INFLUENCE OF PROTONS ON ELECTROCHEMICAL BEHAVIOUR OF THE SYSTEM QUINONE–HYDROQUINONE IN DICHLOROMETHANE

Josef HANZLÍK and Zdeněk SAMEC

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 102 00 Prague 10

Additions of strong acids to a solution of quinone in dichloromethane lead to protolytic equilibria which have a marked influence on its electrochemical behaviour. In the presence of free protons, the electroactive species is the monoprotonated form of quinone, QH^+, and at higher acid concentrations the species QH_2^{2+} is formed with the acidity constant $pK(QH^+/QH_2^{2+}) = 1\cdot2$. The overall equilibrium EC reaction scheme necessarily involves also the protonated forms of hydroquinone, at least the species QH_3^+ which is, in contrast to the inactive hydroquinone, electroactive on the dropping mercury electrode in the medium of dichloromethane.

Quinones play an important role as electron mediators in biological processes including photosynthesis. Also the quinhydrone electrode is reported in textbooks as a tool in pH-metry. Accordingly, the redox properties of the quinone–hydroquinone system have been constantly studied by electrochemical methods, as reported in an exhaustive review by Chambers[1].

The following redox reaction describes formally the electrochemical behaviour of the quinone (Q)-hydroquinone (QH_2) system in water

$$Q + 2e^- + 2H^+ \rightleftarrows QH_2. \qquad (1)$$

The results of its investigations suggest that the system is complicated, since both the reduction and oxidation proceed in a number of steps combined with exchange of a proton or electron and leading to many intermediate products[2].

An important progress was achieved by investigations of the system Q/QH_2 in aprotic media[3], where the concentration of free protons is negligible, and where the simplest scheme of the electrode process is

$$Q \rightleftarrows Q^- \rightleftarrows Q^{2-}. \qquad (2)$$

The reduction proceeds in two consecutive one-electron steps which under the usual conditions are polarographically reversible. The concentrations of the electro-

active species Q, Q^- and Q^{2-} in the diffusion layer may be influenced by chemical reactions; this leads to changes of the recorded $i - E$ curves. Most typical perturbation effects are acid–base equilibria (preprotonation, protonation), formation of ion pairs and complexes, and disproportionation. All these may combine to modify the resulting mechanism[1]. If the influence of a single phenomenon is to be followed, all others must be kept constant during the experiment.

If an aprotic medium is used, the concentration of protons can be controlled and their effect on the redox process followed[4]. This was done in the present work dealing with the Q/QH_2 system in dichloromethane.

EXPERIMENTAL

Apparatus

Voltammetric measurements were carried out on a multipurpose electrochemical equipment[5] with an XY recorder (BAK 4T, Aritma, Prague) and a Tektronix 5103 oscilloscope. The ohmic potential drop between the tip of the Luggin capillary and the working electrode was compensated by a positive feed-back technique[6] using a stabilization circuit[7]. At higher sweep rates in cyclic voltammetry, the XY recorder was connected with a sample-and-hold circuit[8].

All measurements were carried out in a universal kit electrochemical cell[9] with a three-electrode system. The working electrodes were: a) Dropping mercury electrode (DME) with a drop time 3·17 s maintained by a drop time controller; the rate of flow of mercury was 0·559 mg/s at a height of mercury column 68 cm. b) Hanging mercury drop electrode E 410 (Metrohm, Switzerland). c) Stationary Pt electrode formed by a platinum wire of 0·5 mm diameter sealed in glass, planely ground and polished with metalographic emery paper. The reproducibility of the recorded curves was satisfactory.

A 2×2 cm square platinum foil served as auxiliary electrode. The potential values are referred to a calomel electrode OP 830 (Radelkis, Hungary) filled with 0·05 tetrabutylammonium chloride aqueous solution. The electrode was separated from the solution under study by a salt bridge provided with an S5 fritted glass disc. The bridge was filled with a solution of 0·1M tetrabutylammonium hexafluorophosphate in CH_2Cl_2 reaching 2 cm above the fritted glass, and the remaining space of the bridge was filled with an aqueous solution of 0·05M tetrabutylammonium chloride.

All operations and voltammetric measurements were done by using the Schlenk bottle technique[10] in the atmosphere of argon purified by a BTS catalyst (BASF, Ludwigshafen, GFR) and dried by passing over solid KOH and P_2O_5.

Chemicals

Dichloromethane of spectral purity (Uvasol, Merck, GFR) was used as solvent. It was stored over anhydrous calcium chloride and distilled with P_2O_5 through a column prior to use. The base electrolyte, tetrabutylammonium hexafluorophosphate, was prepared by neutralization of dilute hexafluorophosphoric acid (Merck) with 10% aqueous solution of tetrabutylammonium hydroxide. The white precipitate was filtered off, washed several times with water and recrystallized three times from aqueous ethanol (1 : 1). The white crystals were dried in vacuum oven at 100°C for 15 h.

Tetrabutylammonium chloride used for the reference electrode was prepared by neutralization of the base (Lachema, CSSR) with hydrochloric acid with potentiometric indication of the end point. The complex $H_3O[Co(C_2B_9H_{11})_2]$ or oxonium 3,3'-*como*-bis(undecahydro-1,2-dicarba--3-cobalta-*closo*-dodecabor)ate (HDCC) was prepared from its cesium salt as follows: 1 g of the cesium salt was suspended in 50 ml of 30% aqueous H_2SO_4, an equal volume of diethyl ether was added, and the mixture was shaken thoroughly. Shaking with further additions of sulphuric acid was repeated until the cesium passed quantitatively into the aqueous phase. The ether layer was then separated and ether was distilled off on a rotating vacuum evaporator. Drying was completed by using a rotation oil pump. The content of hydrogen ions (oxonium) in the product was determined alkalimetrically.

p-Benzoquinone (Lachema, CSSR) was twice resublimed in vacuum, hydroquinone (Lachema, CSSR) was several times recrystallized from ethanol. Other quinones and trifluoroacetic acid were from Merck.

RESULTS AND DISCUSSION

Electrochemical reduction of quinones in dichloromethane (under exactly aprotic conditions) is analogous to that in other aprotic solvents[4]. The mechanism of the electrode process on mercury electrode corresponds to Eq. (2): two reversible one--electron steps (EE mechanism) leading to the formation of mono- and dianion.

Influence of Water

Addition of water causes a pronounced shift of $E_{1/2}$ of the second polarographic wave (corresponding to the formation of the dianion) to more positive potentials. In the medium of dichloromethane saturated with water (*i.e.* containing 0·238 wt.% water[11]), the shift was 200, 220, and 260 mV for *p*-benzoquinone, vitamine K_1 and K_2, respectively, whereas the value of $E_{1/2}$ for the first reduction step was shifted to more positive potentials by 40 mV in all cases.

Interaction of a weak proton donor, such as water in CH_2Cl_2, with relatively strong bases Q^- and Q^{2-} leads to protonation according to the electrochemical scheme given first by Hoijtink, according to whom the electron affinity of a protonated particle is higher than that of the corresponding nonprotonated form. The shift of the $E_{1/2}$ value is a result of the EC mechanism[12].

Influence of Strong Acids

The concentration of free protons in the medium of CH_2Cl_2 was increased by adding strong acids HDCC or trifluoroacetic acid. The latter is electroinactive in the potential range under study; the anion DCC^- is reduced on DME in a one-electron step at $-1·32$ V and does not interfere with the polarographic effects of interest which occur at more positive potentials. The influence of increasing proton concentration on the polarographic behaviour of *p*-benzoquinone is shown in Fig. 1; curve *1* corresponds to the absence of the acid, the reduction proceeding according to Eq. (2), while

curve *5* corresponds to an excess of hydrogen ions, $[H^+]/[Q] = 50$. In this case, the electrode process proceeds in a single step and the limiting current corresponds to the transfer of two electrons. The difference of the half-wave potentials of the waves *A* and *E* is 1 V. Such a large change of the $E_{1/2}$ value can be explained by assuming profound changes in the chemical structure. This is supported by the fact that the current in the potential region of waves *C* and *D*, which are hardly distinguishable in most cases, is directly proportional to the acid concentration even at the lowest concentrations, and the electrode process is controlled by diffusion. At the same time, the half-wave potential of wave *B* is shifted to more positive potentials and the wave height diminishes. The increase of the current in the region of hydrogen evolution was not observed up to the ratio of $[H^+]/[Q] = 10$, evidence that the concentration of free protons at the electrode was zero. Hence, the protons were consumed in chemical reactions and could not reach the electrode. Analogous voltammetric behaviour was observed on the stationary mercury and platinum electrodes.

Increasing the proton concentration further led to the appearance of another wave *E* with $E_{1/2} = +0.650$ V, which increased with the concentration of protons at the expense of wave *C* until it reached the height corresponding to a two-electron process. Wave *C* with $E_{1/2} = +0.450$ V prevails at $[H^+]/[Q] > 1$. It is clear that waves *C* and *E* correspond to species formed by interaction of the quinone with free protons. Protolytic equilibria lead to the formation of particles QH^+ (wave *C*) and QH_2^{2+} (wave *E*) which are in equilibrium with quinone molecules. From polarographic data the value of $pK(QH_2^{2+}/QH^+) = 1.2$ was calculated.
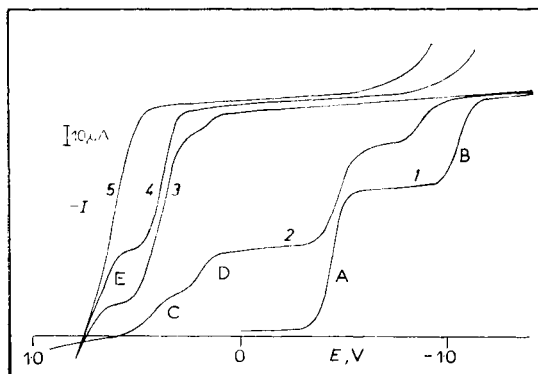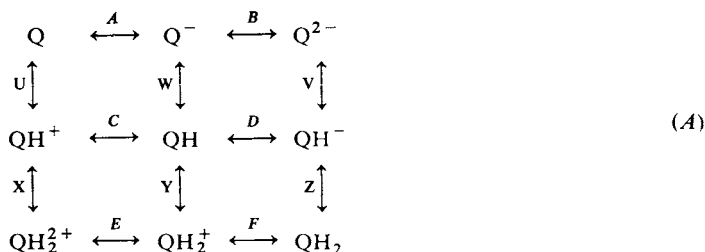

FIG. 1

Influence of trifluoroacetic acid on the polarographic behaviour of *p*-benzoquinone (0.002 mol . . dm^{-3}) in dichloromethane in the presence of 0.1 mol dm^{-3} N(C$_4$H$_9$)$_4$PF$_6$. Molar ratio of $[H^+]/[Q]$: *1* 0; *2* 1; *3* 20; *4* 30; *5* 50

The following scheme involving nine species with hydroquinone QH_2 as the end product of the reduction of quinone in the presence of proton donors was proposed[4].

$$
\begin{array}{ccccc}
Q & \overset{A}{\longleftrightarrow} & Q^- & \overset{B}{\longleftrightarrow} & Q^{2-} \\
U\updownarrow & & W\updownarrow & & V\updownarrow \\
QH^+ & \overset{C}{\longleftrightarrow} & QH & \overset{D}{\longleftrightarrow} & QH^- \\
X\updownarrow & & Y\updownarrow & & Z\updownarrow \\
QH_2^{2+} & \overset{E}{\longleftrightarrow} & QH_2^+ & \overset{F}{\longleftrightarrow} & QH_2
\end{array}
\qquad (A)
$$

However, in contrast to the behaviour of quinone in other solvents[13,14], it was found that hydroquinone in dichloromethane is not oxidized on the DME in the available potential range.

Addition of a strong acid leads to the formation of an oxidation wave with $E_{1/2} = +0.760$ V which increases with the acid concentration while $E_{1/2}$ is shifted to more positive values. Cyclic voltammogram (Fig. 2) shows under these conditions peak H on the anodic branch and at low sweep rates only peak C as in the case of acetonitrile[4]. At sweep rates higher than 0·05 V/s, peak E appears forming a redox couple with peak H. The dependence of the height of peak E on the rate of change of the applied voltage suggests, according to the theory of cyclic voltammetry[16], that the electrode process of peak E proceeds by the ECE mechanism, whereas the current of peak H is controlled by diffusion.

Based on the above facts, the reaction scheme (A) must be supplemented by additional terms involving the protolytic equilibria of hydroquinone, which were ob-
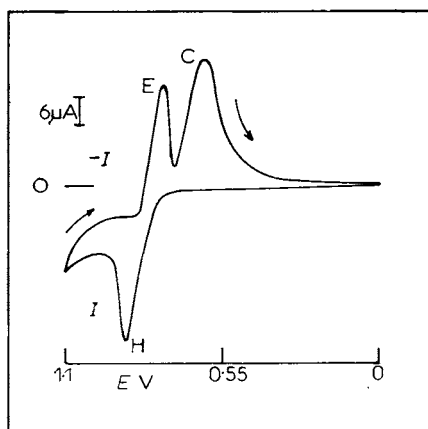

Fig. 2

Cyclic voltammogram of hydroquinone (0·002 mol dm^{-3}) on stationary DME in dichloromethane containing excess of trifluoroacetic acid. Starting potential $+1·10$ V, polarization decreasing to negative values, sweep rate 0·195 V/s, $[H^+]/[QH_2] = 50$

served as yet only in systems of hard acids[15]. At least the particle QH_3^- must be considered in the medium given. With respect to the position of peak E and its kinetic character, the EEC mechanism seems more probable than ECE. Peak E corresponds to reduction of QH_2^{2+} ions formed by two-electron oxidation and splitting off a proton according to

$$QH_3^+ - 2\,e^- \;\rightleftarrows\; QH_3^{3+} \;\rightleftarrows\; QH_2^{2+} + H^+ . \qquad (3)$$
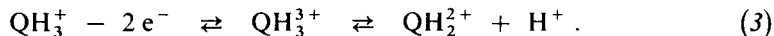
The ion QH_3^{3+} is short lived relative to the time scale of the experiment, and it decomposes to QH_2^{2+}, which is in protolytic equilibrium with QH^+, and this is reduced in peak C. We shall attempt to prove the existence of protonated forms of quinone and hydroquinone in analogous media by using the NMR method.

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