Kinetics of Dimerization of the Reduced Products of Methyl Viologen Dication

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Summary: The rate constants for the dimerization of the reduced products of methyl viologen dication (MV^{2+}) of the processes (a) methyl viologen cation radical ($MV^{+\bullet}$), ($MV^{2+} \xrightarrow{e} MV^{+\bullet}$) and $2MV^{+\bullet} \rightleftharpoons (MV^{+\bullet})_2$ and (b) methyl viologen neutral (MV), ($MV^{+\bullet} \xrightarrow{e} MV$) and $2MV \rightleftharpoons (MV)_2$ were obtained through linear scan- / cyclic- voltammetry and the use of Olmstead-Hamilton-Nicholson theory. The rate constants for the two dimerization processes are reported here. Rate constant for the dimerization process (b) above, of the novel species methyl viologen neutral is being reported first time.

Key Words: Methyl Viologen, Methyl Viologen Neutral, Dimerization Kinetics, Cyclic Voltammetry, Digital Simulation.

Introduction

Methyl viologen – *N*, *N*′-dimethyl-4, 4′-bipyridinium dichloride ($MV^{2+}Cl_2$, the dication notated as MV^{2+}) and its reduced species methyl viologen cation radical $MV^{+\bullet}$ have been extensively studied [1-24]. The higher reduction product, methyl viologen neutral, MV, has been much less studied.[3-4,13-14, 16, 25-27].

There have been reports about dimerization equilibrium processes of $MV^{+\bullet}$ [9,15-16,19,24] as well as of MV [25]. These processes are given in eqs. (1-2)

$$2MV^{+\bullet} \rightleftharpoons (MV^{+\bullet})_2 \qquad K_1 = k_1 / k_{-1} \qquad (1)$$

$$2MV \rightleftharpoons (MV)_2 \qquad K_2 = k_2 / k_{-2} \qquad (2)$$

Equilibrium constant and rate constant subscript numbers refer to equation numbers.

Voltammetry has been used to generate the two reduced species, eqs. (3, 4), and study dimerization of $MV^{+\bullet}$ process as given in eqs. (1).

$$MV^{2+} + e \rightleftharpoons MV^{+\bullet} \qquad (3)$$

$$MV^{+\bullet} + e \rightleftharpoons MV \qquad (4)$$

Theories of linear scan and cyclic voltammetry have been reported for dimerization by some workers, which have not been exploited as much it should have been [28-31]. These workers worked out the EC mechanism of dimerization process, eqs. (5, 6).

$$O + ne \rightleftharpoons R \qquad (5)$$

$$2R \rightleftharpoons R_2;\ K_6 = k_6 / k_{-6} \qquad (6)$$

It is interesting that much less attention has been given to the evaluation of dimerization rate constant in general and of these two species in particular.

In the present study, theory of voltammetry for dimerization process, eqs. (5, 6 for the condition when $k_6 >> k_{-6}$), as proposed by Olmsted, Hamilton and Nicholson, OHN [29], is adopted for the evaluation of the dimerization rate constant of MV, eq. (2). Since the rate constant for dimerization of $MV^{+\bullet}$, eq. (1), is available in literature [19] hence, the efficacy of equation proposed by OHN for dimerization of an electrochemically generated species can be tested. Simulation of experimental CV's can then be carried out with the calculated rate constants to verify the veracity of OHN equation.

Theory

Saveant and Vianello [28] and Olmsted, Hamilton and Nicholson [29] have described in detail the potential sweep response of the process of dimerization of an electrogenerated species R, eqs. (5-6). Olmsted, Hamilton and Nicholson, OHN [29], described the process for various values of l / a; $l = k_6$

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$+ k_{-6}$ and $a = nFv/RT$, v is the scan rate. The pertinent equation is described below.

Under the condition when K **(=** K_6**)** is large, or equivalently $k_6 >> k_{-6}$ Olmstead, Hamilton and Nicholson, OHN, [29] gave an expression for the calculation of the dimerization rate constant, k_6, as

$$n\,(E_p - E^0) = (RT / 3F)\,[\ln \psi - 3.12] \qquad (7)$$

where E^0 is the standard electrode potential (= $E_{1/2}$) for the process given in eq. (5) and E_p is the peak potential associated with the processes eqs. (5 – 6); $\psi = k_6 C_O^* / a$, where C_O^* is the concentration of species O (eq. (5)).

From eq. (7) it is clear that a plot of E_p *vs. ln Co** can give k_6 because all other parameters are supposed to be known. In addition to the Fig (s) and Table(s), given in OHN paper, above equation (eq. (7)) was also to be used in the present study to calculate the dimerization rate constants for $MV^{+\bullet}$, (eq. (1)) and MV, (eq. (2)).

Experimental

Instrument

A CHI 600 Instrument analyzer was used for cyclic voltammetric measurements.

Electrodes

A glassy carbon electrode 3mm in diameter, with an area of 0.0706 cm^2 (BASi) was used as working electrode. A Saturated Calomel Electrode (SCE) was used as reference electrode while a platinum wire (5 cm long, 0.5 mm diameter) was used as counter electrode.

Chemicals

Methyl Viologen (Sigma, 99.9%), Acetonitrile (MeCN) (Fisher, 99.9%), tetrabutylammonium perchlorate (TBAP) (TCI, ≥99 %), Potassium Chloride (KCl) (Merck, 99%) and N,N- Dimethyl foramide (DMF) (Wako, 99.9%) were used. Acetonitrile (MeCN) and N,N- Dimethyl foramide (DMF) were dried over 4A molecular sieve, and passed through an alumina column before use. Water used was deionized water. Methyl viologen, tetrabutylammonium perchlorate (TBAP) and potassium chloride were used without any further purification.

Method

Linear scan / Cyclic voltammetric measurements were recorded for the first and second reduction processes using a standard three electrode assembly, for various concentrations of MV^{2+} (1mM to 10mM in water, 0.5 mM to 5mM in acetonitrile and 0.5 to 4 mM in water + DMF (mixed solution)). For an aqueous and a water + DMF mixed system a solution of $MVCl_2$ with 0.1M KCl as supporting electrolyte was used, whereas for acetonitrile as solvent, a solution of $MVCl_2$ with 0.1M TBAP as supporting electrolyte was used.

Solution was purged with High purity argon for the removal of oxygen. The shift in the E_p with the change in concentration was recorded.

Simulations of the cyclic voltammograms were conducted through BASi Digisim 3.0 software package.

Semi-empirical molecular orbital calculations were carried out with HyperChem 8.0 software package using Austin Model 1(AM1), Parametric Method 3 (PM3) and Reparameterization Method 1 (RM1) methods. The process of geometry optimization of any reduced product of methyl viologen was done at the restricted Hartree-Fock level with Polak- Ribieke minimization algorithm (a conjugated gradient method).

Results and Discussion

Cyclic voltammograms of MV^{2+} recorded in MeCN (Fig. 1) and water + DMF (9:1) solution (Fig. 2), for various concentrations and scan rates, show two completely reversible cathodic and anodic peaks. It is seen that there is no anodic shift in the two cathodic peaks.

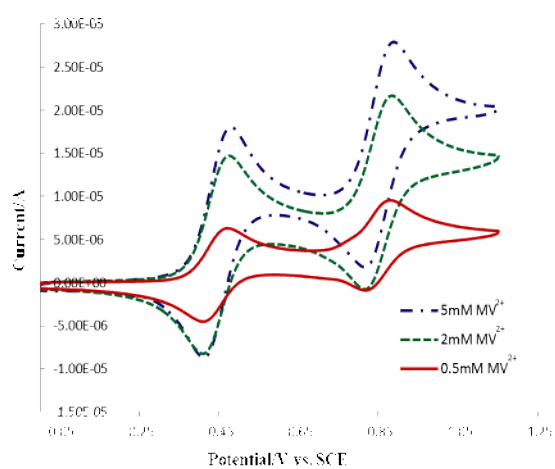

Fig. 1: Cyclic Voltammograms of MV^{2+}, showing both reduction processes for different concentrations of MV^{2+}, in acetonitrile, supporting electrolyte: 0.1M TBAP; working electrode: glassy carbon; scan rate: 0.050V/s; temperature: $25^{O}C$.

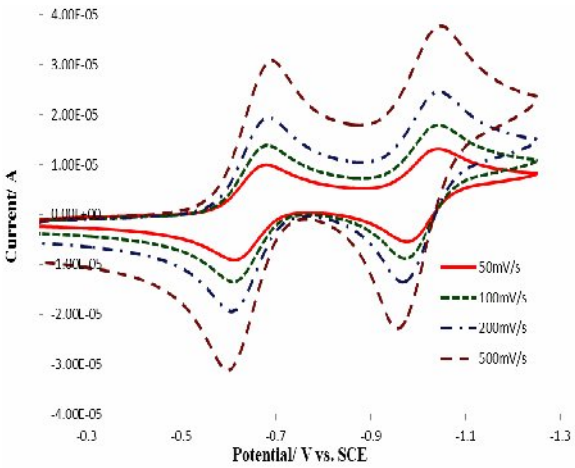

Fig. 2: Cyclic Voltammograms of 2mM MV^{2+}, both reduction processes, in mixed solution of H_2O + DMF (9:1) (0.1M KCl) at various scan rates; potential *vs*. SCE, other conditions are same as in Fig. 1

Cyclic voltammograms of MV^{2+} in water at various concentrations (at 50mV/s) and for different scan rates shown in Figs. (3 and 4). The electrochemical parameters extracted from Figs. 3, for different concentrations of methyl viologen, are collected in Table-1. It is noticed that, unlike the CV's in MeCN and water + DMF (mixed solution) , there is a shift in the peak position depending upon the increase / decrease in the concentration of MV^{2+} which could be attributed to the dimerization of $MV^{+\bullet}$ and MV. Cyclic voltammetric parameters for 5mM MV^{2+} at different scan rates are collected in Table-2.

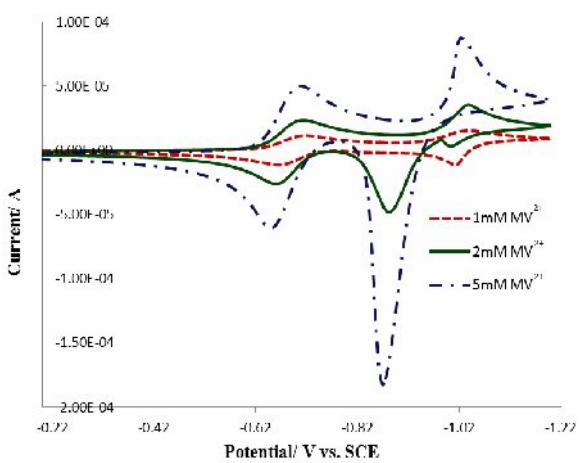

Fig. 3: Cyclic Voltammogram of MV^{2+}, both reduction processes for various concentrations (1mM, 2mM, 5mM) of MV^{2+}, in aqueous system, at 0.05V/s scan rate; other conditions same as in Fig. 1

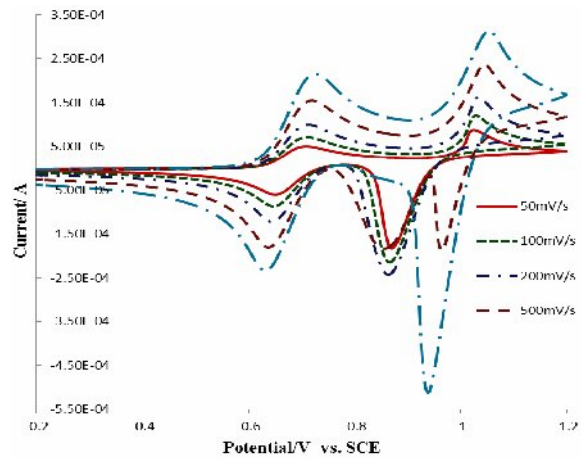

Fig. 4: Cyclic Voltammogram of MV^{2+} (5mM), both reduction processes, in H_2O (0.1M KCl) at different scan rates; potential *vs*. SCE, working electrode: glassy carbon, temperature 25°C.

Table-1: Cyclic Voltammetric data for various concentration of Methyl Viologen (and its reduced products) in water [a,b]

S.No	Concentration (mM)	$E_{pc}1$ (V)	Ep_a1 (V)	$E_{pc}2$ (V)	Ep_a2 (V)	$I_{pa}/I_{pc}1$	$I_{pa}/I_{pc}2$
1	0.1	-0.717	-0.647	-1.042	-0.977	1.11	1.13
2	1	-0.719	-0.667	-1.039	-1.009	0.82	1.80
3	2	-0.712	-0.662	-1.037	-1.004	1.11	--
					-0.882		--
4	5	-0.709	-0.650	-1.023	-0.870	0.91	3.15
5	7.5	-0.706	-0.643	-1.023	-0.860	1.12	3.00
6	10	-0.704	-0.637	-1.022	-0.847	1.11	2.71

[a] Supporting electrolyte 0.1M KCl. [b] All potentials reported *vs.* SCE at scan rate 50mV/s ; *E*rror in the measurement of E_p is $\pm$ 0.001V at low scan rate and $\pm$ 0.002V or more, at higher scan rate ($\geq$200mV/s).

Table-2: Peak potentials for 5mM Methyl Viologen (and its reduced products) at various scan rates (v) in Water [a,b]

S.No	v/ Vs^{-1}	$E_{pc}1$ (V)	Ep_a1 (V)	$E_{pc}2$ (V)	Ep_a2 (V)	$I_{pa}/I_{pc}1$	$I_{pa}/I_{pc}2$
1	0.05	-0.709	-0.650	-1.023	-0.870	0.91	3.15
2	0.1	-0.711	-0.646	-1.029	-0.866	1.13	2.81
3	0.2	-0.713	-0.643	-1.034	-0.864	1.17	2.40
4	0.5	-0.719	-0.637	-1.045	-0.964	1.15	1.60
5	0.7	-0.721	-0.636	-1.049	-0.948	1.11	2.60
6	1.0	-0.726	-0.631	-1.053	-0.939	1.15	2.90

[a] Supporting electrolyte 0.1M KCl. [b] All potentials reported *vs.* SCE; *E*rror in the measurement of E_p is $\pm$ 0.001V at low scan rate and $\pm$ 0.002V or more, at higher scan rate ($\geq$200mV/s).

For all three cases, aqueous, water + DMF (mixed solution) and acetonitrile systems, it is evident from these CV's and electrochemical data that, there is no significant effect of solution resistance on CV's.

Dimerization Rate constants

Methyl Viologen Cation Radical

Rate constants for the dimerization of $MV^{+\bullet}$, in the three solvents, MeCN, mixed medium of water

+ DMF (9:1) and H_2O, were calculated through the use of eq. (7) and from the plot of E_p *vs*. $ln\, C_O^*$ (Fig. 5, for H_2O); C_o^* is the bulk concentration of MV^{2+}. The Rate constants were also calculated using other information provided in Olmstead-Hamilton-Nicholson, OHN, paper [using Fig. 3 and Table-1 of their paper, reference [29]. These results are collected in Table-3. No significant dimerization of $MV^{+\bullet}$ was found to occur in MeCN and H_2O +DMF (9:1). This is in line with previous reports [9, 14, 19]. The value of k_1 (ref eq.(1)) in water, as calculated by Olmstead *et al* [29] method was found to be [O]10^3 $M^{-1}s^{-1}$ ([O] means "order of") which is an orders of magnitude lower as reported by Compton *et al* [19]. This result was obtained using $E_{1/2}$ = - 0.707 (*vs.* SCE) and n = 1. However using $E_{1/2}$ = -0.707 (*vs.* SCE) and n = 1.4, k_1 comes out to be 1.05 $\times 10^4$ $M^{-1}s^{-1}$ - the same order of magnitude as reported by Compton *et al* [19]. $E_{1/2}$ = - 0.707 (*vs.* SCE), used in this calculation, is the one obtained by plotting E_p *vs.* C_O^* and extrapolating to "infinite dilution" (very dilute solution) of MV^{2+} and adding to it 28 mV (for 25°C) (Fig.6*a*). Incidentally this value of $E_{1/2}$ is the same used for simulation also (see later). n = 1.4 was used because this is the "experimental" value of n obtained from the slope of the plot for E_p *vs.* $ln\, C_O^*$.

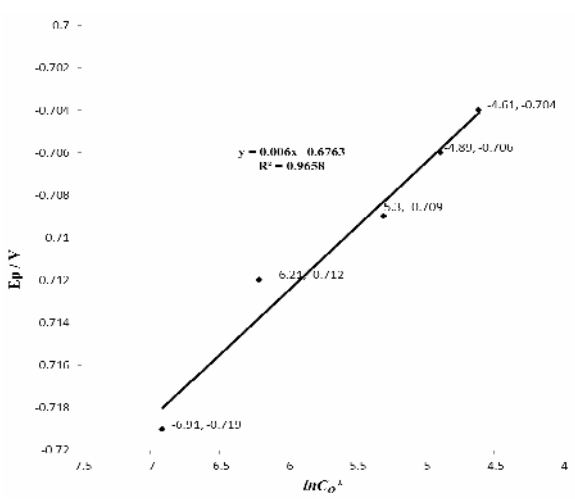

Fig. 5: Peak potential (E_p) vs. $ln\, C_O^*$, plot for first reduction process of MV^{2+} in aqueous system.

For various scan rates, plot of E_p *vs. lna* (a= nFv/RT) gives a good agreement with the literature value and the value of k_1 comes out to be 2.87 × 10^4 $M^{-1}s^{-1}$ through the use of eq. (7).

Methyl Viologen Neutral MV

It is to be noted that so far there is no report of the *rate* of dimerization of MV, methyl viologen neutral, in literature. The dimerization rate constant was obtained through plotting data of Table-4 (Fig. 7), and was found to be quite high, k_2 = [O] 10^5 M^{-1} s^{-1} in water (Table-4), and quite low in MeCN and H_2O +DMF (9:1). Plot of E_p *vs. lna* (a= nFv/RT), for various scan rates, gives a value of k_1 calculated to be 2.86 × 10^5 $M^{-1}s^{-1}$ (from eq. (7)), which further verifies the validity of method used.

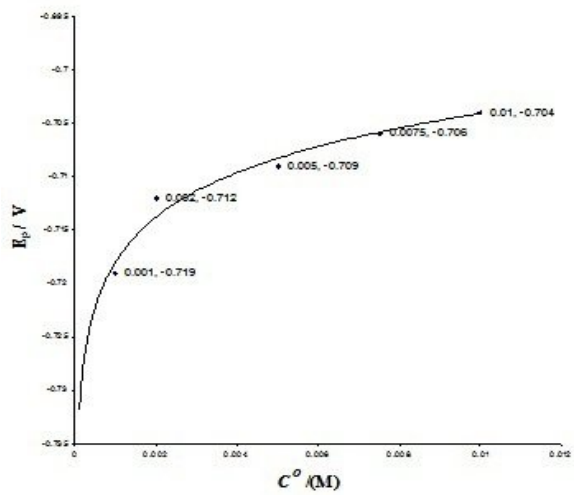

Fig. 6: (*a*) - Peak potential (E_p) *vs.* Concentration (C^O) plot for first reduction process of MV^{2+} in aqueous system (ref. Table III).

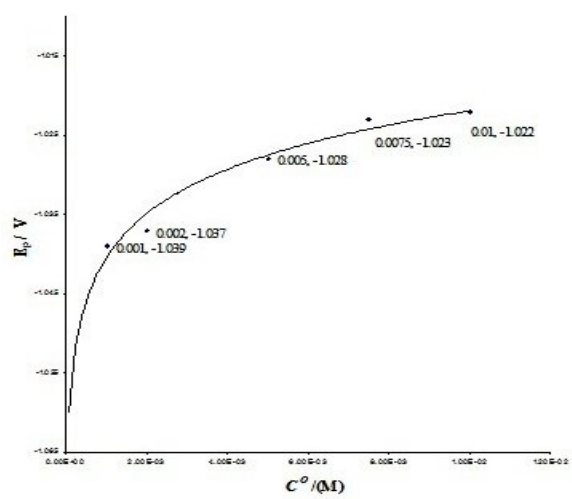

Fig. 6: (*b*)-Peak potential (E_p) *vs.* Concentration (C^O) plot for second reduction process of MV^{2+} in aqueous system (Table-4).

Table-3: Dimerization rate constant of $MV^{+\bullet}$ (k_1) in H_2O.

S.No	Conc. Of MV^{2+} C_O* (mM)	lnC_O*	E_p (V)[a]	k_1 [b] ($M^{-1}s^{-1}$) = from		
				Fig.[c]	Table [d]	Eq (7)[e]
1	1	-6.91	-0.719	7.76×10^3	9.72×10^3	
2	2	-6.21	-0.712	1.41×10^4	1.39×10^4	
3	5	-5.30	-0.709	9.33×10^3	1.95×10^4	1.05×10^4
4	7.5	-4.89	-0.706	1.04×10^4	1.30×10^4	
5	10	-4.61	-0.704	1.15×10^4	9.73×10^3	
Average				$1.06 (\pm 1.1) \times 10^4$	$1.32 (\pm 1.8) \times 10^4$	

[a] $E_{1/2}$= -0.707V (vs. SCE), [b] Literature value [O]10^4 $M^{-1}s^{-1}$ [19], [c] through the use of Fig.3 of ref [29] [d] through the use of Table I of ref. [29], [e] from eq. (7), plot of E_p *vs.* $ln\, C_O^*$ (Fig.5) and the intercept.

Table-4: Dimerization rate constant of MV (k_2) in H_2O [a, b].

S.No	Conc. Of MV^{2+} C_O* (mM)	$ln\, C_O$*	E_p (V)	k_2 [b] ($M^{-1}s^{-1}$) from		
				Fig [b]	Table [b]	Eq (7)[c]
1	1	-6.91	-1.039	2.91×10^5	4.55×10^5	
2	2	-6.21	-1.037	2.05×10^5	2.30×10^5	
3	5	-5.30	-1.028	2.11×10^5	9.10×10^5	1.64×10^5
4	7.5	-4.89	-1.023	2.47×10^5	5.50×10^5	
5	10	-4.61	-1.022	2.59×10^5	4.60×10^5	
Average				$2.43 (\pm 0.2) \times 10^5$	$3.40 (\pm 1.6) \times 10^5$	

[a] $E_{1/2}$= -1.036V (vs. SCE), [b] see foot note (c) and (d) of Table-III, [c] From Eq. (7), and plot of E_p *vs.* $ln\, C_O^*$ (Fig.7) (see text)). Note the concentration of $MV^{+\bullet}$ is taken as 15% of MV^{2+}.

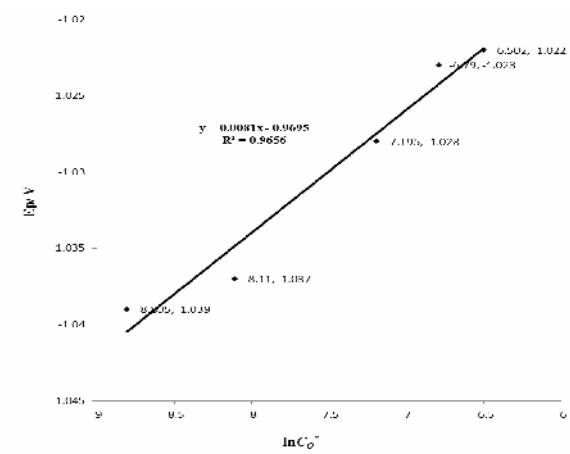

Fig. 7: Peak potential (Ep) vs. $\ln C_O^*$, plot for the second reduction process of MV^{2+} in aqueous system (ref. Table-4).

One would expect the dimerization of neutral MV to be higher in lower dielectric constant medium. Apparently, the subsequent aggregation of MV, after dimerization, in water, pushes the (apparent) rate constant of dimerization to higher k_2 value. No aggregation of $MV^{+\bullet}$ cation radical has been reported in H_2O – at least not in the concentration range and conditions studied here. At the same time it has been noted by all workers that the ratio of anodic to cathodic peak currents for the second reduction process of MV^{2+}, in water, is quite high. This suggests the formation of aggregates. Aggregation has been reported for neutral MV in water [13, 16]. Evans [13] and Kochi [16] have isolated solid crystals / aggregates / thin film of MV in water, but the spectra of dimers had only been reported in hexane by Mohammad [25].

Value of $E_{1/2}$ (- 1.036 (*vs.* SCE)) used for this calculation, is obtained by the same procedure used to find out the value of $E_{1/2}$ for $MV^{+\bullet}$ (by plotting E_p *vs.* C_O^* and extrapolating it to "infinite dilution" (very dilute solution) of MV^{2+} and adding to it 28 mV (for 25°C) (Fig. 6(*b*)). This value of $E_{1/2}$ is used for simulation of cyclic voltammograms as well. For the evaluation of the dimerization rate constant of MV the concentration of $MV^{+\bullet}$ is needed. Concentration of $MV^{+\bullet}$ is taken approximately as 15% of [MV^{2+}] [31-34].

Simulation

All the experimental cyclic voltammograms were successfully simulated for the dimerization process eq. (1) of the *first* reduction process, eq. (3). Parameters used are $E° = E_{1/2} = -0.707$ V (*vs.* SCE), $K_1 = 8.1 \times 10^2$ M^{-1} [9, 16] and $k_1 = 1.05 \times 10^4$ $M^{-1}s^{-1}$. Simulations for the cyclic voltammograms of 5mM $MVCl_2$ at two different scan rates are given in Fig. 8 (*a*).

Simulation of experimental linear scan voltammograms (LSVs) (or equivalently the cathodic part of cyclic voltammograms) for the second reduction process (along with the first) was done for concentrations range from 1-5mM MV^{2+}. Simulations of LSVs for 5mM $MVCl_2$ at 0.05V/s and 0.1V/s are given in Fig.8 (*b*). It is seen that for all concentrations, through simulation, the position as well as the shape, of both cathodic part of LSVs are well reproduced for the dimerization mechanism, as given in eq. (4). Parameters used are $E° = E_{1/2} = -1.036$ V (*vs.* SCE), $K_2 = 7.5\times10^4 M^{-1}$ and $k_2 = 1.64\times10^5 M^{-1} s^{-1}$, for the second reduction process.

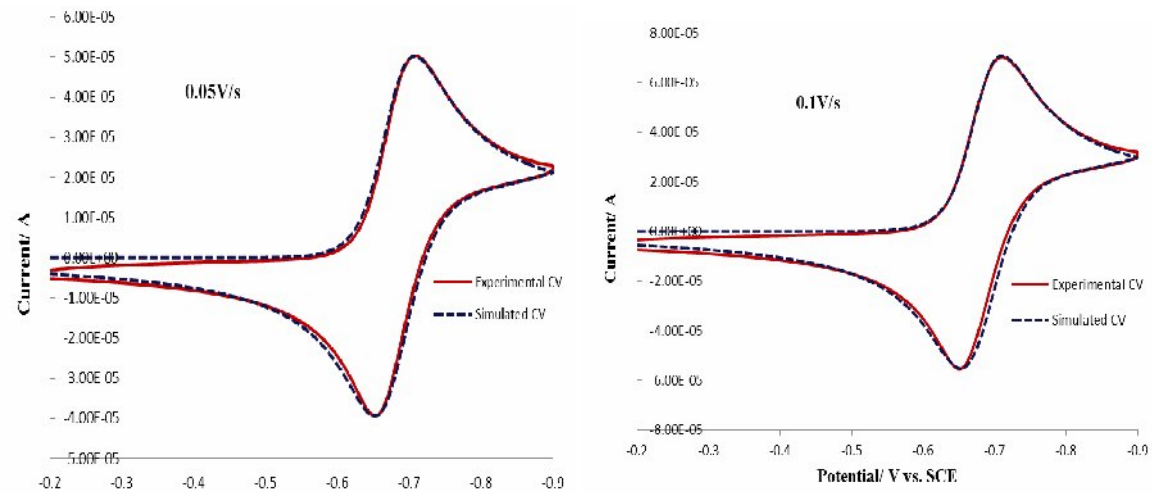

Fig. 8: (*a*) – Simulation of Cyclic voltammograms for first reduction processes of 5mM MV^{2+} in aqueous system at room temp, at two different scan rates. Experimental CVs are shown by solid curves and the corresponding simulations are represented by dotted lines.

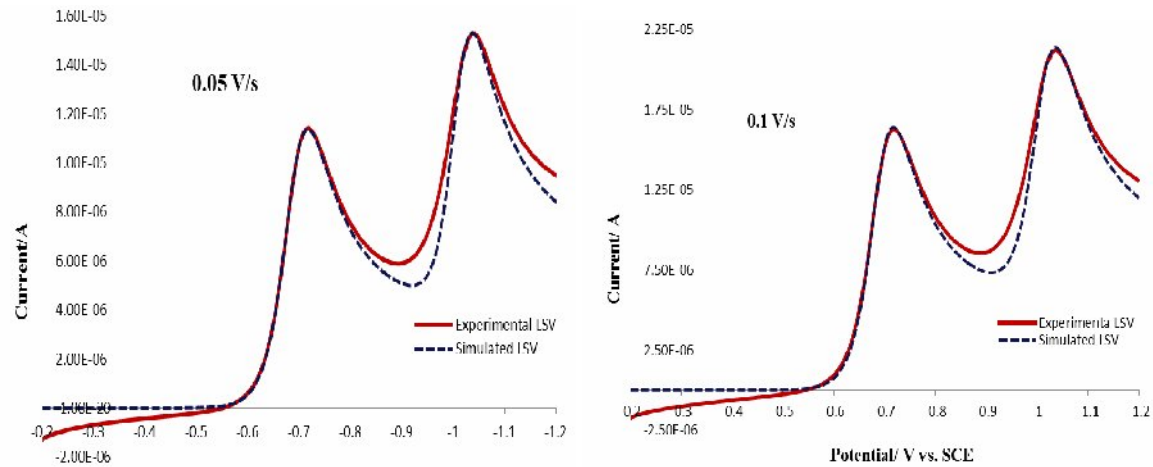

Fig. 8: (b) – Simulation of LSVs for second reduction processes of 5mM MV^{2+} in aqueous system at room temp, at two different scan rates. Experimental CVs are represented by solid curves and the corresponding simulations are shown by dotted lines.

Linear scan voltammograms (LSVs) (or equivalently cathodic part of cyclic voltammograms) were selected for simulation. This helped to avoid the simulation of anodic side (of the cyclic voltammogram) which is not the subject of present study. True study of the anodic part of MV is important in its own right, but it is not of much concern of the present study.

All these simulations of voltammograms of first and second reduction processes further strengthen the evaluated values of k_1 and k_2 of dimerization processes.

Quantum Chemical Calculations

Geometry optimization, of the built molecule structure (in Hyperchem 8.0 program) calculates the possible structure of methyl viologen radical cation or methyl viologen neutral (Fig. 9). Data collection starts from standard bond lengths and bond angles for a single molecule and then compares it with the experimental one [16]. These data for the geometric parameters of the two reduced species are collected in Table-5.

Table-5: The geometric parameters calculated for methyl viologen radical cation and methyl viologen neutral at 6-311G *ab initio* calculations and PM3 and RM1 methods.

Bond Lengths, Å	Methyl viologen radical cation				Methyl viologen neutral			
	6-311G[a]	PM3[b]	RM1[b]	X-ray[c]	6-311G[a]	PM3[b]	RM1[b]	X-ray[c]
N1-C1	1.3440	1.3777	1.3718	1.343	1.3884	1.4135	1.4011	1.375
N1-C5	1.3481	1.3761	1.3733	1.370	1.3884	1.4144	1.3996	1.387
N1-C6	1.4816	1.4811	1.4865	1.494	1.4477	1.4688	1.4612	1.447
C1-C2	1.3696	1.3870	1.388	1.353	1.3340	1.3502	1.3497	1.325
C2-C3	1.3970	1.4035	1.3978	1.439	1.4699	1.4519	1.4483	1.461
C3-C4	1.3976	1.4006	1.3980	1.437	1.4699	1.4520	1.4481	1.444
C4-C5	1.3669	1.3886	1.3872	1.329	1.3340	1.3497	1.3503	1.336
N2-C7	1.3835	1.4241	1.4000	1.385	1.3884	1.4144	1.3996	1.382
N2-C11	1.3833	1.4234	1.4000	1.388	1.3884	1.4135	1.4011	1.383
N2-C12	1.4584	1.4802	1.4718	1.495	1.4476	1.4688	1.4612	1.451
C7-C8	1.3297	1.3428	1.3453	1.356	1.3341	1.3497	1.3503	1.329
C8-C9	1.5209	1.4952	1.4899	1.401	1.4699	1.4520	1.4481	1.465
C9-C10	1.5134	1.4918	1.4879	1.396	1.4700	1.4519	1.4483	1.452
C10-C11	1.3306	1.3438	1.3453	1.331	1.3340	1.3502	1.3497	1.330
C3-C9	1.5260	1.5088	1.5072	1.440	1.3554	1.3678	1.3586	1.363

[a] Calculations performed on *ab initio* method with 6-311G basis set on Hyperchem 8.0, [b] calculations done with semiempirical methods on Hyperchem 8.0, [c] experimental values [16].

Table-6: Calculated total energies in kcal/mol of the proposed structure (found with lowest energy) for $(MV^{+\bullet})_2$ and $(MV)_2$

System	PM3		AM1		RM1	
	Binding Energy kcal/mol	Dipole (D)	Binding Energy kcal/mol	Dipole (D)	Binding Energy kcal/mol	Dipole (D)
$MV^{+\bullet}$	-2851.6725598	8.606	-2841.7827549	7.974	-2866.9569783	7.825
MV	-2934.8972695	0.000	-2918.5310127	0.000	-2938.6137017	0.000
$(MV^{+\bullet})_2$	-5539.5956423	1.787	-5514.0402420	1.026	-5582.2546283	1.350
$(MV)_2$	-5875.6932826	0.271	-5837.7207375	0.320	-5878.0905050	0.411

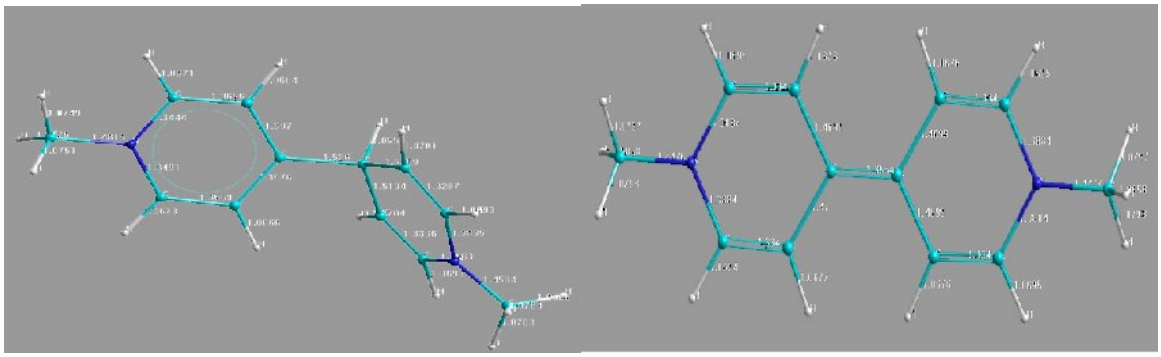

Fig. 9: Bond lengths of the two reduced products of methyl viologen (a) methyl viologen radical cation and (b) methyl viologen neutral using *ab initio* with 6-311G basis set.

Thus from the comparison of the (results of) two methods with experimental one, it is evident that there is not much difference found between the two methods, *ab initio* and semi empirical (SE). This makes it possible to use SE methods for further calculation of dimers of the two reduced products.

But it is important to note that all the calculations done are referred to "*in vacuum*" and the results obtained are only approximations.

The bond energies were calculated for the proposed structure of radical cation and neutral. From different SE methods lowest energy structure of the two dimers can be determined. Table-6 represents the binding energies as well as dipole moments of the single and dimer molecules.

Hence, through above mentioned semi-empirical methods, an attempt was made to correlate experimental results with the one obtained through the calculations with reduced computational time. Furthermore structural representation of the two dimers was another task to achieve. In comparison of the three methods AM1, RM1 and PM3, RM1 gives the lowest energies for the single as well as dimers of the two reduced products. Structural representation of the two dimmers, $(MV^{+\bullet})_2$ and $(MV)_2$ is given in Fig. 10.

Equilibrium as well as kinetics of the dimerization of methyl viologen cation radical $MV^{+\bullet}$ have been studied electrochemically and otherwise, and reported by earlier workers [9, 15-16, 19], but so far, there has been no report on kinetics of dimerization of methyl viologen neutral MV (eq. 2). Thus, it was considered proper to explore the use of those theories of stationary electrode voltammetry /

polarography which are available in the literature for the evaluation of kinetic parameters for the dimerization of MV. To apply these theories it was decided to first test them to the dimerization of methyl viologen cation radical $MV^{+\bullet}$, eq (1). The literature value of k_1 for $MV^{+\bullet}$ were well reproduced using eq, (7) and other aides (Figs and Table) given in ref. [29]. Thus eq. (7) and other aides given by OHN [29] (could also be used with confidence to evaluate k_2 for dimerization of MV (eq. (4)). The use of Olmstead *et al* equation (eq. (7)) to evaluate k_1 for $MV^{+\bullet}$ was worth trying because the OHN equation, eq.(7), can be considered as valid for the condition when $k_6 >> k_{-6}$ which in the present case is, fortunately, true: K_1 (= K_6) is large, $[O]10^2$, which means k_{-6} can be neglected as compared to k_6. It can be seen that our attempt to use OHN formalism [29] including eq. (7) to evaluate k_1 for (the dimerization of) $MV^{+\bullet}$ (eq (1)) was justified: values of k_1 of $MV^{+\bullet}$ thus calculated was of the same order of magnitude $[O]\ 10^4\ M^{-1}\ s^{-1}$ as reported by Compton *et al* [19] and it could be successfully used in the simulation of the CV.

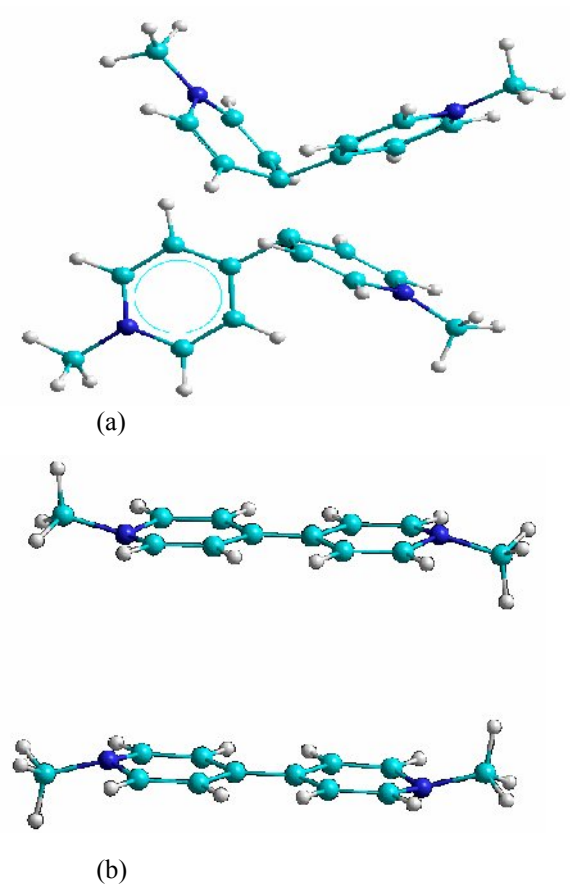

Fig. 10: Estimated structure of (a) $(MV^{+\bullet})_2$ and (b) $(MV)_2$; mode of coupling optimized using RM1.

Thus it was so satisfying to see results obtained through OHN formalism were in line with the reported values as well as those used in simulations.

For eq. (1), the value of K_1 is well established to be $[O]\ 10^2\ M^{-1}$, where [O] means order of [9, 16, 24]. This means the equilibrium is largely shifted to right side and in extreme case the process of dimerization, eq. (1) could equivalently be interpreted as

$$2MV^{+\bullet} \xrightarrow{k_f} (MV^{+\bullet})_2 \qquad (8)$$

Two questions then arise (a) if the dimerization process is actually described by eq.(8) then how experimentally *reversible* waves could be obtained for the process, eq.(1), (b) if k_f is indeed obtained by using OHN equation then what is its status in the present case.

Taking first question first, even if dimerization processes do follow eqs. (1-2), still it is possible to observe a reversible wave if, say, $(MV^{+\bullet})_2$ also gets oxidized at the same redox potential of MV^{2+}, eq. (9), as is the case of dimerization of $Br^{\bullet}$ atom free radical [30].

$$(MV^{+\bullet})_2 = [(MV^{+\bullet})_2]^{+\bullet} + e \qquad (9)$$

Which may or may not be followed by a very rapid reaction

$$[(MV^{+\bullet})_2]^{+} \longrightarrow MV^{+\bullet} + MV^{2+} \qquad (10)$$

The other interpretation is that if K is large and l/a is also large then a reversible wave will be observed [29-36]. This may very well be the case in dimerization of both $MV^{+\bullet}$ and MV (both forward and reverse rate constants are large as compared to the scan rate).

Now coming to question (b); in answering question (a), it can be claimed that the use of eq. (7) is justified as was in the case of dimerization of bromine atom free radical [30]. However there is another aspect.

In our investigation of the process of hydrogen bonding of anion radical and dinaions [35], we used the theory of stationary electrode polarography / voltammetry of Nicholson and Shain for E_rC_r and E_rC_i [see cases V and VI, ref. 36]. While using case V formalism (eq. (81 of ref. 36), it was found that as K increased, l (= $k_f + k_r$) and hence k_f

also increased, at a fixed (slow) scan rate. When $K >> 1$, k_f reached a limit, same as obtained by using equation for E_rC_i process (eq. 83 of ref. 36). Extending this argument of E_rC_i (or equivalently E_rC_r with large K) to OHN equation it can be assumed that the values of k_f obtained using eq.(7) gives a limiting value - may be upper limit - of rate constant for forward rate of reaction.

It can thus be assumed that in the case of dimerization of $MV^{+\bullet}$ a rapid dimerization occurs but with large K values; k_f calculated through OHN equation, eq. (7), gives a limiting value (perhaps an upper limit) of the rate constant. Nevertheless values obtained by using eq. (7) for k_1 is of the same order of magnitude as obtained by Compton, obtained by a much more elaborate method [19]. Also this k_1 is the same as used in the simulation of CV's of 1st reduction-dimerization process of MV^{2+}. In the present case k_f is the same as k_6 (and k_1 or k_2). There is no reason why k_2 obtained for the dimerization of MV is not taken to be correct.

It is evident from binding energies of the various species obtained from the semiempirical calculations that, at least this level of approximations, the dimer $(MV)_2$ is stable. From geometry consideration it looks that $(MV)_2$ is a stacked one over another MV a *pi*-mer, whereas the structure of $(MV^{+\bullet})_2$ is more complicated. The latter phenomenon could be due to electrstatic repulsions in each moiety.

Conclusion

The rate of dimerization of an electro-generated species can be studied through cyclic voltammetric technique and the use of theory of stationary electrode polarography / voltammetry. The technique and the theory were applied successfully to the case of dimerization of methyl viologen cation radical $MV^{+\bullet}$. This simple but elegant method was then employed in determining the rate constant for dimerization of methyl viologen neutral MV. The rate constants for dimerization processes of first and second processes are the same as used in the simulation of CV's of the two reduction processes. It is the first time the rate constant as well as the semiempirical calculaions for dimerization of the novel species methyl viologen neutral is being reported.

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