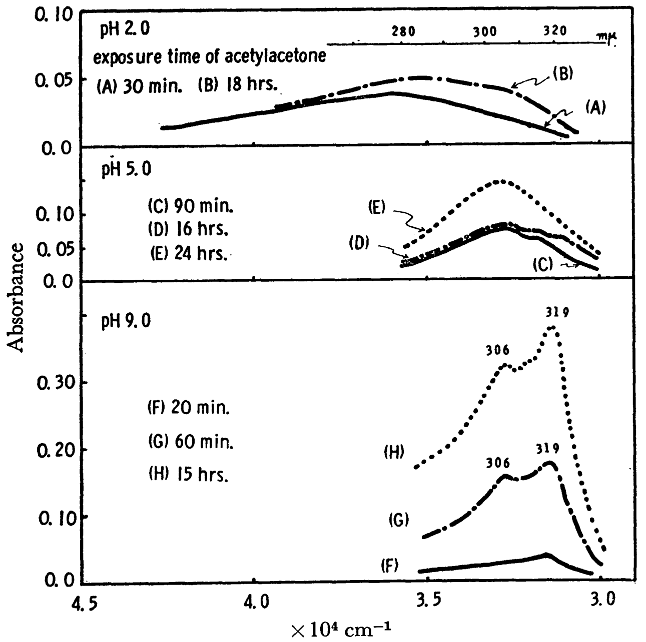

Fig. 2. Ultraviolet spectra of acetylacetone adsorbed on nickel film with preadsorbed D-tartaric acid at pH 2.0, 5.0, and 9.0.

to acetylacetone, and the band maximum shifted to a longer wavelength after 18 hr. In the modification at pH 5.0, absorption peaks were observed at 306, 316, and 322 mμ after 16 hr; these peaks became one at 303—306 mμ after 24 hr. In the treatment at pH 9.0, three intensive bands were observed at 306, 313, and 319 mμ after 15 hr.

The maximum peak at 303 mμ was assigned to an absorption peak of the π-π^* transition of adsorbed acac$^-$ in the study by Kishi *et al.*[2] of the absorption spectrum of Hacac adsorbed on the unmodified nickel film.

Tanabe,[4] one of our research group, suggested that, in the modification with a free tartaric acid aqueous solution (pH 2.0), one of the carboxyl groups of tartaric acid is bound to the catalyst surface, while the other, being undissociated, stretches out from the nickel surface and is dissociated by the neutralization, with an increase in the modifying pH.

On the basis of the above information, the results in Fig. 2 can be explained by the following proposition. In the modification at pH 2.0, the acidic β-carboxyl group stretching out from the nickel surface could hinder the enolization of Hacac, which would favor Hacac making a stable adsorption with a chelation from on the nickel surface; consequently, enol-form Hacac could hardly adsorb on the nickel surface. Hence, we observed the shift of adsorption maximum at 303 mμ, which was seen in the adsorption of Hacac on the unmodified nickel surface, to at shorter wavelength position.

In the modification at pH 5.0, the acidity of the β-carboxyl group of tartaric acid should be mostly neutralized; therefore, acetylacetone can adsorb with a stable pseudo aromatic ring on the nickel surface because there is little hindrance by the acidity of the β-carboxyl group, and the absorption band can be considered to show a maximum peak at 303—306 mμ.

In the treatment at pH 9.0, both carboxyl groups of tartaric acid were mostly neutralized, the amounts of tartaric acid adsorbed were moderately small compared with the amounts adsorbed in the modification at pH 5.0,[5] and acetylacetone would adsorb more easily

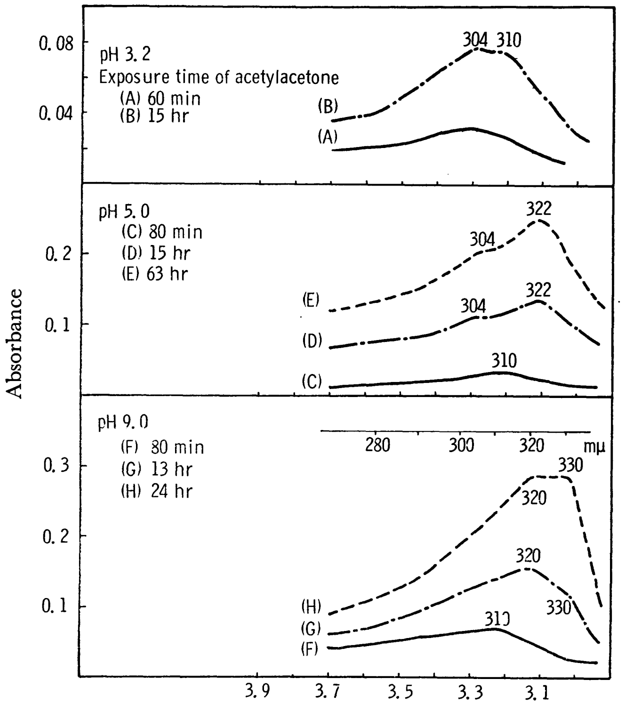

Fig. 3. Ultraviolet spectra of acetylacetone adsorbed on nickel film with preadsorbed L-glutamic acid at pH 3.2, 5.0, and 9.0.

---

4) T. Tanabe, This Bulletin, to be published.

5) S. Tatsumi, This Bulletin, **41**, 408 (1968).

than at pH 5.0. Thus, the chemical circumstances on the catalyst surface at pH 9.0 were different from those at pH 5.0. Therefore, the absorption spectrum of Hacac at pH 9.0 is considerably different from that at pH 5.0 as is shown in Fig. 2.

Figure 3 displays the absorption spectra of Hacac adsorbed on the nickel film modified with L-glutamic acid at pH 3.2, 5.0, and 9.0. As is illustrated in Fig. 3, in the modification at pH 3.2 two weak bands, at 304 mμ and 310 mμ, were observed after 15 hr's exposure to acetylacetone.

With an increase in the modifying pH value, the bands of adsorbed Hacac shifted to longer wavelength positions and their intensities increased. The above shift of the adsorption bands with an increase in the modifying pH must be due to the effect or γ-carboxyl group of L-glutamic acid, as in the modification with tartaric acid.

On the basis of the above facts and discussion, it is clear that the approaching form of the substrate was affected by the chemical circumstances of the modifying reagent on the nickel surface; that is, in acidic circumstances acetylacetone could hardly take the enol form while in neutral or basic circumstances acetylacetone could take the enol form and could stably adsorb with a pseudo aromatic ring on the nickel surface.

Moreover, a remarkable difference between Figs. 2 and 3 was observed at the same modifying pH. That is, at both pH 5.0 and pH 9.0 the absorption spectra in the modification with tartaric acid were different from those in the modification with glutamic acid. This important difference in the absorption spectra is due to the difference in chemical interaction between the substrate and the modifying reagent, probably because of the difference in reactivity to the substrate between the amino group of amino acid and the hydroxy group of hydroxy acid. For example, the amino group can behave as a base to the substrate, acetylacetone, the enol form of which may act as an acid, and can also form a Schiff base with the ketone group of the substrate, while the hydroxy group acting as an acid can make a hydrogen bond with the ketone group of the substrate.

This difference in chemical interaction between the amino and the hydroxy groups and the carbonyl group of the substrate seems to result in a difference in asymmetric direction between the catalysts modified with L- (or D-) amino acid and L- (or D-) hydroxy acid. As a matter of fact, the catalysts modified with L-aspartic acid show (—) asymmetric activity, while the catalysts modified with L-malic acid show (+) asymmetric activity, in the asymmetric hydrogenation of methyl acetoacetate.[6]

In conclusion, the above phenomenon supports strongly the idea that, in the asymmetric hydrogenation, the substrate approaching the catalyst surface is perturbed and affected asymmetrically by the modifying reagent on the catalyst surface.

2) *Adsorption of Methyl Acetoacetate.* Figure 4 illustrates the absorption spectra of methyl acetoacetate (MAA) adsorbed on the unmodified nickel film. As is illustrated in Fig. 4, a broad band was observed at 285 mμ. The band did not disappear upon the use of a liquid nitrogen trap, although the band at 239 mμ due to vapor MAA disappeared upon the use of a liquid nitrogen trap. In addition, the intensity of the band increased with an increase in the time of exposure to MAA, and upon exposure to acetic acid vapor the band disappeared instantly.

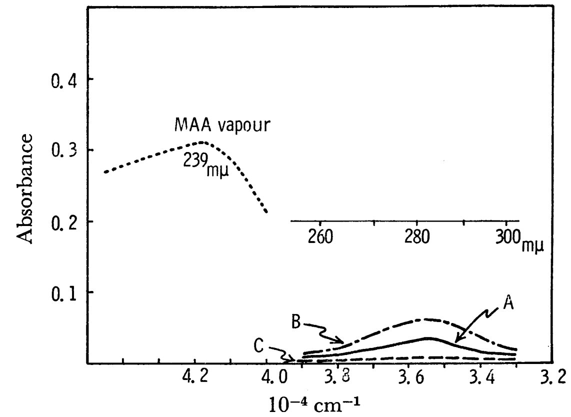

Fig. 4. Ultraviolet spectra of methyl acetoacetate adsorbed on nickel film (without preadsorption).
A: 60 min B: 18 hr C: 30 sec after AcOH

The above facts support the idea that the band at 285 mμ is to be ascribed to the chemisorbed species of MAA on the nickel film. Further, from the fact that the position of the band maximum of chemisorbed MAA (285 mμ) is near that of nickel methyl acetoacetate (278 mμ in methanol), MAA can be concluded to chemisorb like a chelation form with a pseudo aromatic ring on the nickel surface.

Figure 5 shows the absorption spectra of MAA adsorbed on nickel film modified with L-valine, L-glutamic acid, L-histidine, and D-tartaric acid. As is shown in Fig. 5, the intensities of the absorption spectra originating from MAA adsorbed on the nickel surfaces modified with valine, glutamic acid, and histidine

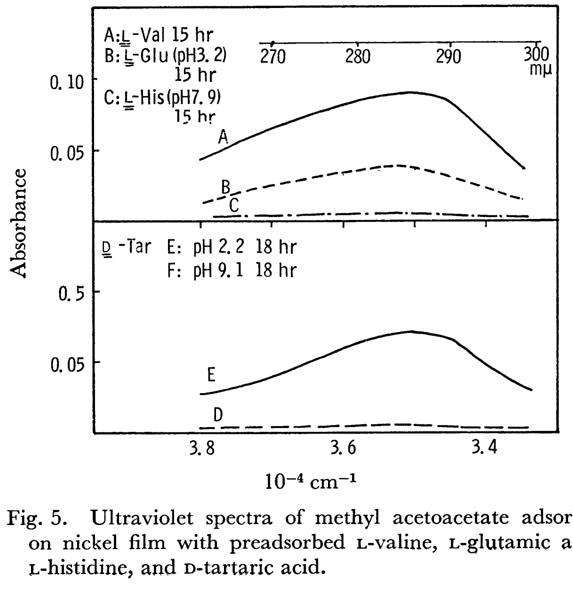

Fig. 5. Ultraviolet spectra of methyl acetoacetate adsorbed on nickel film with preadsorbed L-valine, L-glutamic acid, L-histidine, and D-tartaric acid.

---

[6] Y. Izumi, S. Yajima, K. Okubo, and K. K. Babievsky, *ibid* **44**, 1416 (1971).

decreased in the following order; valine>glutamic acid≫ histidine. This order seems to be related to the hydrogenation rate of MAA in the presence of a catalyst modified with L-valine, L-glutamic acid, or L-histidine. That is, the hydrogenation of MAA with the catalyst modified with L-histidine took at least 2 times as long as the hydrogenation with catalysts modified with neutral L-amino acids.

Histidine can chelate strongly on the nickel surface because histidine can act as a tridentate chelating reagent,7) while neutral L-amino acids acts as bidentate reagents. As a result, it can be considered that a nickel atom of the catalyst surface on which a histidine molecule should absorb strongly can hardly attract the substrate, while a nickel atom on which a neutral amino acid should adsorb can attract the substrate rather easily.

Therefore, the MAA substrate will probably approach the nickel surface modified with L-histidine with more difficulty than that modified with neutral L-amino acids.

In the modification with D-tartaric acid, the adsorption intensity at pH 2.2 was far weaker than that at pH 9.1. The phenomenon is probably due to the reason mentioned in the case of acetylacetone; that is, at pH 2.2, the β-carboxyl group, being undissociated, should hinder the enol-form adsorption of MAA, while at pH 9.1 the β-carboxyl group of D-tartaric acid is mostly neutralized and MAA can adsorb easily with the enol from on the nickel surface. The above results correspond to the facts shown in Fig. 6.

In Fig. 6, the percentage of hydrogenation is plotted against the hydrogenation time in the asymmetric hydrogenation with the catalysts modified with D-tartaric acid at pH 2.2 and pH 9.5 at 0°C. As is shown in Fig. 6, the hydrogenation rate in the modification at pH 2.2 is smaller than that as pH 9.5. From the above discussion, it is clear that the asymmetric hydrogenation rate of MAA depends on the degree of hindrance of the modifying reagent, which probably contains at least two factors, the strength of the chelation ability for amino acids and the acidity of the β-carboxyl group for a tartaric acid, in relation to a the substrate approaching the catalyst surface.

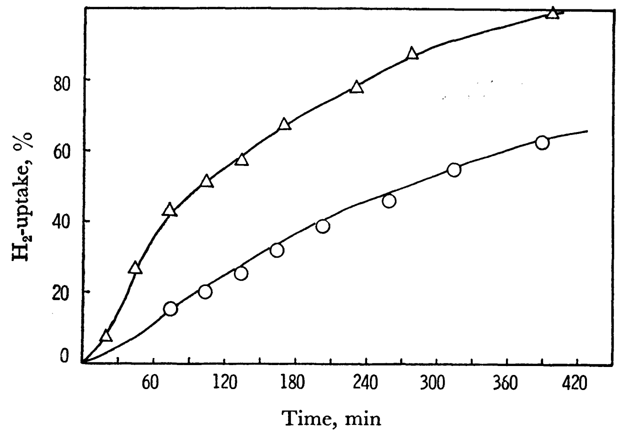

Fig. 6. Effect of modifying pH on hydrogenation rate. (modification with D-tartaric acid at 0°C)
—△—: pH 9.5; —○—: pH 2.2

The author wishes to express his sincere thanks to Professor Yoshiharu Izumi, Professor Shigero Ikeda, and Dr. Kosaku Kishi for their valuable advice and encouragement throughout this work.

---

7) R. Leberman and B. R. Rabin, *Ttans. Faraday Soc.*, **55**, 1660 (1959).