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PULSE RADIOLYSIS STUDIES OF ELECTRON TRANSFER BETWEEN POLYMER AND ZWITTERIONIC VIOLOGEN RADICALS(1)

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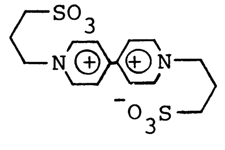
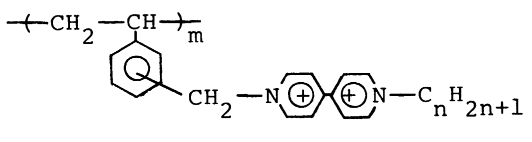
The reaction between viologen polymer radicals($PV^{+\cdot}$) and $Ru(NH_3)_6^{3+}$ via zwitterionic viologen as excellent mediator, has been studied using the pulse radiolysis technique. Kinetic analysis provided quantitative measurement of the rate of electron transfer between the viologen radicals of zwitterionic viologens and PV^{2+} and vice versa. These also allowed determination of the redox potential of the polymer system. Implications to the photochemical charge separation system are discussed.

The recent use of viologen systems (4,4'-bipyridinium salts) as electron relay systems in photochemical conversion devices(2-4) has been added to the long standing interest in the viologens as electron mediators in biological systems and as herbicides.(5) In a typical photoconversion model system, a viologen (V^{2+}) molecule quenches an excited state of a photosensitizer (e.g. $Ru(bpy)_3^{2+}$ or a porphyrin(6)) to yield a stable viologen radical ($V^{+\cdot}$) and an oxidized sensitizer. The latter will then react either with a sacrificial electron donor or with a catalyst to oxidize water.(7) The $V^{+\cdot}$ radical on the other hand, can react with a platinum catalyst to reduce water to molecular hydrogen.

An underlying problem in such systems is the back electron transfer reaction from $V^{+\cdot}$ to the oxidized photosensitizer. In an effort to overcome this problem a variety of V^{2+} molecules have been synthesized and tested.(8,9) These include the zwitterionic viologen, propyl sulfonate viologen(10)(ZV 1) and several viologen polymer (PVC_n^{2+} 2) systems.(11) In a recent report, incorporation of both ZV and PV^{2+} into a system containing $Ru(bpy)_3^{2+}$ or $Ru(phen)_3^{2+}$ was found to surpass the



1 ZV



2 PVC_n^{2+} : n = 3 or 6

Table 1. Kinetic Parameters for Electron Transfer in the ZV, PV^{2+}, and $Ru(NH_3)_6^{3+}$ System[a)]

Reaction							k /$M^{-1}s^{-1}$ b)
(1)	$ZV^{-\cdot}$	+	$Ru(NH_3)_6^{3+}$	$\longrightarrow$	ZV	+ $Ru(NH_3)_6^{2+}$	9.5×10^8
(2) (a)	$PVC_3^{+\cdot}$	+	$Ru(NH_3)_6^{3+}$	$\longrightarrow$	PVC_3^{2+}	+ $Ru(NH_3)_6^{2+}$	4.2×10^5
(b)	$PVC_6^{+\cdot}$	+	$Ru(NH_3)_6^{3+}$	$\longrightarrow$	PVC_6^{2+}	+ $Ru(NH_3)_6^{2+}$	2.9×10^5
(3) (a)	$ZV^{-\cdot}$	+	PVC_3^{2+}	$\longrightarrow$	ZV	+ $PVC_3^{+\cdot}$	1.1×10^8
(b)	$ZV^{-\cdot}$	+	PVC_6^{2+}	$\longrightarrow$	ZV	+ $PVC_6^{+\cdot}$	9.5×10^7
(4) (a)	ZV	+	$PVC_3^{+\cdot}$	$\longrightarrow$	$ZV^{-\cdot}$	+ PVC_3^{2+}	4.5×10^4
(b)	ZV	+	$PVC_6^{+\cdot}$	$\longrightarrow$	$ZV^{-\cdot}$	+ PVC_6^{2+}	2.5×10^4

a) All experiments were done in the presence of 1% 2-propanol and pH= 6.8(5 mM phosphate buffer), $\mu = 2 \times 10^{-2}$; $[Ru(NH_3)_6^{2+}] = 5 \times 10^{-5}$M and $[V^{2+}] = 0.1$-1 mM. b) Accuracy, ±10%, 1 M = 1 mol dm^{-3}.

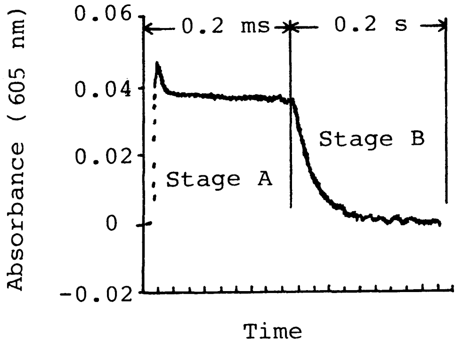


Fig. 1. Decay of the absorption of $ZV^{-\cdot}$ by electron transfer to $Ru(NH_3)_6^{3+}$ and to PVC_3^{2+} (fast decay in Stage A) and decay of the viologen radical equilibrate system by electron transfer to $Ru(NH_3)_6^{3+}$ (slow decay in Stage B). Experimental conditions: $[PVC_3^{2+}] = 5$ mM, [ZV] =1 mM, $[Ru(NH_3)_6^{3+}] = 5 \times 10^{-5}$M; $[V^{+}] = 5.7$ µM; 1% 2-propanol at pH = 6.8; Ar saturated.

parent methyl viologen (MV^{2+}) system in efficiency of production of $V^{+\cdot}$ radicals.[12)] Presumably in the combined system the effecient quencher ZV mediates the photo-liberatd electrons to the PV^{2+} system which, due to its polycationic nature and higher redox potential, will back react rather slowly with $Ru(bpy)_3^{3+}$. In the present study we attempt to obtain some quantitative information on the electron transfer rate and equilibrium constants in the ZV/PV^{2+} system.[13)]

The radicals $ZV^{-\cdot}$ and $PV^{+\cdot}$ were produced using the pulse radiolysis technique[14)] and the rate of electron transfer from these radicals to $Ru(NH_3)_6^{3+}$ was measured by following the decay of their absorbance at 605 nm. The Ru(III)hexamine provides a chemically stable model system for $Ru(bpy)_3^{3+}$, while the latter is well known to react with water. The use of the pulse radiolysis technique overcomes problems associated with low efficiency of quenching of the excited state of $Ru(bpy)_3^{2+}$ by PV^{2+} or low yield of photoproduction of $ZV^{-\cdot}$ in this system.[15)] The lower redox potential of $Ru(NH_3)_6^{3+}$ (E^0=0.24 V) as compared to the tris(bipyridine) complex is, however, reflected also in the rate constants of electron transfer from $V^{+\cdot}$.

In Table 1 we summarize the kinetic parameters for electron transfer between the $V^{+\cdot}$ radicals and $Ru(NH_3)_6^{3+}$ and among themselves. The rate constants for reactions 1 and 2 were measured in the presence of one of the corresponding V^{2+} alone. The back reactions in the viologen polymer systems are thus inhibited by more than three orders of magnitude. When both, PV^{2+} and ZV, are present in the solution, production of $ZV^{-\cdot}$ is favoured initially over the production of $PV^{+\cdot}$ since the rate constant for the reaction of the primary radicals (e_{aq}^- and $(CH_3)_2\dot{C}OH$)

with PV^{2+} is slower than with ZV. The equilibration between $ZV^{-\cdot}$ and $PV^{+\cdot}$ (reactions 3, 4 in Table 1) is difficult to follow directly due to the similiarity in absorption spectra of the two viologen radicals. However, in the presence of low concentration of $Ru(NH_3)_6^{3+}$ (excess ZV) competition between reaction 1 and the equilibrium reaction can be observed (see Fig. 1, fast decay in Stage A). The observed rate constant for this decay fits well the expected equation $k_{f,obsd} = k_1 [Ru(III)] + k_2[PV^{2+}]$ in the concentration range $[PV^{2+}] = (0.1-2) \times 10^{-3}$ M. Rate constants for the electron transfer from $ZV^{-\cdot}$ to two PV^{2+} are given in Table 1.

Once the above described fast decay (Stage A) is completed and the exchange equilibrium is established, $Ru(NH_3)_6^{3+}$ slowly reacts with $PV^{+\cdot}$ and with the low steady state concentration of $ZV^{-\cdot}$ (slow decay in Stage B). Under these conditions the overwhelming majority of the viologen radicals are in the form of $PV^{+\cdot}$, the steady state approximation for $ZV^{-\cdot}$ yields Eq. 1. The observed rate constant for

$$k_{s,obsd} = k_2 + \frac{k_1 k_2 [ZV]}{k_3[PV^{2+}] + k_1[Ru(III)]} [Ru(III)] \qquad (1)$$

$V^{+\cdot}$ disappearance at constant $[PV^{2+}]$ and [Ru(III)] was found to be linear with [ZV] and provides a route to calculate k_4 (Table 1). The redox equilibrium constant $K_{eq} = k_3/k_4$ could thus be evaluated for the two viologen polymers. We thus obtain $K_{eq} = 2.4 \times 10^3$ for PVC_3^{2+} and $K_{eq} = 3.8 \times 10^3$ for PVC_6^{2+}.

The redox potential for ZV was determined both by cyclic voltammetry and by pulse radiolysis[16)] to be $E^0_{ZV/ZV^{-\cdot}} = -0.345$ V. From K_{eq} we obtain $E^0_{PV^{2+}/PV^{+\cdot}} = -0.145$ V for PVC_3^{2+} and $E^0_{PV^{2+}/PV^{+\cdot}} = -0.134$ V for PVC_6^{2+}. These values may be compared with cyclic voltammetry results for viologen copolymers.[17)] It should however be pointed out that adsorption peaks are evident in the cyclic voltammograms previously reported[17a)] as well as in our own experiments. The higher redox potential of PV^{2+} than that of benzyl viologen ($E^0_{BV^{2+}/BV^{+\cdot}} = -0.354$ V[18)]) indicates increased thermodynamic stability of the $PV^{+\cdot}$, which maybe related to charge migration among the V^{2+} units along the polymer chain. Slightly higher stabilization of the longer chain viologen radical ($PVC_6^{+\cdot}$) as compared to the polymer radical ($PVC_3^{+\cdot}$), is obtained by hydrophobic interactions of the former with local aggrerates along the polymer chain. When further stabilization through dimerization of $V^{+\cdot}$ is considered,[19)] a radical of more negative redox potential than $PV^{+\cdot}$ as an electron relay will be required for photoproduction of molecular hydrogen. Further implication to the photochemical system, where a combination of ZV and PV^{2+} is used, could be deduced from the kinetic results of the present study. The high charge density of the polyelectrolyte viologen is sufficient to suppress the back reaction under the experimental conditions of the photochemical experiment so that charge transfer, from $ZV^{-\cdot}$ to PV^{2+}, dominates. Furthermore, in the combined system the back reaction will proceed through the small steady state concentration of $ZV^{-\cdot}$.

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