

## CYCLOVOLTAMMETRIC STUDY OF THE HOMOGENEOUS KETO-ENOL EQUILIBRIUM OF DIHYDROXYFUMARIC ACID IN ACID AND NEUTRAL MEDIA

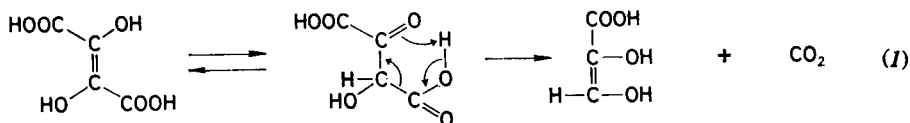
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The keto-enol equilibrium of dihydroxyfumaric acid (DHF) was investigated in acid and neutral buffer solutions by cyclic voltammetry. The keto-form decreases with increasing pH, so that in neutral region (pH = 6–8) the equilibrium is totally shifted to the enol-form of the acid. The thermodynamic constant,  $K_k$ , of the equilibrium: enol-DHF  $\rightleftharpoons$  keto-DHF, was estimated at different pH and temperatures. The thermodynamic parameters  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  of the above equilibrium were also determined in 0.5M-H<sub>2</sub>SO<sub>4</sub> solution.

In a recent study the decomposition of dihydroxyfumaric acid (DHF) in acid solutions has been investigated and the decomposition rates of the undissociated, the mono-anionic and the di-anionic forms of the acid have been calculated<sup>1</sup>. This decomposition is attributed to the decarboxylation of the keto-form of DHF according to the reaction:



The existence of an equilibrium between the keto- and the enol-form of DHF in aqueous solutions has also been proposed by other authors<sup>2,3</sup>.

From the two tautomer forms of DHF only the enol-form can be electrochemically oxidized to diketosuccinic acid<sup>4</sup>, which in aqueous solutions is converted to its hydrated form, the dihydroxytartaric acid<sup>1,5-7</sup>.

In the present study the keto-enol equilibrium of DHF in acid and neutral buffered solutions is investigated using cyclic voltammetry on a hanging mercury drop electrode (HMDE).

### EXPERIMENTAL

Cyclic voltammetric  $i$ - $E$  curves at a HMDE were obtained as described previously<sup>1</sup>.

Dihydroxyfumaric acid "Pract" (Fluka) and "zur Synthese" (Merck) were purified by multiple recrystallizations from absolute ethanol until the final samples showed exactly the same electrochemical behaviour in a buffer  $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$  ( $\text{pH} = 7.4$ ) solution.

In order to avoid possible auto-oxidation or decomposition of DHF, and for minimizing the dissolution time of DHF in a buffer solution, a fresh solution of DHF in pure pre-deaerated methanol was prepared. This solution was continuously kept in an Ar atmosphere. After the deaeration of the supporting electrolyte (40 ml), 2 ml of this solution was removed and the same quantity of the methanolic solution of DHF was added. Then, the cyclic voltammogram was immediately recorded.

Different buffer solutions at a constant ionic strength of  $0.3\text{M}$  were used such as citric acid-potassium citrate ( $\text{pH} = 2-5$ ) and  $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$  ( $\text{pH} = 5-8$ ), all obtained from Fluka A.G. (Swiss). The DHF solubility is very low in the presence of  $\text{Na}^+$  on the contrary to the  $\text{K}^+$  used, where the acid is sufficiently soluble. Sulfuric acid and the other chemicals were of the highest purity available and were dissolved in triply distilled water.

The pH of each solution was checked after the DHF dissolution with a Radiometer PHM 64 pHmeter.

## RESULTS AND DISCUSSION

Curve 1 of Fig. 1 shows the cyclic voltammogram of DHF ( $10^{-3}$  mol/l) taken at pH 7.3 by dissolving the appropriate amount of depolarizer in the pre-deaerated supporting electrolyte. In this pH region (6-8) the  $i_p$  of DHF remained unchanged in an inert atmosphere even after 12 hours, showing no decomposition. This wave is diffusion controlled and its peak current is proportional to the DHF concentration.

It is well known that the keto-enol equilibrium is an acid-base catalyzed reaction and that the keto-form of DHF, as a  $\beta$ -ketoacid, undergoes decarboxylation. So, as the pH of the solution decreases the equilibrium is shifted to the keto-form and the decarboxylation takes place according to the kinetic equation of a first order reaction. Extrapolating to the zero time the  $\log i_p - t$  diagram, the peak current at zero time,  $(i_p)_0$ , can be determined. This value was found to vary with pH and it was identical with the corresponding  $i_p$  value of the voltammogram as it has been described in the experimental section (Fig. 1, curves 2-4). These voltammograms are also irreversible and controlled by diffusion. The peak current varied linearly with  $v^{1/2}$  and DHF concentration with a temperature coefficient of about 1.7%, showing no kinetic character. Here must also be pointed out that the 5% (v/v) content of methanol in the final solution had no effect on the shape and height of the wave.

On the other hand, the peak current at zero time at a certain pH is proportional to the enol-form of DHF, since only this form is oxidizable, and its difference from the  $i_p$  at  $\text{pH} = 7$  expresses the concentration of the keto-form of the acid at the same pH. From these two concentrations the constant of the keto-enol equilibrium can easily be calculated.

The % amount of the enol and keto forms of DHF at  $25^\circ\text{C}$  in the pH region

studied is shown in Fig. 2. From this plot it can be seen that the quantity of the enol-form levels off at its maximum value at pH 6–8, where no decomposition of the acid occurs.

TABLE I

Percentage of enol and keto forms of DHF and values of equilibrium constant in 0.5M-H<sub>2</sub>SO<sub>4</sub> at different temperatures

$t, ^\circ\text{C}$	% Enol	% Keto	$K_k$
15	87.65	16.87	0.19
20	81.71	18.29	0.22
25	77.69	22.31	0.29
30	74.24	25.76	0.35
35	71.78	28.22	0.39

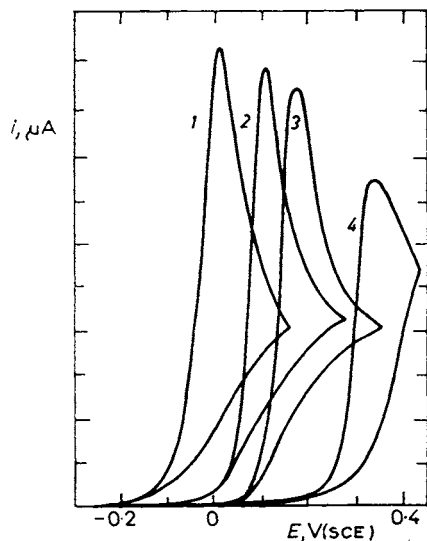


FIG. 1

Cyclic voltammograms of  $2.5 \cdot 10^{-3}$  mol/l DHF on a HMDE ( $A = 3.51 \cdot 10^{-2}$  cm<sup>2</sup>) at zero time: 1 pH = 7.3; 2 pH = 3.75; 3 0.005 mol/l H<sub>2</sub>SO<sub>4</sub>; 4 1 mol/l H<sub>2</sub>SO<sub>4</sub>.  $v = 100$  mV/s

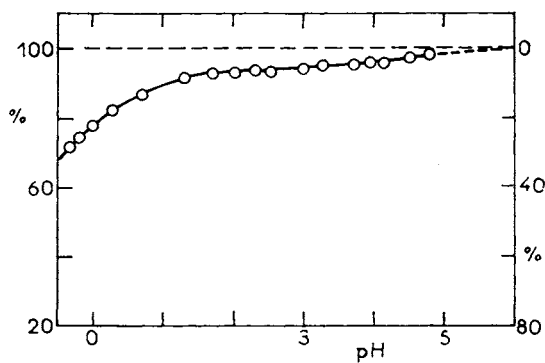


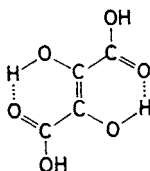
FIG. 2

Variation of the percent enol-keto forms of DHF with pH; left-hand side enol-DHF form, right-hand side keto-DHF form

Following the same procedure at different temperatures the ratio of the keto-enol tautomers and hence the equilibrium constant was also determined in 0.5M sulfuric acid. The above experimental data are gathered in Table I.

In our experiments the temperature was varied between 15°C and 35°C and from the slope and intercept of the  $\log K_k - 1/T$  diagram the values of  $\Delta H = 27.6$  kJ/mole and  $\Delta S = 82.4$  J/mole deg were calculated. Using  $K_{k(25)}$ , a value of 3.1 kJ/mole for  $\Delta G$  was also obtained. These values agree reasonably well with the corresponding values of other keto-enol equilibria already given in literature<sup>8</sup>.

From the  $\Delta G$  value of the equilibrium enol-DHF  $\rightleftharpoons$  keto-DHF results that the enol-form of DHF is the more stable one. This form is stabilized by a double internal hydrogen bonding, which is unavailable to the keto-form.



The existence of DHF only as the enol-form of the *trans* isomer in its solid state, could be also explained by the above-mentioned intramolecular two six-membered rings, since hydrogen bonds can also exist in the solid phase<sup>9</sup>.

It is also well known that the keto-enol equilibrium is greatly affected by solvent and temperature. Thus, in acid aqueous solutions the keto-form is about 30%, while in pure methanol the equilibrium is totally shifted to the enol-form. Furthermore, the enol-form becomes less stable with increasing temperature (Table I) suggesting that the intramolecular hydrogen bondings are increasingly broken up at a higher temperature.

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