Investigation on the Electrode Process of Acetophenone by Faradaic Rectification Method

by

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The periodic variation of electrode potential about a mean potential when the electrode is polarized by a sinusoidal current was found by Doss and Agarwal¹⁾, and is known as rectification by electrode reaction. This rectification which is generally known as the faradaic rectification was analyzed from asymmetrical current-potential curves with respect to the equilibrium potential. Barker and his coworkers devised the method which measures the rectification voltage when the electrode is polarized by an amplitude-modulated radio frequency current. The inherently fast electrode processes were studied by this method²⁾. Delahay and his coworkers discussed the faradaic rectification of the fast electrode processes and the electrode processes with preceding chemical reaction³⁾ or with adsorption⁴⁾. Using the faradaic rectification method, Agarwal found that the transfer coefficient of quinhydron is affected by hydrogen ion⁵⁾.

In this paper the electrode process of acetophenone in acid medium was studied by the same method as was devised by Barker and his coworkers. The experimental rectification voltage of acetophenone was calculated from square wave and radio frequency polarograms⁷⁾. On the other hand, assuming that the protonization of acetophenone plays the part of preceding chemical reaction⁶⁾ and this backward rate is very great, a theoretical rectification voltage was derived for charge transfer reaction with preceding chemical reaction³⁾. The experimental rectification voltage was discussed from this theoretical rectification voltage. It is concluded that the rectification voltage of acetophenone is not affected by the hydrogen ion.

Theoretical Consideration

Relationship between the mean potential of mercury electrode and the bulk concentration of reactants—Assuming that the electrode process is represented by eqs. (1) and (2) in acid medium⁶⁾, eqs. (3), (4) and (5) are introduced from Fick's differential equation.

$$\frac{\partial C_a(x, t)}{\partial t} = D_a \frac{\partial^2 C_a(x, t)}{\partial x^2} - k_1[\text{H}^+]C_a(x, t) + k_2C_o(x, t) \quad (3)$$

$$\frac{\partial C_o(x, t)}{\partial t} = D_o \frac{\partial^2 C_o(x, t)}{\partial x^2} + [k_1\text{H}^+]C_a(x, t) - k_2C_o(x, t) \quad (4)$$

$$\partial C_r(x, t)/\partial t = D_r \partial^2 C_r(x, t)/\partial x^2 \quad (5)$$

where x is the distance from the electrode and t the elapsed time. In eqs. (3) and (4), k_1 and k_2 are the forward and backward rate constant of protonization (1), respectively. In eqs. (3), (4) and (5), $C_a(c, t)$, $C_o(x, t)$ and $C_r(x, t)$ are the bulk concentration of acetophenone, protonized acetophenone cation and acetophenone free radical, respectively, and D_a , D_o and D_r the diffusion constant of acetophenone, protonized acetophenone cation and acetophenone free radical, respectively.

When the initial and boundary conditions are $C_a(x, 0) + C_o(x, 0) = C$, $C_r(x, 0) = 0$, $C_o(x, 0)/C_r(x, 0) = K (= [H^+][k_1/k_2])$, $C_a(\infty, t) + C_o(\infty, t) = C$, $C_r(\infty, t) = 0$, $C_o(\infty, t)/C_r(\infty, t) = K$, $\partial C_a(0, t)/\partial x = 0$, $\partial C_o(0, t)/\partial x = -\partial C_r(0, t)/\partial x = \text{const. } t^{-1/2}$, and then $[H^+][k_1 + k_2] \gg 1$ and $C_o(0, t)/C_r(0, t) = \exp\{nF(E - E_0)/RT\}$ where n is number of electrons, F the Faraday constant, E the mean potential of mercury electrode, E_0 the standard potential, R the gas constant and T the absolute temperature, one obtains eqs. (6), (7) and (8).

$$C_a(0, t) = CP/\{K + (1 + K)P\} \quad (6)$$

$$C_o(0, t) = CKP/\{K + (1 + K)P\} \quad (7)$$

$$C_r(0, t) = CK/\{K + (1 + K)P\} \quad (8)$$

where $P = \exp\{nF(E - E_0)/RT\}$.

The theoretical rectification voltage of acetophenone— When $k_1/k_2 \ll 1$, a theoretical rectification voltage for the electrode process of eqs. (1) and (2) can be obtained for a charge transfer reaction with preceding chemical reaction³⁾ from the bulk concentration of eqs. (6), (7) and (8). It is expressed as ΔE_∞ in eq. (9).

$$\Delta E_\infty = (nF/RT) V^2 \left[\frac{2\alpha - 1}{4} + \frac{r_s \{(1 - \alpha)r_R - r_o\} + y_s \{(1 - \alpha)y_R - y_o\}}{2(r_s^2 + y_s^2)} \right] \quad (9)$$

where V is the amplitude of alternating voltage, $r_s = r_o + r_R + r_{ct}$, $y_s = y_o + y_R$, $r_o = (\omega^{-1/2} + f)$, $y_o = (\omega^{-1/2} + g)/P$, $r_R = y_R = \omega^{-1/2}$ and $r_{ct} = (2D)^{1/2}/k_a P^{1-\alpha}$. In the above eqs., k_a is the apparent standard rate constant, α the transfer coefficient, $f = \{(\omega^2 + k_2^2)^{1/2} + k_2\}^{1/2}/(\omega^2 + k_2^2)^{1/2}$ and $g = \{(\omega^2 + k_2^2)^{1/2} - k_2\}^{1/2}/(\omega^2 + k_2^2)^{1/2}$ where ω is angular frequency. Eq.(9) does not involve the hydrogen ion concentration as parameter.

Experimental

A Yanagimoto Radio Frequency Polarograph PF-500 was used throughout experiments. All the chemicals were of reagent grade. The electrolytic solutions which contained 0.1mM acetophenone, 1M KCl and 1.0% ethanol in acid medium (pH 2.50–4.23) were prepared.

After dissolved oxygen in the electrolytic solution was removed by bubbling nitrogen gas, direct current, square wave and radio frequency polarograms were measured at $25 \pm 0.5^\circ\text{C}$ in electrolytic cell with the dropping mercury electrode and the mercury pool electrode.

Results

Examination on the rate constant of the protonization by direct current polarographic method—The half wave potential was measured at pH 2.50–4.23 and the relation-

Fig. 1. Relationship between pH and half wave potential.
0.1mM acetophenone+1M KCl+1.0% ethanol Temperature ; 25°C.

Fig. 3. Relationship between wave height and amplitude of square wave at various mean potential of mercury drop.
Parallel capacitance ; $1\mu\text{F}$. Recorder sens. : $0.2\mu\text{A}/\text{mm}$. Amplifier sens. ; $1/100$, Gate : 1-9, Time constant ; 110 0.1mM acetophenone+1M KCl+1.0% ethanol at pH 3.60 Temperature : 25°C.

Fig. 2. Square wave and radio frequency polarograms at various pH.
Parallel capacitance ; $1\mu\text{F}$. Recorder sens. ; $0.2\text{A}/\text{mm}$. Amplifier sens. ; $1/100$, Gate ; 1-9 Time constant ; 110 (without r.f. pol.) 0.1 mM acetophenone+1 M KCl+1.0% ethanol Temperature ; 25°C.

Fig. 4. The rectification voltage of acetophenone.
Experimental rectification voltage : 0.1 mM acetophenone+1 M KCl+1.0% ethanol at pH 3.00-4.15 and at temp. 25.0°C. $\circ$ —0.455Mc/sec, $\bullet$ —1Mc/sec. Theoretical rectification voltage : $\alpha=0.4$ $D^{1/2}/k_a=7 \times 10^{-3} \text{ sec}^{1/2}$ and $k_2 \gg 10^6 \text{ sec}^{-1}$. —0.455Mc/sec, ---- 1Mc/sec.

ship between the half wave potential and pH is shown in Fig.1.

Square wave and radio frequency polarograms—Square wave and radio frequency polarograms were measured at pH 3.00–4.15 and are shown in Fig.2. The wave height of the square wave and radio frequency polarogram were expressed in an arbitrary unit.

Calculation of the experimental rectification voltage⁷⁾— The wave height of square wave polarogram was measured at the amplitude of square wave as great as 5–20mV and at various mean potentials of the mercury electrode. A linear relationship in Fig.3 exists between the wave height of the square wave polarogram and the amplitude of the square wave at pH 3.00–4.15. The experimental rectification voltage of acetophenone was calculated from such a linear relationship and the wave height of the radio frequency polarogram.⁷⁾ Its value is the same at the same pH and at the same mean potential of the mercury electrode and a relationship is shown in Fig. 4 in an arbitrary unit.

Discussion

Examination on the rate constant of the protonization by direct current polarographic method—Eq. (10) can be derived for eqs. (1) and (2) at 25.0°C.

$$E_{1/2} = E_0 + 0.0591 \log (k_1/k_2) + 0.0591 \log [H^+] - 0.0591 \log (1 + [H^+]k_1/k_2) \quad (10)$$

where $E_{1/2}$ is the half wave potential. According to eq. (10), one obtains $k_1/k_2 \ll 1$ from Fig. 1.

Square wave and radio frequency polarograms—The summit potential of the square wave polarogram shifts toward negative potential with increase of pH, but the shape of square wave polarogram is independent of pH and radio frequency polarograms show that the positive rectification effect decreases and the negative rectification effect increases with increase of pH (Fig. 2). When the positive rectification effect is equal to the negative rectification effect, the mean potential of mercury electrode is independent of pH. Its value is -1.33 V at 1MC and -1.35 V at 0.455 MC. This phenomenon can not be explained from Barker's discussion for single electrode process, $O + ne \rightleftharpoons R^{2)}$. Accordingly the other electrode process for acetophenone must be considered.

The rectification voltage—The experimental rectification voltage is independent of the hydrogen ion concentration (Fig. 4). According to eqs. (1) and (2), when $k_1 \ll k_2$, the theoretical rectification voltage in eqs. (9) will not involve the hydrogen ion concentration as the parameter. It can be inferred that the rectification voltage of acetophenone is equal to the theoretical rectification voltage in eqs. (9). Therefore, the electrode process of acetophenone is given by eqs. (1) and (2).

The rectification voltage of acetophenone is independent of the hydrogen ion concentration, but the square wave polarogram shifts negative potential with decrease of the hydrogen ion concentration. Accordingly the radio frequency polarogram varies with the variation of the hydrogen ion concentration (Fig. 2).

When $\Delta E_\infty = 0$ in eq. (9), eq. (11) is derived.

$$P^2 + (2\alpha - 1)D/k_a^2 P^2 + \{(2\alpha - 1)\omega^{1/2} - (1 - \alpha)\omega f\} (2D)^{1/2}/k_a P^{1+\alpha} - \{(1 + \omega^{1/2}f)^2 + (1 + \omega^{1/2}g)^2\}/2 = 0 \quad (11)$$

According to eq. (9) and (11), the theoretical rectification voltage in Fig. 4 can be calcu-

lated when $\alpha=0.4$, $D_{1/2}/k_a = 7 \times 10^{-3} \text{ sec}^{1/2}$ and $k_2 \gg 10^6 \text{ sec}^{-1}$.

Conclusion

From the experimental rectification voltage of acetophenone and the theoretical rectification voltage for eqs. (1) and (2), it was proved that the protonization of acetophenone plays the preceding chemical reaction.

According to eq. (9), the transfer coefficient of the electrode process of acetophenone is equal to 0.4 in acid medium.

The theoretical rectification voltage was calculated by NEC 2203. The author thanks Dr. M. Kito for this calculation.

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ファラダイック整流作用によるアセトフェノンの電極反応に関する研究

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Doss と Agarwal によって発見されたファラダイック整流作用を利用してアセトフェノンの電極反応の解析を試みた。装置は Barker らによって考案された、整流電圧を矩形波ポーログラフ法の矩形波振幅として利用する方法をとる柳本高周波ポーログラフ PF 509型である。

この装置によってアセトフェノンのポーログラムを測定すると、図2に示したように、矩形波ポーログラムは pH の増大とともに負電位に移行するがその波形はほとんど変化しない。他方高周波ポーログラムは pH の増大とともに正の整流効果が減少し負の整流効果が増す。この原因は、電極反応のもっとも単純な系 $O + ne \rightleftharpoons R$ に対する Barker の報告によると、転移係数の水素イオン濃度依存性が非常に大きいものと考えうるが、アセトフェノンの酸性溶液中の電極反応を単純な電極反応系として考えるにはつぎの二点で不可能と思われる。第1は周波数と高周波ポーログラムの関係について、pH 3.00 から 3.60 の間で負の整流電圧は 1MC/sec のときが 0.455MC/sec のときより大きい。第2は正の整流電圧と負の整流電圧が等しくなる電位は pH に依存しない。そこで整流電

圧を矩形波ポーログラムと高周波ポーログラムの波高より求めると図4に示す pH に依存しないものであった。

これらの点を説明できる系として、酸性溶液中のアセトフェノンの電極反応を Mauanovskuu らの報告から(1)と(2)式で示されるものとした。整流電圧は各々複極剤の電極界面濃度を Delahay らにより求められた化学反応が先行する整流電圧の方程式にあてはめることにより求めた。この時 $k_1/k_2 \ll 1$ とした。この(9)式の特徴は水素イオン濃度が変数として含まれていないことである。この式から pH に依存しない整流電圧第4図は説明できる。また前の2点は pH に依存しない整流電圧を矩形波振幅としたため、そして矩形波ポーログラムが pH の増大とともに負電位に移行すると考えればよい。そうすれば当然 pH に対して変化に富んだ高周波ポーログラムが観察されることになる。

以上よりアセトフェノンの電極反応は(1)と(2)式として考えることができる。そこで(9)式にしたがい $\alpha = 0.4$, $D_{1/2}/k_a = 7 \times 10^{-3} \text{ sec}^{1/2}$, $k_2 \gg 10^6 \text{ sec}^{-1}$ のとき整流電圧を計算した。この結果は図4に示す。