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# Liquid-Phase Catalytic Hydrogenation of Unsaturated Compounds: A New View on the Causes of the Zero Order of the Reaction

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The hydrogenation of maleic acid has been studied as a model hydrogenation of unsaturated double-bond compounds in aqueous and alcoholic 1 $M$ $H_2SO_4$ solutions. The curves of hydrogenation uptake time and catalyst potential time show that as the reaction proceeds the degree of surface coverage by the organic substance decreases with the logarithm of its bulk concentration. The kinetic equation derived for the reaction indicates that the decrease in the surface coverage is offset by a change in the catalyst potential or in the chemical potential of adsorbed hydrogen, resulting in a constant hydrogenation rate and zero-order reaction with respect to the unsaturated compound.

## INTRODUCTION

The liquid-phase hydrogenation of unsaturated compounds has been studied by many workers, and many relationships have been proposed to describe the reaction kinetics (*1–3*). The simplest and most widely used kinetic equation is that of the Langmuir–Hinshelwood type (*4*), with the hydrogenation rate expressed as (*5*)

$$-(V/WS)(da_A/dt) = r_h = k_A K_A a_A K_H a_H / (1 + K_A a_A + K_H a_H + K_P a_P + K_S a_S), \quad (1)$$

where $V$ is the volume of liquid reaction mixture, $W$ is the catalyst mass, $S$ is the catalyst specific surface area, $t$ is the time, $a_A$, $a_P$, $a_H$, and $a_S$ are the activities of the unsaturated compound, product, hydrogen, and solvent, respectively, $K_A$, $K_P$, $K_H$, and $K_S$ are the adsorption coefficients of the respective components, and $k_A$ is the rate constant. Concentrations rather than activities are used when ideal behavior of the reaction mixture is assumed.

Assuming that

$$K_A c_A \gg (1 + K_P c_P + K_H c_H + K_S c_S), \quad (2)$$

the kinetic equation (1) can apparently be simplified to a zero-order equation with respect to the concentration, $c_A$, of the compound hydrogenated. The solvent concentration, $c_S$, is usually substantially greater than $c_A$, and the product concentration, $c_P$, during the hydrogenation is comparable with $c_A$. Hence, in order for condition (2) to be satisfied, it is necessary that the adsorption coefficients $K_S$ and $K_P$ be much smaller than $K_A$ ($K_S, K_P \ll K_A$). In view of the lower adsorbabilities of saturated compounds and the solvents commonly used (alcohols, saturated hydrocarbons, etc.) (*6*), we may assume that this condition can be fulfilled. Some difficulties are encountered with the term $K_H c_H$. The concentration of dissolved hydrogen in the solvents used is small, because of its low solubility. By increasing the hydrogen pressure, the concentration of dissolved hydrogen can be enhanced by up to two orders of magnitude, with a proportionate increase in the term $K_H c_H$. However, even under these conditions the hydrogenation remains a zero-order reaction with respect to the compound hydrogenated. Since in the usual hydrogenation systems it is not possible to measure simultaneously the hydrogen adsorption and consequently the value of the hydrogen adsorption coefficient is not available, it is assumed that $K_H$ is also substantially smaller than the adsorption coefficient of the unsat-

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urated compound, $K_H \ll K_A$, and hence $K_H c_H \ll K_A c_A$. However, a number of studies (see, for example, Refs. (*6, 7*)) have indicated that under hydrogenation conditions the degrees of coverage of, for instance, a platinum surface by unsaturated compounds and by hydrogen are comparable. Apparently, the hydrogenation of unsaturated compounds in this medium should not occur as a zero-order reaction, because condition (2) is not fulfilled. Nevertheless, a number of studies (for example, Ref. (*8*)) have demonstrated that the opposite is true for many unsaturated compounds in the medium of an aqueous solution of sulfuric acid.

If condition (2) is satisfied, then Eq. (1) simplifies to

$$r_h = k_A K_H c_H. \qquad (3)$$

When hydrogenation under constant hydrogen pressure is carried out in the presence of, say, a platinum catalyst in an excess of solvent, the concentration of dissolved hydrogen remains constant. Under these conditions, the term $K_H c_H$ is also constant and we obtain an equation for zero-order reaction. During hydrogenation in the medium of a conducting electrolyte such as sulfuric acid solution, changes in the activity of adsorbed hydrogen $a_{H,ad}$ can be easily determined by measuring the potential of the catalyst on which the hydrogenation occurs, as on the platinum surface the reaction ($H_{ad} \rightleftharpoons H^+ + e$) proceeds relatively fast and equilibrium between adsorbed hydrogen and $H^+$ ions is attained rapidly. The relation between the activity of adsorbed hydrogen and the potential $E$ is governed by the Nernst equation

$$E = E^0 + (RT/F) \ln(a_{H^+} \cdot a^0_{H,ad}/a^0_{H^+} \cdot a_{H,ad}). \qquad (4)$$

At constant pH, the change in the electrode potential is governed by the change in the activity of adsorbed hydrogen:

$$\Delta E = (RT/F) \ln a^1_{H,ad}/a^2_{H,ad}. \qquad (5)$$

As the activity of adsorbed hydrogen is related to the activity of dissolved hydrogen, which in the course of the hydrogenation remains constant, it is necessary for the activity of adsorbed hydrogen to be also constant, i.e., $a^1_{H,ad} = a^2_{H,ad}$, and consequently for the reaction to be of zero order it is also necessary that $\Delta E = 0$.

The aim of the present work was to verify whether $\Delta E$ is indeed zero in the range where the hydrogenation occurs as a zero order reaction and also to try to explain why the reaction is of zero order even under experimental conditions where inequality (*2*) is not satisfied.

## EXPERIMENTAL

Various kinds of platinum black, prepared by reduction of chloroplatinic (IV) acid by formaldehyde or sodium borohydride, were used as catalysts. Samples of low surface areas were obtained by annealing the originally prepared catalysts at 900°C for various times. In this way, catalysts with surface areas ranging from 2.9 to 28.6 $m^2/g$ were obtained. The hydrogenation was carried out in the medium of 1 *M* $H_2SO_4$ in aqueous or 50% methanol solution. The sulfuric acid solutions wer prepared by mixing concentrated $H_2SO_4$ with distilled water or with analytical grade methanol. Analytical grade maleic acid purified by crystallization was used as the model hydrogenation compound and the reaction was carried out using electrlytic hydrogen taken from a cylinder. The hydrogenation rate was measured by means of an apparatus described elsewhere (*9*), which permitted continuous automatic recording of hydrogen consumption and catalyst potential.

## RESULTS AND DISCUSSION

Figure 1 shows a typical hydrogenation curve of hydrogen consumption versus time and a simultaneously recorded curve of the catalyst suspension potential as a function of time. With the exception of the cases described below, such dependences

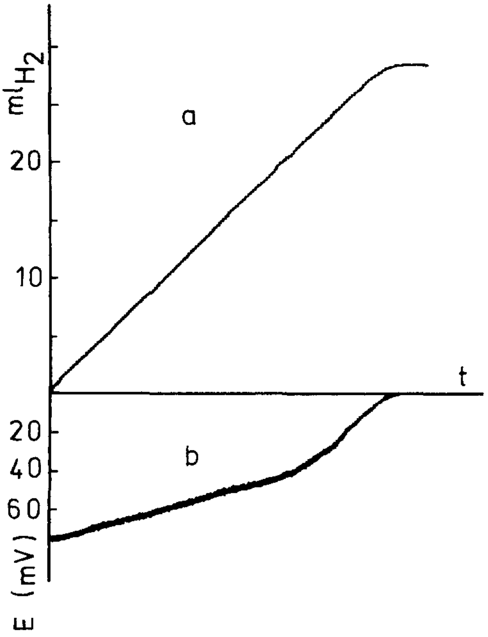

FIG. 1. Hydrogenation of maleic acid, initial concentration $c_A^0 = 0.029$ *M*, 1 *M* $H_2SO_4$, Pt black with $S_{Pt} = 12.2$ m$^2$/g. (a) Dependence of hydrogen consumption on time; (b) variation in potential with time.

are obtained for all catalysts with different specific surface areas, in both the aqueous and methanolic media. From the measured dependence of hydrogen consumption on time, data for the suspension potential and hydrogenation rate as a function of the logarithm of maleic acid concentration have been calculated. As seen in Fig. 2, the $E - \ln c_A$ plot is linear over as much as two orders of magnitude in maleic acid concentration. The values of $\partial E/\partial \ln c_A$ vary from 0.02 to 0.050 V/decade. Within the linear portion of the $E - \ln c_A$ plot, the hydrogenation rate is, in most cases, also independent of the concentration and the hydrogenation occurs as a zero-order reaction.

With catalysts having lower surface areas, under otherwise the same conditions, the hydrogenation may no longer proceed as a zero-order reaction. This is illustrated in Fig. 3, which shows the behavior of a platinum black catalyst with a small specific surface area, $S_{Pt} = 2.9$ m$^2$/g. For the ratio of maleic acid concentration in solution to the total catalyst surface area in the reaction mixture $R \lesssim 5 \times 10^{-8}$ mol/cm$^5$, the hydrogenation is zero order, with a linear variation in $E$ as a function of $\ln c_A$. At higher $R$ or in repeated hydrogenation using this low-surface-area catalyst at the same ratio, the catalyst becomes poisoned, and the hydrogenation rate diminishes with time and consequently with decreasing concentration of maleic acid. In this case, the $E - \ln c_A$ plot is no longer linear, the rapid decrease in the hydrogenation rate being paralleled by a rapid decrease in $E$. The above critical value of $R$ applies approximately also to catalysts with higher specific surface areas. For example, with platinum black having a specific surface area of 12.0 m$^2$/g and a solution with the initial concentration $c_A = 0.1$ *M*, in which rapid poisoning occurs for a catalyst with $S_{Pt} = 2.9$ m$^2$/g, the hydrogenation proceeds in the usual manner as a zero-order reaction. It is not until the initial concentration is increase to $c_A = 0.24$ *M* at $R = 1.0 \times 10^{-7}$ mol/cm$^5$ that a gradual catalyst poisoning occurs and the hydrogenation rate diminishes continuously with time.

The results displayed in Figs. 1 to 3 and confirmed by a large number of additional measurements, as well as some results published in the literature (*8*), demonstrate unambiguously that the catalyst potential $E$ changes by even more than 50 mV during hydrogenation in the region of constant $r_h$. Accordingly, the activity of hydrogen adsorbed on the catalyst surface changes by as much as an order of magnitude. Thus it is clear that Eq. (3), which formally accounts well for the experimental data, does not satisfy its underlying physical assumptions.

An equation for zero-order hydrogenation with respect to the concentration of unsaturated compound which satisfies the physical assumptions can be derived on the basis of the concepts and results of Vassiliev *et al.* (*7*) for the electrochemical reduction of unsaturated compounds. If we consider the hydrogenation as a process in

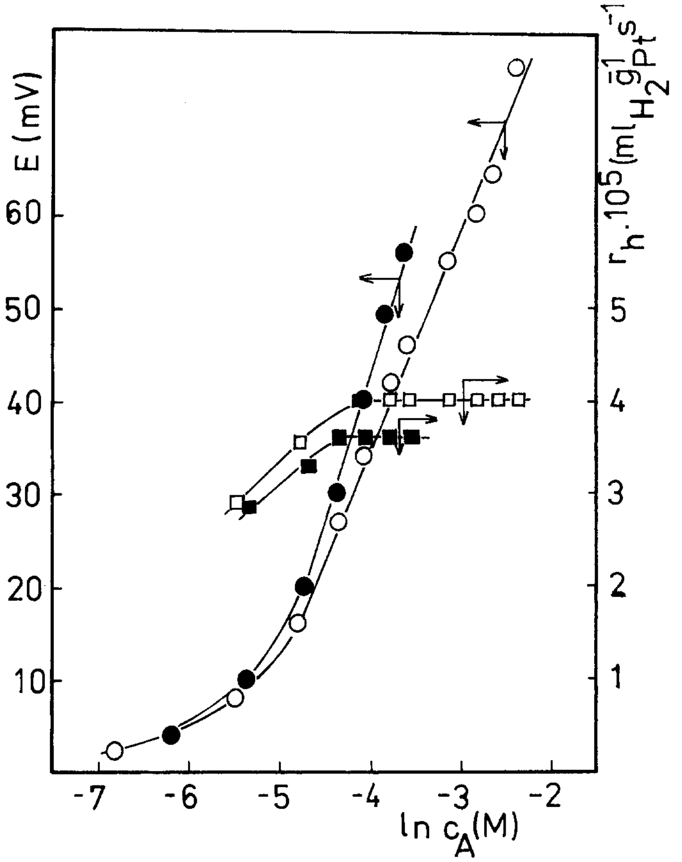

FIG. 2. Potential (○, ●) and hydrogenation rate (□, ■) as a function of maleic acid concentration. Initial concentrations $c_A^0 = 0.026\ M$ (●, ■) and $c_A^0 = 0.091\ M$ (○, □), 1 $M$ $H_2SO_4$, Pt black with $S_{Pt} = 12.2\ m^2/g$.

which the rate-determining elementary step is the reaction between the adsorbed unsaturated compound and hydrogen, then the hydrogenation rate may be expressed as

$$r_h = k\theta_H\theta_A \exp(-\beta\Delta Q), \qquad (6)$$

where $\theta_H$ and $\theta_A$ are the degrees of catalyst surface coverage by hydrogen and the reactant, respectively, $\beta$ is a coefficient (*7*), and the term $\Delta Q$ is the activation energy for the reaction, which includes the effect of the adsorption energies of both the chemisorbed species. For $\Delta Q$ we can write

$$\Delta Q = \Delta Q_H^0 + \Delta Q_A^0 - g_H\theta_H - g_A\theta_A, \quad (7)$$

where the coefficients $g_H$ and $g_A$ include the mutual interactions of the chemisorbed species. Equation (6) may now be written in the form

$$r_h = k'\theta_H\theta_A \exp \beta(g_H\theta_H + g_A\theta_A). \quad (8)$$

For the chemical potential of adsorbed hydrogen at an intermediate coverage with adsorbed species of the organic compound present on the surface, we can write (*10*), taking into account the mutual interactions of the chemisorbed species,

$$\mu_H = RT(f_H\theta_H + f_A\theta_A) + \mu_H^0. \quad (9)$$

In a medium involving hydrogen ions, the adsorbed hydrogen is in equilibrium with the ions, so that

$$f_H\theta_H = a - EF/RT - f_A\theta_A. \quad (10)$$

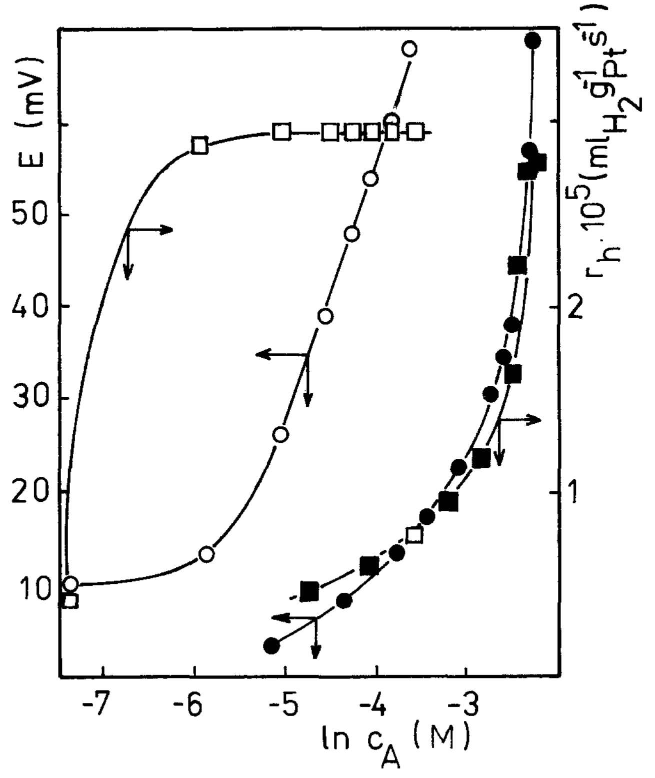

FIG. 3. Potential (○, ●) and hydrogenation rate (□, ■) as a function of maleic acid concentration. Initial concentrations $c_A^0 = 0.026$ *M*, $R = 4.55 \times 10^{-8}$ mol/cm$^5$ (○, □) and $c_A^0 = 0.103$ *M*, $R = 1.77 \times 10^{-7}$ mol/cm$^5$ (●, ■), 1 *M* $H_2SO_4$, Pt black with $S_{Pt} = 2.9$ m$^2$/g.

Combining Eqs. (8) and (10), we obtain

$$r_h = k''\theta_H\theta_A \exp(-\beta g'_H EF/RT + \beta g''_A\theta_A), \quad (11)$$

where $k'' = k' \exp \beta g_H a/f_H$, $g'_H = g_H/f_H$, and $g''_A = g_A - g'_H f_A$. In hydrogenation of an unsaturated compound at a potential of about 0.05 V (versus an equilibrium hydrogen electrode in the same medium), the surface coverage by the adsorbed compound and hydrogen is intermediate, so that the preexponential term is negligible with respect to the magnitude of the exponential term and can be omitted (*6, 7*). Thus Eq. (11) can be rewritten as

$$r_h = k''' \exp(\beta g''_H EF/RT). \quad (12)$$

It has been established (*11, 12*) that the variation in the adsorption of an organic compound with its concentration in solution can be described by the Temkin isotherm

$$\theta_A = a_A + (1/f) \ln c_A, \quad (13)$$

where $a_A$ is a constant, and $f$ is a factor related to the surface heterogeneity. However, the degree of surface coverage by adsorbed organic compound depends on the potential, especially in the potential region where hydrogen can be adsorbed simultaneously, so that Eq. (13) only holds for a constant value of the potential. Based on experimental values for $\theta_A$ and $\theta_H$ (*7*) on platinum black, the dependence of $\theta_A$ on $c_A$ and $E$ at potentials $E \lesssim 0.2$ V can be expressed by the approximate empirical relationship

$$\theta_A = a_A + k_E(E - E^0) + (1/f) \ln c_A. \quad (14)$$

Combining Eqs. (14) and (12), we obtain for the hydrogenation rate

$$\ln r_h = k_h + (\beta g''_A/f)\ln c_A - \beta\gamma E, \quad (15)$$

where $k_h = \ln k''' + \beta g''_A a_H - \beta g''_A k_E E^0$, and $\gamma = g'_H F/RT - k_E g''_A$. Equation (15) indicates that the condition for the hydrogenation to proceed as a zero-order reaction is that $\partial E/(\partial \ln c_A)$ = constant in the region of constant $r_h$. The experimentally determined dependences represented in Figs. 2 and 3 demonstrate that this condition is fulfilled. Equation (15) also indicates that the hydrogenation rate should decrease with decreasing concentration of unsaturated compound and the corresponding reduction in $\theta_A$. The decrease in the hydrogenation rate is, however, offset by an acceleration of the reaction rate due to a shift of the catalyst potential in the negative direction.

Relationships similar to Eqs. (14) and (15) can be derived on the basis of the hydrogenation model proposed by Horiuti and Polanyi (*13*), according to which hydrogen adsorbed on the catalyst surface by a disproportionation reaction reacts with the adsorbed unsaturated compound:

$$H_{2,g} \rightarrow H_{2,s} + M \rightarrow 2H_{ad} \quad (A)$$

$$A_s + M \rightarrow A_{ad} \quad (B)$$

$$A_{ad} + H_{ad} \rightarrow AH_{ad}. \quad (C)$$

The semihydrogenated species $AH_{ad}$ then reacts with another adsorbed hydrogen to yield the final product

$$AH_{ad} + H_{ad} \rightarrow AH_2. \quad (D)$$

In the presence of $H^+$ ions, the following equilibrium is set up in the reaction medium:

$$H_{ad} \rightleftharpoons H^+ + e. \quad (E)$$

The adsorption rate of the unsaturated compound can be described by the Roginsky–Zeldovich equation (*11, 12*)

$$\vec{r}_B = \vec{k}_B c_A \exp(-\alpha_A\theta_A). \quad (16)$$

In the steady state, we have

$$r_C = r_D = r_A = \vec{r}_B - \overleftarrow{r}_B. \quad (17)$$

If the adsorbed compound is removed from the surface at a sufficient rate, then $\vec{r}_B \gg \overleftarrow{r}_B$, and the adsorption rate equals the hydrogenation rate, for example, $r_C$. The reaction rate $r_C$ can be expressed by

$$r_C = r_h = k''\theta_A\theta_H \exp\beta(g_A\theta_A + g_H\theta_H),$$

which is Eq. (8).

On the basis of Eq. (16), we can write

$$\vec{k}_B c_A \exp(-\alpha_A\theta_A) = k''\theta_A\theta_H \exp(g_A\theta_A + g_H\theta_H). \quad (18)$$

For the equilibrium of reaction E, we have

$$\theta_H/(1 - \theta_T)\exp(f_A\theta_A + f_H\theta_H) = \text{constant } c_{H^+}\exp(-EF/RT). \quad (19)$$

Neglecting the preexponential term in Eq. (19), we obtain the above Eq. (10). If the species involved in equilibrium (E) are the same as those taking part in reaction (C), then the respective coefficients $f$ and $g$ should be identical (*14*). Under these conditions, however, we cannot arrive at Eqs. (14) and (15). If, on the other hand, the reaction involves the formation of a surface complex (*14*), or if we invoke the concept of catalytic domains (*15*), i.e., areas of immediately adjacent species $A_{ad}$ and $H_{ad}$ and islands comprising species of one kind only, then $g_H \neq f_H$ and $g_A \neq f_A$. The experimental results only conform to the latter concept, so we can assume that this model is real. Combining Eqs. (18) and (10) and neglecting the preexponential terms $\theta_A$ and $\theta_H$, we obtain

$$\theta_A = a'_A + (1/f)\ln c_A + (g'_H/f)EF/RT, \quad (20)$$

where $a'_A = (1/f)\ln \vec{k}_B/k'$ and $f = g''_A + \alpha_A$. This relationship is equivalent to Eq. (14). Substitution of this expression into Eq. (12) for the hydrogenation rate $r_h$ leads to a relationship equivalent to Eq. (15). (The same results are obtained for $r_C \gg r_D$).

The derivative of Eq. (20) leads to a fundamental conclusion. The adsorption isotherm described by Eq. (20) does not represent a conventional thermodynamic equilibrium between $\theta_A$ and $c_A$, but a steady-state value of $\theta_A$ attained when the rate of adsorption equals the rate of hydrogenation. Such a steady-state adsorption isotherm, formally identical with the Temkin equilibrium adsorption isotherm, has been derived and considered by Biegler and Koch (*16*) for the electrochemical oxidation of methanol on a platinum electrode.

The concept of a steady-state value of $\theta_A$ immediately suggests an explanation for the fact that in systems with high $R$ the hydrogenation does not occur as a zero-order reaction, but instead the hydrogenation rate decreases markedly with time. Apparently, the reason for this is that in a reaction mixture with a high concentration of unsaturated compound, the balance between the adsorption and hydrogenation rates is disrupted, with the result that the unreacted unsaturated compound A accumulates on the catalyst surface, blocking increasingly larger surface area of the catalyst.

When no $H^+$ ions are present in the reaction medium, as is the case with nonpolar solvents, one cannot speak of the electrochemical potential, since no equilibrium between $H^+$ and $H_{ad}$ is set up on the catalyst surface. Nevertheless, as implied by Eq. (9), the chemical potential of adsorbed hydrogen is influenced by the adsorbed unsaturated compound. Thus, as the concentration $c_A$ decreases, the corresponding change in the chemical potential instead of an electrochemical potential change accelerates the hydrogenation reaction. However, those changes cannot be measured experimentally.

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