Calculation of Rate Constant of Dimerization of an Electrochemically Generated Species

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Summary: The rate constant for the dimerization process of an electrochemically generated species- (methyl viologen radical cation $MV^{+\bullet}$), have been determined by linear scan/ cyclic voltammetry technique. Methyl viologen radical cation $MV^{+\bullet}$, an unstable radical cation, is known to undergo dimerization process in aqueous solution. Nicholson and Shain theory and equation for E_rC_i with the appropriate approximation was used for the evaluation of dimerization kinetic parameter(s). The bimolecular rate constant for the dimerization process of methyl viologen radical cation, was found to be 4.3 ($\pm$ 1.0) $\times$ 10^4 $M^{-1}s^{-1}$ for the E_rC_i formalism. The results are consistent with the values reported earlier in the literature.

Key word: Methyl Viologen, Dimerization, Kinetics, Nicholson and Shain, E_rC_i.

Introduction

Information about the rate of dimerization of an ion-radical or neutral free radical or other reactive intermediates (eq. (1)) is of interest to physical chemists.

$$2A^n \underset{}{\overset{k_2}{\rightleftharpoons}} (A^n)_2 \qquad (1)$$

where n = 0, ±1 or ±2. Thus A can be a neutral molecule or a neutral free radical (n = 0 in both cases) or it can be a cation or an anion radical (n = ± 1) or a dication or a dianion (n = ± 2).

To an electrochemist**,** dimerization of an electrochemically generated species is of interest (eq (2)).

$$O + ne \rightleftharpoons R$$

$$2R \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2 \qquad (2)$$

$$K_2 = [R_2] / [R]^2 = k_2 / k_{-2}$$

The subscript corresponds to the equation number.

Saveant–Vianello's [SV] treatment of the process given in eq. (2) is most extensive [1], while Olmstead–Hamilton–Nicholson's [OHN] [2] treatment is confined to the same process but for $k_2 >> k_{-2}$, this is equivalent, to

$$2R \xrightarrow{k_2} R_2 \qquad (3)$$

A very simple expression is given by OHN to calculate k_2 for the process given in eq (3) [2].

Nicholson and Shain [3], in their treatment of a reversible electron transfer followed by an irreversible chemical reaction, (eq. (4)), have given some simple expressions for the calculation of k_f.

$$O + ne \rightleftharpoons R$$

$$R \xrightarrow{k_f} Z \qquad (4)$$

For the process given in eq. (4), Nicholson and Shain's expression for the evaluation of k_f through (the use of) linear scan/ cyclic voltammetry, is as follows:

$$E_p = E_{1/2} - \frac{RT}{nF} [0.780 - ln \sqrt{\frac{k_f}{a}}] \qquad (5)$$

where E_p is the observed peak potential of the voltammogram. $E_{1/2}$ is the half wave potential of the electrode process O + ne $\rightleftharpoons$ R**;** $a = nFv / RT$ and v is the scan rate.

Thus k_f can be very easily calculated, from the measured E_p, provided that $E_{1/2}$ of the electrode process is known. $E_{1/2}$ has to be somehow obtained from the experimental voltammogram.

$E_{1/2}$ for an electrode process, can be obtained as

$$E_{1/2} = \frac{1}{2}\,[(E_p)_c + (E_p)_a] \tag{6}$$

This relationship may very well be used for the case when dimerization is limited, which is true for dilute solution.

Now it's left to be shown that k_2 (eq. (3)) can be obtained from k_f of eq. (5).

Methyl viologen dication (MV^{2+}), an extensively studied moiety [4-9], have received much attention due to its favorable redox properties, along with their wide and enormously varied applications [4-9]. Methyl viologen undergoes two step single electron transfer process eq. (7-8).

$$MV^{2+} + e \rightleftharpoons MV^{+\bullet} \tag{7}$$

$$MV^{+\bullet} + e \rightleftharpoons MV: \tag{8}$$

$MV^{+\bullet}$ is known to dimerize in water [4-15], eq. (9). Formation of dimer is most likely due to the increased hydrophobic nature of the radical cations in contrast with their parent dications [14]. Thus

$$2\,MV^{+\bullet} \overset{K_D}{\rightleftharpoons} (MV^{+\bullet})_2 \tag{9}$$

Whereas experimental K_D is already known [10,12,15].

Compton *et al* have reported the rate of dimerization k_{2D} of $MV^{+\bullet}$, eq. (10) through impedance technique and simulation [16].

$$2\,MV^{+\bullet} \xrightarrow{k_{2D}} (MV^{+\bullet})_2 \tag{10}$$

It is now to be shown that k_{2D} ($=k_2$ of eq. (3)) of dimerization of $MV^{+\bullet}$, can be obtained through k_f (ref. eq. (4)), whereas k_f can be obtained using eq. (5) (E_rC_i formalism).

Dimerization rate constant k_2 = (k_{2D}) for $MV^{+\bullet}$ dimerization (eqs. (3,10)) can be obtained as follows,

$$A + A \xrightarrow{k_2} B \tag{11}$$

$$-\frac{dA}{dt} = k_2\,[A]\,[A] \tag{12}$$

Also consider a unimolecular reaction

$$A \xrightarrow{k_1} Z;\; k_1 = k_f \text{ (of eq. (4))} \tag{4,13}$$

$$-\frac{dA}{dt} = k_1\,[A] \tag{14}$$

From eq. (12) and (14), one can obtain

$$-\frac{dA}{dt} = k_2[A]^2 + k_1[A] \tag{15}$$

When the product is same, it can be shown [17]

$$k_2 = \frac{k_1}{[A]} \tag{16}$$

And for dimerization of $MV^{+\bullet}$, one will have

$$k_2 = k_{2D} = \frac{k_1}{[MV^{+\bullet}]} = \frac{k_f}{[MV^{+\bullet}]} \tag{17}$$

The next problem in evaluating k_2 is the (evaluation of the) concentration of $MV^{+\bullet}$ radical cation, the electrochemically generated species R of the process given in eq. (7)).

The concentration of $MV^{+\bullet}$, radical cation, around the electrode is not the same as that of MV^{2+} in the bulk, whereas dimerization process is taking place around the electrode.

For the electrode process O + ne $\rightleftharpoons$ R, it had been shown that [R] is some 5% to 10% of [O] [18,19]. This estimated concentration of $MV^{+\bullet}$ radical cation, can be used for the calculation of k_2, ($=k_{2D}$), the rate constant of dimerization of $MV^{+\bullet}$ (eq. (10)), once k_f is obtained.

Result and Discussion

The complete cyclic voltammograms of MV^{2+} for various concentration of MV^{2+} (in water) are depicted in Fig. 1. In the present case the first reduction process is of interest (eq. (7)). The E_p values for various concentrations of MV^{2+} are collected in Table-1. k_f as calculated using eq. (5) and k_2 using eq. (17) are also collected in Table-1. The concentration of methyl viologen radical cation $MV^{+\bullet}$ is taken as 5% of MV^{2+} concentration [18,19]. The average value of k_2 is obtained as 4.3 (± 1.0) × 10^4 $M^{-1}s^{-1}$ using eq. (5) and (16,17). This value is of the same order of magnitude as the one reported by Compton et al [16].

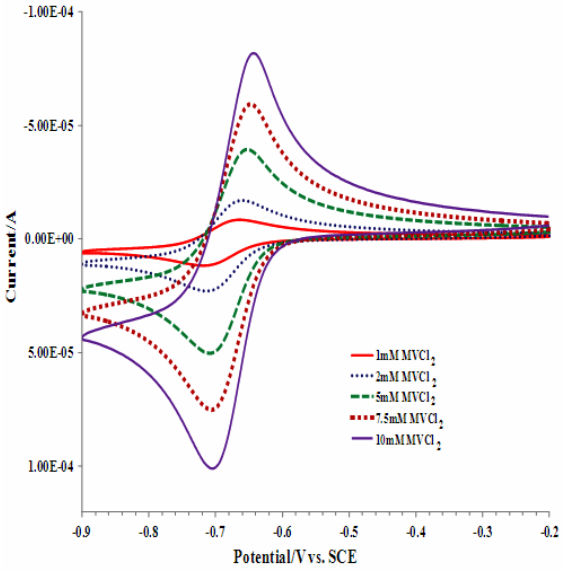

Fig. 1: Cyclic voltammograms for the different concentrations of methyl viologen (MV^{2+}) and its reduced product, methyl viologen radical cation ($MV^{+\bullet}$) in water.

The numerical value of k_2, as obtained from eqs. (4), (5) and (17), and as referred to Olmstead-Hamilton and Nicholson [OHN] theory [2] (eq (3)), illustrates the importance of the basic assumption on which eq. (5) is based. In eq. (5) the dimerization is considered as a chemically irreversible process (E_rC_i formalism).

The value of k_{2D} ([O] 10^4 $M^{-1}s^{-1}$) obtained by Compton *et al*, has been obtained from the simulation and reflects more an irreversible chemical dimerization process. Physically, even in water, K_D is large but not overwhelming – it is order of 10^2 M^{-1} [10]. In the present study it is shown that simple Nicholson and Shain equation (eq. (5)) can also be used to evaluate the rate constant of chemically irreversible (E_rC_i) dimerization of an electro generated species.

Table-1: Dimerization rate constant k_f and k_2 for $mv^{+\bullet}$ in H_2O.

S. No.	Conc. of MV^{2+} (mM)	E_p (V)	$E_{1/2}$- E_p [a] (V)	k_f [b] (s^{-1})	k_2 [b] $M^{-1}s^{-1}$
1	1.0	-0.719	-0.012	3.62	7.28×10^4
2	2.0	-0.712	-0.005	6.28	6.28×10^4
3	5.0	-0.709	-0.002	7.92	3.16×10^4
4	7.5	-0.706	0.001	10.04	2.68×10^4
5	10	-0.704	0.003	11.74	2.35×10^4
					$4.3 (+ 1.0) \times 10^4$

(*a*) $E_{1/2}$= -0.707V *vs.* SCE., (*b*) From eq. (5) and $k_2 = k_f / [MV^{+\bullet}]$; $[MV^{+\bullet}] = 0.05\ [MV^{2+}]$ (eq. (17)).

In addition, simulation technique was used to verify the results for the rate of dimerization process (eqs. (3), (10)) of methyl viologen radical cation $MV^{+\bullet}$. One such simulated cyclic voltammogram for 7.5mM MV^{2+} is given at Fig.2 (other parameters are E^O= -0.707, K_D= 4 × 10^2 M^{-1} [10] and k_f = 4.3 × 10^4 $M^{-1}s^{-1}$). This gives confidence in the use of Nicholson and Shain formalism in the calculation of dimerization rate constant of an electrochemically generated species.

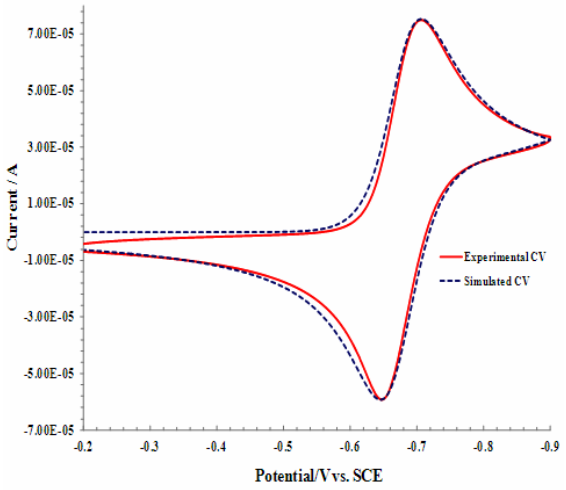

Fig. 2: Simulated cyclic voltammograms for the 7.5mM of methyl viologen (MV^{2+}) and its reduced product, methyl viologen radical cation, ($MV^{+\bullet}$) in water.

Experimental

Experimental details have been described in earlier publication [19]. However they are reviewed here.

Instrument

Cyclic voltammograms were recorded on a CHI Electrochemical analyzer with CHI 600C software on a 3 electrode configuration system.

Materials

Electrodes

A glassy carbon electrode 3mm in diameter (BASi) was used as working electrode, a platinum coil (10 cm long, 0.5 mm diameter) was used as counter electrode and a saturated calomel electrode (SCE), was used as reference electrode.

Chemicals

Methyl viologen (Sigma, 99.9%), potassium chloride (Merck, 99.9%) were used as received (without further purification), deionized water was used.

Procedure

Details are given elsewhere [19]. Cyclic voltammogram were recorded for the first reduction process for various concentrations of MV^{2+} (1 to 10mM), while using KCl as supporting electrolyte in water. Solution was purged with high purity argon. The change or shift in the E_p with the change in concentration was noted.

Conclusion

It had been envisaged that the rate constant of dimerization of an electrochemically generated species could also be obtained through linear scan / cyclic voltammetry using Nicholson and Shain equation and the proper approximation for the concentration of the electrochemical-generated species *R*. The concept was successfully tested with the dimerization process of $MV^{+\bullet}$ (Methyl Viologen radical cation).

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