A New Electron Mediator: Reduction by $Na_2S_2O_4$ in Organic Media of a Novel Viologen Functionalized with Crown Ether Structure

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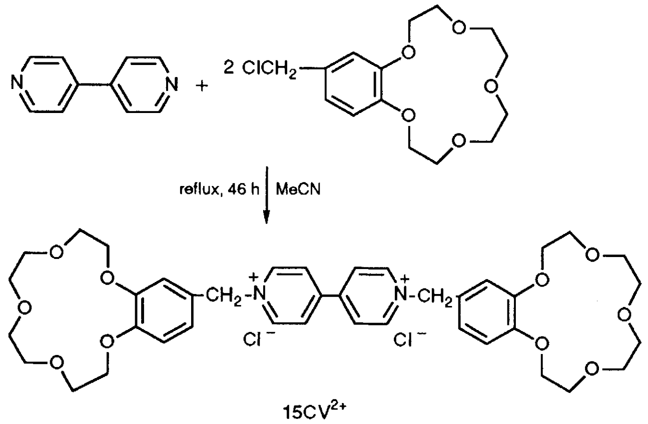
Synthesis of a novel viologen functionalized with two 15-crown-5 units, and its reduction by sodium dithionite in organic media, were conducted; the viologen is efficiently reduced to its monomeric cation radical owing to the solubilisation of sodium dithionite in the organic solvent by the 15-crown-5 moiety.

Viologens (4,4′-bipyridinium salts) are efficient electron mediators in the photoinduced reduction of protons,[1] reductions of various organic compounds[2] and biomimetic electron relay systems.[3] These electron relays have been studied mainly in aqueous, or aqueous–organic two phase systems. The reduction of organic compounds by sodium dithionite ($Na_2S_2O_4$) in dichloromethane has been successfully achieved using viologen polymers containing polyether units, that acted as non-cyclic crown ethers to solubilize $Na_2S_2O_4$ efficiently in the medium.[4] In the case of redox systems using the viologen polymers, viologen cation radicals ($V^{+\bullet}$) reduced by $Na_2S_2O_4$ contained both the monomeric and dimeric $V^{+\bullet}$, the latter formed intramolecularly between the neighbouring monomeric units present in the polymer. Since $V^{+\bullet}$ dimers are not active for reduction of substrates,[5] selective formation of monomeric $V^{+\bullet}$ as electron mediators is required to construct an effective redox system. Macrocyclic receptor molecules containing azobenzene units,[6] and redox-active molecules



15CV^{2+}

Scheme 1

functionalized with crown ether units have been reported.[7,8] We designed a viologen derivative having crown ether units which is considered to be reduced selectively by $Na_2S_2O_4$ to its monomeric cation radicals in organic solvents. In this communication, we report the synthesis and reduction by $Na_2S_2O_4$ in organic solvents of a novel viologen functionalized with two crown ether units.

The novel viologen derivative (15CV^{2+})† containing two benzo-15-crown-5 groups was prepared by the reaction of 4,4′-bipyridine with 4′-chloromethylbenzo-15-crown-5 in acetonitrile for 46 h (Scheme 1).

15CV^{2+} is soluble in ethanol, methanol and dimethyl sulfoxide at a concentration of *ca.* 0.02 mol dm^{-3}, although a reference compound, benzyl viologen (BzV^{2+}), is insoluble in ethanol. 15CV^{2+} was also partially soluble in warm acetonitrile (MeCN) and dichloromethane at the same concentration.

The reduction of 15CV^{2+} was conducted in methanol as follows; $Na_2S_2O_4$ (2 mg) was measured into a quartz cell, and the cell was flushed with Ar. A solution of 15CV^{2+} (4 ml, *c.* 0.1 mmol dm^{-3}) degassed with Ar was added to the quartz cell, and then the solution was stirred at room temperature under Ar. The monomeric cation radical (15CV$^{+\bullet}$, λ_{max} = 605 nm) of 15CV^{2+} was produced immediately; this was ascertained by comparing its electronic spectrum with that of authentic cation radicals of viologens. The concentration of the 15CV$^{+\bullet}$ produced increased rapidly and 15CV^{2+} was reduced to 15CV$^{+\bullet}$ quantitatively after one minute. In contrast, in the reduction of BzV^{2+} the corresponding cation radical (BzV$^{+\bullet}$) was formed more gradually, and the conversion of BzV$^{+\bullet}$ reached 80% after 2 min. $Na_2S_2O_4$ seems to be soluble slightly in methanol owing to the presence of traces of water, and consequently BzV^{2+} would be reduced by the $Na_2S_2O_4$ dissolved in methanol. Next, we attempted to reduce 15CV^{2+} with $Na_2S_2O_4$ in MeCN, but it was not sufficiently soluble. Thus, the reduction of 15CV^{2+} was carried out in MeCN containing 2 vol% of water (MeCN–2% H_2O); 15CV$^{+\bullet}$ was produced gradually after about 1 min, and 15CV^{2+} was reduced to 15CV$^{+\bullet}$ quantitatively after 5 min. Attempted reduction of BzV^{2+} in MeCN–2% H_2O similarly led to only a slight production of BzV$^{+\bullet}$ after 3 min. Reduction of a mixture of BzV^{2+} and benzo-15-crown-5 (B15C5) by $Na_2S_2O_4$ in MeCN–2% H_2O gave only a small amount of BzV$^{+\bullet}$ after 3 min. After 3 min BzV$^{+\bullet}$ formed, and the conversion attained about 50% after 5 min. The efficiency of the reduction of 15CV^{2+} is clearly higher than that of a mixture of B15C5 and BzV^{2+} (Fig. 1). These results suggested

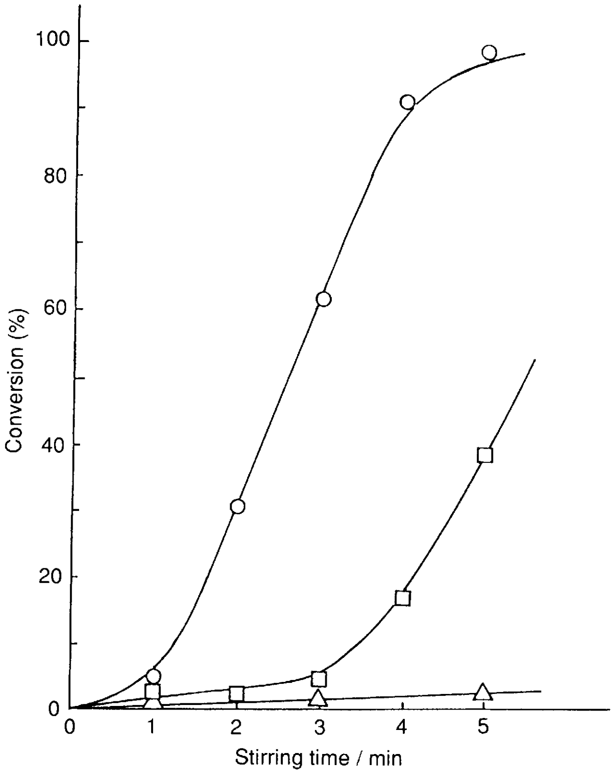


Fig. 1 Formation of cation radicals in MeCN–2% H_2O: 15CV^{2+} (○); BzV^{2+} (△); mixture of BzV^{2+} and B15C5 (□), conc. = 0.1 mmol dm^{-3}, $Na_2S_2O_4$ = 280 mol%

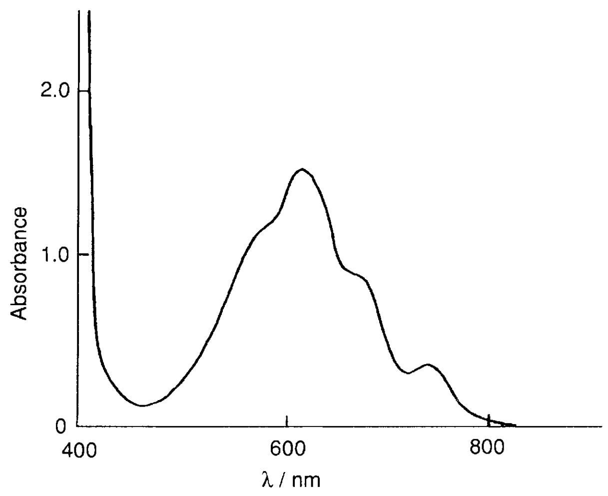


Fig. 2 Electronic spectrum of 15CV$^{+\bullet}$ in MeCN–2% H_2O; concn. = 0.1 mmol dm^{-3}

that the 15-crown-5 moiety of 15CV^{2+} efficiently formed a complex with $Na_2S_2O_4$ to make $Na_2S_2O_4$ soluble into the solvent; subsequently, the viologen could be reduced by the solubilised $Na_2S_2O_4$.

As previously mentioned, cation radical dimers of viologens showing an absorption at *ca.* 550 nm are more stable than the corresponding monomeric cation radicals, and have low potential for reductions of substrates.[5] Since 15CV^{2+} is reduced selectively to the monomeric cation radical by $Na_2S_2O_4$ (Fig. 2) it is a very suitable electron mediator for electron-transfer systems in organic solvents.

Attempts to estimate the redox potential of 15CV^{2+} by cyclic voltammetry (CV) in MeCN–2% H_2O with tetraethyl-

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† IR (KBr) ν/cm^{-1} 2920, 2872, 1635, 1517 and 1176. ^{1}H NMR (250 MHz, D_2O) δ 3.77–4.27 (m, 32 H), 5.90 (s, 4 H), 7.18 (m, 6 H), 8.55 (m, 4 H), 9.15 (m, 4 H). Satisfactory elemental analyses were obtained for the compound.

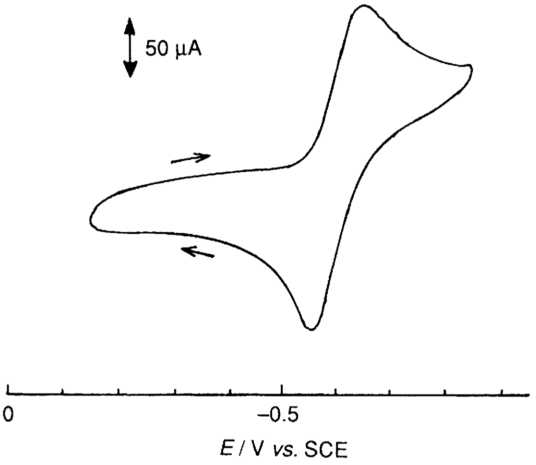

Fig. 3 Cyclic voltammetry of 15CV^{2+} in water; Et_4NCl, 0.2 mol dm^{-3}; scan rate, 2.0 × 10^2 mV s^{-2}

ammonium perchlorate as a supporting electrolyte could not be carried out because of the solubility of 15CV^{2+} under the measurement conditions, and so the redox potential was measured in ion-exchanged water containing tetraethylammonium chloride. A reversible CV profile (Fig. 3) was observed similar to that for BzV^{2+}. From the profile, the redox potential ($E_{\frac{1}{2}}$) of 15CV^{2+} to the corresponding cation radical (15CV$^{+\cdot}$) was estimated to be −0.59 V *vs* SCE (SCE = saturated calomel electrode), which was almost the same as that of BzV^{2+} (−0.58 V). CV measurements on 15CV^{2+} in water containing an excess of NaCl led to a similar reversible curve as in the absence of NaCl, and the $E_{\frac{1}{2}}$ for reduction of 15CV^{2+} to 15CV$^{+\cdot}$ was equal to that (−0.59 V) in the absence of NaCl. These results demonstrate that 15CV^{2+}, in which the 15-crown-5 moiety formed a complex with NaCl, was reduced electrochemically with equal ease as free 15CV^{2+}.

Thus, efficient production of the monomeric cation radical of a viologen by $Na_2S_2O_4$ in organic solvents was successfully accomplished by designing the novel viologen (15CV^{2+}) functionalized with 15-crown-5 units. 15CV^{2+} should provide a basis for the construction of new redox systems in organic media.

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