Kinetic Studies on Hydrogen Bonding in Quinone Anion Radical and the Dianion of Tetramethyl-1,4-Benzoquinone

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Summary: The kinetic of hydrogen bonding of tetramethyl-1,4-benzoquinone (duroquinone, DQ) anion radical and dianion with methanol and ethanol was investigated in DMSO. The hydrogen bonding equilibrium constant and the (hydrogen bonding) rate constants were evaluated through the use of linear scan- and cyclic- voltammetry. It was found that the monoanion radical hardly undergoes any hydrogen bonding with the above mentioned hydrogen bonding agents. The hydrogen bonding equilibrium constant, K_{eq}, for the process $DQ^{-\bullet} + e \rightleftharpoons DQ^{2-}$, $DQ^{2-} + m\,[HB] \rightleftharpoons DQ^{2-}(HB)_m$, (where HB is a hydrogen bonding agent and [ ] means large excess concentration) was found to be in the range of $2.3 \times 10^5\ M^{-m}$ to $2.2 \times 10^6\ M^{-m}$, whereas the rate constants k_m were found to be [O] $10^6\ M^{-m}\ s^{-1}$ for ethanol and [O] $10^7\ M^{-m}\ s^{-1}$ for methanol. The hydrogen bonding number m was found to be ~3 for both alcohols.

Keywords: Dianion, Hydrogen Bonding, Hydrogen Bonding Kinetics, Duroquinone, Hydrogen Bonding number.

Introduction

There has been a growing interest in the electrochemistry of quinones, substituted quinones and nitroarenes, and their electrochemically reduced products – anion radicals and dianions [1-6]. This interest is due to (a) the facile electron accepting property of quinones substituted quinones and nitroarenes and the stability of their anion radicals and dianions, (b) the ease with which these anion radicals and dianions can undergo hydrogen bonding and (c) the possibility of hydrogen bonding of these anion radicals and dianions with biologically important compounds [4-5].

Generally it is hydrogen bonding equilibrium process which has been studied and equilibrium constant determined [1-6]; kinetics of hydrogen bonding has, for some reasons, attracted less attention of workers.

Thus the kinetics of hydrogen bond formation and the number of hydrogen bonds formed in quinone anion radicals / dianion offers attractive area of study. It should be noted that a quinone has two electron attracting centers (two "O" atoms) thus this aspect - the geometry of hydrogen bonded complex could also be of some interest.

Cyclic voltammetry has been previously employed to study hydrogen bonding equilibrium process in quinone and nitroarenes anion radicals and dianions [5-7]. At the same time theories to deal with chemically coupled electrochemical processes for stationary electrode voltammetry (polarography, linear scan and cyclic-voltammetry) have been worked out and are available in the literature [8-10]. Thus it is attractive to explore the use of linear scan- / cyclic- voltammetry in studying the kinetics and equilibrium process of hydrogen bonding of anion radical and dianion of a quinone and thus to obtain the kinetics as well as equilibrium parameters. Also through linear scan- / cyclic- voltammetry one can obtain the number of hydrogen bonds formed.

Tetramethyl-1,4-benzoquinone also called duroquinone (DQ) exhibits two well defined reversible cyclic voltammograms in aprotic solvents [1-6]; thus DQ is a suitable substrate for the present study. The reduction processes of DQ, in the absence of any protic agent, are described as:

$$DQ + e \rightleftharpoons DQ^{-\bullet} \quad (1)$$

$$DQ^{-\bullet} + e \rightleftharpoons DQ^{2-} \quad (2)$$

where $DQ^{-\bullet}$ is the anion radical and DQ^{2-} the dianion of duroquinone.

Reduced species of DQ, could in the presence of H-bonding agent, undergo following processes [6]:

$$DQ^{-\bullet} + nHB \overset{K_1}{\rightleftharpoons} DQ^{-\bullet}(HB)_n \ ; \ K_1 = \frac{k_1}{k_{-1}} \quad (3)$$

$$DQ^{-\bullet}(HB)_n + e \rightleftharpoons DQ^{2-}(HB)_n \quad (4)$$

$$DQ^{2-}(HB)_n + (m-n)HB \overset{K_2}{\rightleftharpoons} DQ^{2-}(HB)_m; \ K_2 = \frac{k_2}{k_{-2}} \quad (5)$$

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Subscript numbers to K and k correspond to hydrogen bonding process of anion and dianions respectively.

Processes as given in eq. (1, 3-5) are E_rC_r (a reversible electron transfer followed by a reversible chemical reaction) processes and both k_1 and k_2 are pseudo-first order rate constants, hydrogen bonding agents being in large excess. Both E_rC_r and the complementary E_rC_i (a reversible electron transfer followed by an "irreversible" chemical reaction) processes have been investigated, studied – voltammetrically - and the format extensively used since early days of voltammetry [6-15].

Thus the present study focuses on obtaining a little *more detail* information on the dynamics of the H-bonding process of anion radical and dianion of a quinone. By more *detail* information it is meant, evaluation of K, k and m which can help us in understanding the mechanism of hydrogen bonding in biological systems [4, 5]. The quinone selected is DQ and HB are ROH (R = CH_3, C_2H_5).

Theory

According to Gupta and Linschitz [6], K_1 and K_2 can be evaluated through cyclic voltammetry from the expressions given in eqs. (6,7).

$$K_1 [HB]^n = \exp [f (\Delta E_{1/2})_1] - 1 \qquad (6)$$

where f = F/RT and $(\Delta E_{1/2}) = (E_{1/2})_1 - (E°_{1/2})_1$, where "1" denotes the first reduction process eqs. (1,3), $(E_{1/2})_1$, $(E°_{1/2})_1$ are half wave potential of eq. (1) in the presence and the absence of HB.

$$\exp [f (\Delta E_{1/2})_2] = \frac{1+K_2 [HB]^m}{1+K_1 [HB]^n} \qquad (7)$$

where $(\Delta E_{1/2})_2$ pertains eqs. (2) and (5); n and m are hydrogen bonding numbers for anion radicals and dianion respectively. As mentioned earlier $K_1 = 0$ means no hydrogen bonding of anion radical occurring. In such a case it is straight forward to evaluate K_2 from an equation analogous to eq. (6), replacing $(\Delta E_{1/2})_1$ by $(\Delta E_{1/2})_2$. An interesting limiting case is when $K_{1 \text{ or } 2} [HB]^{n \text{ or } m} >> 1$ and thus the number "1" can be ignored. In that case a plot of $(\Delta E_{1/2})_{1 \text{ or } 2}$ vs *ln* [HB] would give $K_{1 \text{ or } 2}$. From such a plot n or m can also be obtained [6]. E_rC_r equilibrium case, have been dealt by Nicholson and Shain [8] in detail, eqs. (8-9).

$$O + e \rightleftarrows R \text{ ; one electron transfer} \qquad (8)$$

$$R \overset{K_{NS}}{\rightleftarrows} Z \qquad (9)$$

where $K_{NS} = k_f / k_r$. Also $k_f + k_r = l$, and f and r symbolize forward and reverse reactions. NS means Nicholson and Shain.

For the above electrochemical process, eqs. (8-9), for the condition $K_{NS}\sqrt{a / l}$ and l/a both large, Nicholson and Shain [8] gave a useful equation eq. (10), (for n=1) relating E_p (peak potential), K_{NS}, l and a.

$$E_p = E°_{1/2} - \frac{RT}{F} [0.780 + ln \frac{K}{1+K} + \frac{1}{2} ln\, a - \frac{1}{2} ln\, l] \qquad (10)$$

where E_p is the observed peak potential pertaining to the processes given in eqs. (8-9), a = Fv/RT (for one electron transfer), v is the scan rate.

Process as given in eq. (1,3) is equivalent to the process given in eq. (8-9) since in the present case [HB] >> [R]. This turns eq. (3 or 9) to be "pseudo-first order" reaction and k_f to be considered pseudo-first order rate constant. Also K_{NS} of eq. (9) is identified as $K_{NS} = K_{1 \text{ or } 2} [HB]^{n \text{ or } m}$.

When $K_{NS} >> 1$, or equivalently when $k_f >> k_r$ then eq. (10) reduces to E_rC_i process.

$$E_p = E°_{1/2} - \frac{RT}{F} [0.78 - \frac{1}{2} ln\, k_f + \frac{1}{2} ln\, a] \qquad (11)$$

Rate constants $k_{n \text{ or } m}$ can be obtained from k_f as $k_{n,m} = k_f / [HB]^{n,m}$.

Equilibrium constants K_1 and K_2 can be evaluated from experimental linear- or cyclic-voltammograms using eq. (7) or its variants as described earlier. K_{NS} (= $K_{1 \text{ or } 2} [HB]^{n \text{ or } m}$) can then be used to evaluate l and hence k_f eqs. (10,11). In eq. (10) when $K_{NS} >> 1$, then eq. (11) can be used to *estimate* k_f from which $k_{n \text{ or } m}$ can be evaluated. If a monoanion radical does not undergo hydrogen bonding, then eqs. (4-5) can be modified as:

$$DQ^{-\bullet} + e \rightleftarrows DQ^{2-}$$

$$DQ^{2-} + m[HB] \overset{K_2}{\rightleftarrows} DQ^{2-}(HB)_m \qquad (12)$$

The H-bonding reaction of DQ^{2-} can be depicted as eq. (12), k_m can be conveniently obtained

through the use of the eq. (11). It is also be noted that $K_2' \equiv K_2$.

Since the reaction eq. (12) may be notated as,

$$R + m[HB] \rightleftharpoons Z \qquad (13)$$

where [HB] is in large excess, and under condition $k_f' >> k_r'$ where k_f' being a pseudo-first order rate constant, a rate constant k_m can now be defined as:

$$k_m = \frac{k_f'}{[HB]^m} \qquad (14)$$

Results and Discussion

The Hydrogen Bonding Equilibrium Constant

No significant hydrogen bonding was observed for $DQ^{-\bullet}$ anion radical by any of the two hydrogen bonding agents used in the present study. ($K_1 \rightarrow 0$), hence all calculations were done on the hydrogen bonding process of DQ^{2-}, eq. (12).

The H-bonding process is treated as E_rC_r process in the present case, hence equilibrium constant and H-bonding number could be obtained using the usual voltammetric equation as, say, used by Gupta and Linschitz [6]. The effect of added MeOH on the CV of $DQ^{-\bullet}$/ DQ^{2-} system is given in Fig 1. Similar CV was obtained for EtOH with hydrogen bonding agents. The plot of ($E_{1/2} - E°_{1/2}$) versus *ln* [HB] for H-bonding agent, CH_3OH, is given in Fig. 2. Similar plots were obtained for EtOH (figures not given). From such plots / data K_2' ($\equiv K_2$) (eq. 12) and m values are obtained. Values of K_2' ($\equiv K_2$) and m obtained from these plots are 2.2×10^6 M^{-m} and 2.3×10^5 M^{-m} for MeOH and EtOH H-bonding agents respectively; m values being 3.1 and 2.8 respectively which for calculation purpose may be rounded as m = 3 for MeOH and EtOH.

The values of K_2 and m (Table-1) seem to be of the right order of magnitude for MeOH and EtOH. Values for K_2 for the hydrogen bonding of DQ^{2-} by EtOH have been reported by Gupta and Linschitz [6] as 8.5×10^9. It is however noted that the values reported by Gupta and Linschitz are for the solvent PhCN (Z-value = 66) [15-16]. K_2 – values reported by Gupta and Linschitz for various substituted quinones in various solvents, are found to be quite sensitive to solvent polarity parameter Z–values. For example K_2 for DCBQ (Dichloro-Benzoquinone) is reported as 2.5×10^6 in PhCN (Z = 66); 1.2×10^4 in acetonitrile (Z = 71.3) and 1.9×10^3 in DMSO (Z = 71.1). In the present study DMSO has been used as the solvent, hence lower values of K_2 (and m) in the present case are not surprising. The reason for high values of K_2 in low Z–value solvent is obvious: hydrogen bonded species – a less polar moiety – is more stabilized in a less polar solvent.

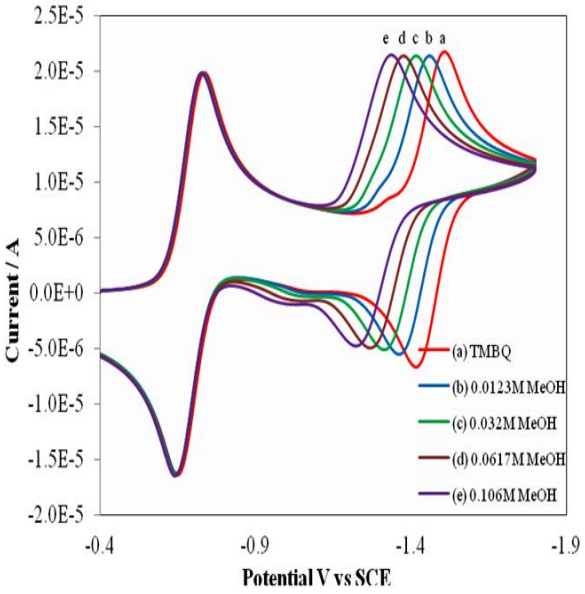

Fig: 1: Cyclic voltammogram of DQ in the absence and presence of MeOH as hydrogen bonding agent, concentration of DQ = 2mM in DMSO (0.1M TBAP); all potentials vs SCE. From a $\rightarrow$ e concentration of MeOH was added in the manner of 0M, 0.0123, 0.032, 0.0617, 0.106M MeOH.

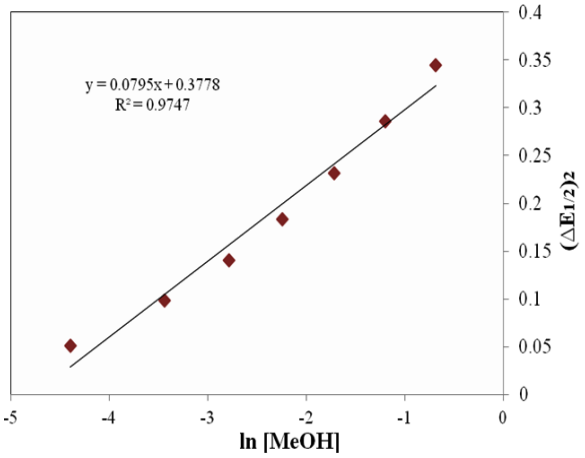

Fig. 2: Plot of $(\Delta E_{1/2})_2$ vs ln [MeOH] in DMSO.

Table-1: [a,b] Hydrogen Bonding Number (m), Equilibrium Constant (K_2) and Rate Constants (k_m) for DQ^{2-} - (MeOH, EtOH) Systems.

HB-agents	m [c]	K_2 [c] M^{-m}	k_m [d,e] $M^{-m}\,s^{-1}$	$k_{m=3}$ [d,f] $M^{-3}\,s^{-1}$	$k_{m=4}$ [d,g] $M^{-4}\,s^{-1}$
MeOH	3.1 (≅3)	2.2×10^6	$2.2(\pm2.0)\times10^7$ (m=3.1)	$1.6(\pm1.6)\times10^7$	$4.0(\pm1.4)\times10^8$
EtOH	2.8 (≅3)	2.3×10^5	$3.0(\pm2.1)\times10^6$ (m=2.8)	$4.9(\pm2.9)\times10^6$	$8.5(\pm4.5)\times10^7$

(a) Solvent DMSO, all potential referred to SCE, ***(b)*** $E°_{1/2}$ = -1.460V in the absence of HB agents for MeOH and EtOH respectively, ***(c)*** values obtained by plotting ($E_{1/2} - E°_{1/2}$) vs. *ln* $[HB]^m$, with statistical R^2 value 0.97, ***(d)*** $k_m = k_f' / [HB]^m$, average + SD values ***(e)*** k_m when m = 3.1 and 2.8 for MeOH and EtOH respectively, ***(f)*** $k_{m=3}$, when m = 3, ***(g)*** $k_{m=4}$, when m = 4.

The fractional or odd number of m could be due to an average value of equilibrium between two m-values – time averaged. For example m = 3 for MeOH (Table-1) could be due to the fast equilibrium between m = 2 and m = 4.

The Hydrogen Bonding Rate Constant

The most important part of H-bonding process is its kinetics, which, surprisingly, has not been paid attention to by earlier workers. This, kinetics study, has been an important and integral part of the present study. Thus evaluation of the hydrogen bonding rate constants has been carried out. The "pseudo-first order" rate constant k_f**'** were calculated [eq. (11)] from which, k_m defined as $k_f'/[HB]^m$, eq. (14), were calculated for the hydrogen bonding agents, MeOH and EtOH and are collected in Table-1. Rate constant values k_m were $2.2(\pm2.0)\times10^7$ $M^{-m}.s^{-1}$ (m = 3.1) and $3.0(\pm2.1)\times10^6$ $M^{-m}.s^{-1}$ (m = 2.8) for MeOH and EtOH respectively. For m = 3, the values of $k_{m=3}$ were $1.6(\pm1.6)\times10^7$ and $4.9(\pm2.9)\times10^6$ and for m = 4, the values of $k_{m=4}$ were $4.0(\pm1.4)\times10^8$ and $8.5(\pm4.5)\times10^7$ for MeOH and EtOH respectively.

It was noted that, for the two hydrogen bonding agents, fairly constant values of k_m were obtained. At very high concentration (for [MeOH] $\geq$ 0.062M and [EtOH] $\geq$ 0.12M) the value of k_m also gets very high and don't give constant values. The reason for such behavior could be either aggregation of H-bonded complexes, or higher m-values or a side reaction of the dianion which becomes prominent at higher concentration of H-bonding agents.

Hydrogen Bonding Number

An important parameter "hydrogen bonding number" or number of hydrogen bonds formed per anion radical / dianion of quinone, n or m respectively, has been almost totally neglected by earlier workers. It may be noted that only through this hydrogen bonding number a 3-dimentional structure or geometry of hydrogen bonded complex can be proposed and investigated theoretically, by, say, using MO calculations. As mentioned earlier no significant hydrogen bonding was found to occur in the case of the anion radical, $DQ^{-\bullet}$ hydrogen bonding number, m, of DQ^{2-} for MeOH and EtOH were calculated [ref. eqs. (6-7)] and collected in Table-1.

Poposed Mechanism

DQ^{2-} has two oxygen centers with high electron density, hence at a time two hydrogen bonding molecules can attach to DQ^{2-}. Notating DQ^{2-} as A and hydrogen bonding moiety as B, the following mechanism can tentatively be proposed, for m = 3.

$$A + 2B \rightleftharpoons AB_2 \quad \text{fast equilibrium} \qquad (15)$$

$$AB_2 + 2B \rightleftharpoons AB_4 \quad \text{also fast equilibrium} \qquad (16)$$

which is equivalent to

$$AB_2 + AB_4 \rightleftharpoons 2AB_3 \quad \text{fast} \qquad (17)$$

The two equilibrium (15) and (16) together may be manifesting equilibrium (17) thus giving m = 3 on the cyclic voltammmetric time scale.

Experimental

Instrument, Electrode and Chemicals

Experimental details have already been described in an earlier publication [7].

Duroquinone (97%) was purchased from Acros Organics and was used directly without further purification. High purity argon gas was used for purging the solution. All potentials were referred to saturated calomel electrode (SCE).

Conclusion

A simple electrochemical approach for studying hydrogen bonding reaction rates has been proposed and used to evaluate rate constants for such H-bonding reactions. The method was used to evaluate the rate constants k_m, the equilibrium

constant K_m (≡ K_2 for m-value) as well as the hydrogen bonding number m, for the system DQ^{n-} + mHB $\rightleftharpoons$ [DQ^{n-},$(HB)_m$], where n = 1,2 and HB are CH_3OH, C_2H_5OH. It was found that hydrogen bonding of monoanion radical of DQ is insignificant. To explain the values of hydrogen bonding number (m = 3) a tentative mechanism has also been proposed.

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