

Redox Behaviour of Hydroquinone in Aqueous and Non-aqueous Solutions

L R SHARMA* & ARUN SHARMA

Department of Chemical Engineering & Technology
and

GURCHARAN SINGH

Department of Chemistry, Panjab University, Chandigarh 160 014

Received 12 May 1986; accepted 29 January 1987

Cyclic voltammetry of hydroquinone has been studied in aqueous and non-aqueous solutions at plain graphite electrode. The highly irreversible nature of the redox couple obtained in each case has been shown to be due to the electrogeneration of the redox system: hydroquinone \rightleftharpoons quinhydrone and not due to hydroquinone \rightleftharpoons benzoquinone as generally believed. The number of electrons involved in the overall anodic oxidation of hydroquinone to quinhydrone is one per molecule of hydroquinone.

Anodic oxidation of hydroquinone has been studied by several investigators in aqueous and non-aqueous solutions¹⁻¹⁹ and diverging opinions have been expressed whether the electrode reaction involves one-electron¹⁻⁴ or two-electron transfer. Views in favour of two-electron transfer to yield benzoquinone are now generally accepted. The redox behaviour of hydroquinone has been reported to be highly irreversible at solid microelectrodes^{6,10,13}, for which, however, no explanation appears to have been offered so far. The title investigation is an attempt in this direction. An attempt has also been made to resolve the controversy about the exact mechanism of the electrode reaction.

Materials and Methods

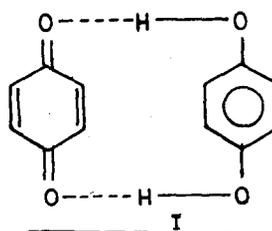
Hydroquinone (AR) was subjected to anodic cyclic voltammetry at plain compressed graphite electrode (specpure), both in aqueous and non-aqueous media. Sulphuric acid solutions of concentrations 1.0 M and 0.1 M, Britton-Robinson buffers of pH 2.2, 4.15, 6.0 and 8.5 and acetonitrile containing 0.2 M sodium perchlorate were used as the background solutions. Instrumentation, electrode assembly and experimental details are essentially the same as described earlier²⁰.

Results and Discussion

Cyclic voltammograms obtained for anodic oxidation of hydroquinone in all the background solutions were found to be almost similar exhibiting in each case a single redox couple. This has been attributed^{6,13} to the redox system: hydroquinone \rightleftharpoons benzoquinone + 2H⁺ + 2e⁻. Contrary to expectations, this redox system has been found to be highly irrever-

sible in all the background solutions with a distinct difference of over 450 mV between anodic and cathodic peak potentials. This indicates that the oxidation product is not benzoquinone but some other compound which reduces at a more cathodic potential than benzoquinone. This compound appears to be quinhydrone which is formed by the combination of electrogenerated benzoquinone with hydroquinone present in the diffusion layer. This contention is supported by our observation that exhaustive electrolysis of hydroquinone in all the background solutions at appropriate potentials invariably yields quinhydrone as the end product. Formation of quinhydrone from anodic oxidation of hydroquinone has also been reported by some other investigators as well^{6,14,15}.

The redox system generated during anodic cyclic voltammetry of hydroquinone is, thus, hydroquinone \rightleftharpoons quinhydrone and not hydroquinone \rightleftharpoons benzoquinone. Quinhydrone has the probable structure (I)



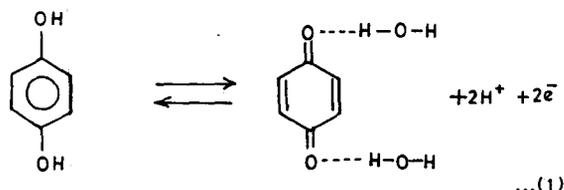
It is evident that (I) would undergo reduction at a more cathodic potential than benzoquinone. The above observations lead to an obvious conclusion that the number of electrons involved in overall anodic oxida-

tion of one molecule of hydroquinone to yield quinhydrone (I) is 1 since for the formation of (I), one needs 2 molecules of hydroquinone in accordance with the redox system: $2 \text{Hydroquinone} \rightleftharpoons \text{I} + 2\text{H}^+ + 2\text{e}^-$.

This contention is supported by the fact that the magnitude of anodic peak current for hydroquinone is found to be almost exactly half of that obtained for *o*-dianisidine ($n=2$) in aqueous solutions under identical conditions of concentration and potential scan rate. This conclusion negates the general belief that the number of electrons involved per molecule in anodic oxidation of one molecule of hydroquinone is 2.

Evidently, if during cyclic voltammetry, the electrogenerated benzoquinone is not in a position to combine with hydroquinone to form quinhydrone, the redox system generated should be hydroquinone \rightleftharpoons benzoquinone which shall give rise to a reversible redox couple. Such a situation does get created during cyclic voltammetry of quinhydrone. At the commencement of the voltammetric cycle, quinhydrone gets exposed to zero potential which is sufficiently cathodic to cause reduction of quinhydrone to hydroquinone. During the first forward scan it is this hydroquinone (and not quinhydrone) which undergoes oxidation to give benzoquinone. Since now there is no hydroquinone in the vicinity of the electrode surface, the electrogenerated benzoquinone does not get converted into quinhydrone.

Unexpectedly, however, the cyclic voltammograms of quinhydrone as obtained in sulphuric acid as well as in buffer solutions still exhibit a considerable difference of 310-350 mV between oxidation and reduction peak potentials. A probable explanation for this unexpected behaviour appears to emerge from the appreciable solubility of benzoquinone in water. It is very likely that benzoquinone gets hydrated through hydrogen bonding at the C=O groups thereby becoming not only hydrophilic and more soluble in water but also reluctant to get reduced like quinhydrone. Accordingly, hydrated benzoquinone also would undergo reduction at a more cathodic potential than benzoquinone. The redox system generated in this case is represented by Eq. (1).



The above observations readily suggest that if cyclic voltammetry of hydroquinone is carried out under conditions in which neither excess hydroquinone nor water is available in the diffusion layer to form quin-

hydrone or hydrated benzoquinone, as the case may be, the electrogenerated benzoquinone would remain as it is and the redox couple would behave completely reversibly. In order to verify this contention, cyclic voltammetry of quinhydrone was carried out in anhydrous acetonitrile containing 0.2 M sodium perchlorate as the supporting electrolyte. It is interesting to note that the cyclic voltammogram obtained under these conditions exhibited a redox couple which is almost completely reversible with a difference of only 40 mV between oxidation and reduction peak potentials.

An interesting point emerges from the above observations that the reversible redox system hydroquinone \rightleftharpoons benzoquinone is generated only during cyclic voltammetry of quinhydrone (and not of hydroquinone) and that too in non-aqueous medium. Anodic cyclic voltammetry of hydroquinone always generates an irreversible system hydroquinone \rightleftharpoons quinhydrone, whether the medium is aqueous or non-aqueous.

Effect of acidity of medium on redox potentials of hydroquinone

Cyclic voltammograms of hydroquinone obtained in various background solutions showed distinct shift in peak potentials with change in acidity of the medium particularly in the pH range of 2 to 8 (Table 1).

The oxidation peak potential remains the same in solutions of comparatively high acidity (entries 1-3 in Table 1). In solutions of low acidity (entries 4-6), there is a gradual shift of oxidation peak potentials in cathodic direction with increase in pH. This behaviour may be explained as follows:

In an oxidation reaction in which proton transfer follows the electron transfer step, the oxidation mechanism is represented by Eqs. (2) and (3)



According to Meites²¹, $E_{1/2}$ for the above oxidation reaction is given by Eq. (4)

Table 1—Redox Peak Potentials in Cyclic Voltammetry of Hydroquinone in Different Background Solutions

Sl No.	Background solution	Peak potentials (V)	
		Anodic	Cathodic
1	1.0 M H ₂ SO ₄	0.63	0.18
2	0.1 M H ₂ SO ₄	0.64	0.18
3	Buffers pH 2.2	0.64	0.10
4	pH 4.15	0.52	-0.01
5	pH 6.0	0.41	-0.10
6	pH 8.5	0.26	-0.18

$$E_{1/2} = E^0 + \frac{0.05915}{n} \log \frac{[H^+]^x K_c}{[H^+]^x K_c + 1} \quad \dots (4)$$

where K_c is the equilibrium constant for reaction (3). With some approximation, $E_{1/2}$ can be replaced by E_p , i.e., the peak potential.

For anodic oxidation of hydroquinone in 1.0 M and 0.1 M H_2SO_4 and buffer of pH 2.2, due to comparatively high $[H^+]$, the factor $[H^+] K_c$ is presumably much greater than unity so that Eq. (4) reduces to Eq. (5)

$$E_p = E^0 \quad \dots (5)$$

Accordingly, in these background solutions, the oxidation peak potential should remain unchanged as is actually the case (see Table 1).

In buffer solutions of pH 4.15, 6.0 and 8.5 due to low $[H^+]$, the factor $[H^+] K_c$ is presumably much smaller than unity so that Eq. (4) takes the form (6)

$$\frac{d(E_p)}{d(pH)} = \frac{0.05915}{n} \text{ at } 25^\circ\text{C} \quad \dots (6)$$

Accordingly, in these buffers, the oxidation peak potential should change by 0.05915 V for every one unit change in pH. That it is actually so is evident from the data given in Table 1. The numerical values of the factor $d(E_p)/d(pH)$ come out to be 0.061, 0.059 and 0.060 V in the pH ranges 2.2-4.15, 4.15-6.0 and 6.0-8.5, respectively. These values are in good agreement with the theoretical value of 0.05915 V.

The data in Table 1 show that the reduction peak potentials are also pH-dependent. However, their variation is not in accordance with Eq. (6). Since in the reduction process, proton transfer appears to pre-

cede the electron transfer step, some different equation would presumably be required to lend support to the reduction peak potential data. Nevertheless, it has not been possible so far to explore such an equation.

Acknowledgement

The authors are grateful to the UGC, New Delhi, for their liberal financial assistance.

References

- 1 Vetter K J, *Z Electrochem*, **56** (1952) 797.
- 2 Elving P J & Krivis A P, *Anal Chem*, **30** (1958) 1645.
- 3 Loshkarev M A & Tomilov B I, *Zh Fiz Khim*, **34** (1960) 1753; **36** (1962) 132, 1902.
- 4 Eggins B R, *Chem Commun*, (1972) 427.
- 5 Turner W R & Elving P J, *J Electrochem Soc*, **112** (1965) 1215.
- 6 Eggins B R & Chambers J Q, *Chem Commun*, (1969) 232.
- 7 Parker V D, *Electrochim Acta*, **18**(8) (1973) 519.
- 8 Parker V D, *Chem Commun*, (1969) 716.
- 9 Parker V D & Ebersson L, *Chem Commun*, (1970) 1289.
- 10 Adams R N, *Electrochemistry at solid electrodes* (Marcel Dekker, New York) 1969, pp. 366.
- 11 Ryba O, Petranek J & Pospisil J, *Colln Czech chem Commun*, **30** (1965) 843, 2157.
- 12 Muller O H & Baumberger J P, *Trans electrochem soc*, **71** (1937) 181.
- 13 Reddy S J & Krishnan V R, *Trans SAEST*, **16** (1981) 189.
- 14 Ely R E, *Ind Engng Chem (Anal Ed)*, **15** (1943) 284.
- 15 Gupta G L, *Curr Sci*, **33** (1964) 680.
- 16 Bagotsky V S & Vasilyev Yu B, *Electrochim Acta*, **9** (1964) 869.
- 17 Santhanam K S V & Krishnan V R, *Z phys Chem (Frankfurt)*, **39** (1963) 10.
- 18 Hale J M & Parsons R, *Trans Faraday Soc*, **59** (1963) 1429.
- 19 Morris J B & Schompf J M, *Analyt Chem*, **31** (1959) 286.
- 20 Sharma L R, Singh G & Sharma A, *Indian J Chem*, **25A** (1986) 345.
- 21 Meites L, *Polarographic techniques* (Wiley-Interscience, New York) 1965.