5.12 (t, 1 H), 5.48 (dd, 1 H), 7.46 (m), 7.76 (br); IR (KBr) 3420, 3280, 2930, 1895, 1620, 1210, 1065 cm^{-1}. Anal. Calcd for $C_{24}H_{27}N_3O_6S$: C, 59.37; H, 5.60; N, 8.65, S, 6.60. Found: C, 59.26, H, 5.66; N, 8.63; S, 6.66.

7-[(2-(2-Pyridyl)ethyl)oxy]-9a-methoxymitosane (25): yield 31%; ^{1}H NMR (pyridine-d_5) δ 1.68 (s, 3 H), 1.68 (br, 1 H), 2.72 (br, 1 H), 3.08 (br, 1 H), 3.20 (t, 2 H), 3.20 (t, 3 H), 3.50 (d, 1 H), 3.92 (dd, 1 H), 4.16 (d, 1 H), 4.92 (m), 5.38 (dd, 1 H); IR (KBr) 3430, 3300, 2930, 1715, 1625, 1210, 1060 cm^{-1}. Anal. Calcd for $C_{22}H_{24}N_4O_6$: C, 59.99, H, 5.49; N, 12.72. Found: C, 59.94; H, 5.66; N, 12.63.

Registry No. **4**, 4055-39-4; **5**, 7041-61-4; **7**, 21124-13-0; **8**, 109-73-9; **9**, 75-31-0; **10**, 2038-03-1; **11**, 109-85-3; **12**, 1007-54-1; **13**, 2706-56-1; **14**, 53477-45-5; **15**, 50707-41-0; **16**, 104376-54-7; **17**, 104393-20-6; **18**, 104376-55-8; **19**, 104376-56-9; **20**, 56981-64-7; **21**, 56981-61-4; **22**, 103864-79-5; **23**, 76079-90-8; **24**, 103840-03-5; **25**, 103840-02-4; p-$MeC_6H_4N_2^+Cl^-$, 2028-84-4.

Reduction of Acrylonitrile in the Presence of Viologen Derivatives

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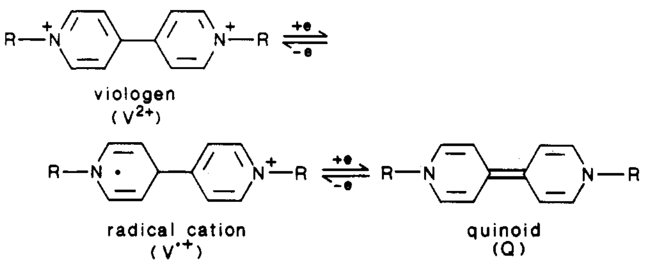
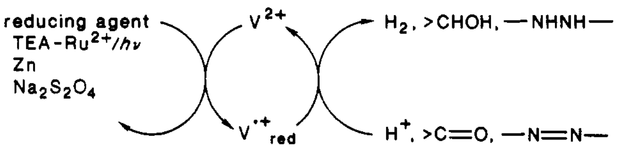
Viologen (N,N-dialkyl-4,4′-dipyridinium, V^{2+}) is well-known to produce the blue radical cation ($V^{\cdot+}$) and quinoid (Q) by one-electron and two-electron reduction, respectively, and show redox behavior as below. The reduction of some substrates is of great interest using V^{2+} as electron-transfer catalyst (ETC). Methyl viologen (MV^{2+}) and viologen polymers (P-V^{2+}) have been studied as an effective electron mediator in hydrogen production,[1-4] the reduction of quinones or α-keto ester by zinc (Zn).[5,6] Further, we have also reported the reduction of azobenzene[7] by Zn, aromatic aldehydes, and ketones by sodium dithionite ($Na_2S_2O_4$)[8] in the presence of V^{2+} as ETC.



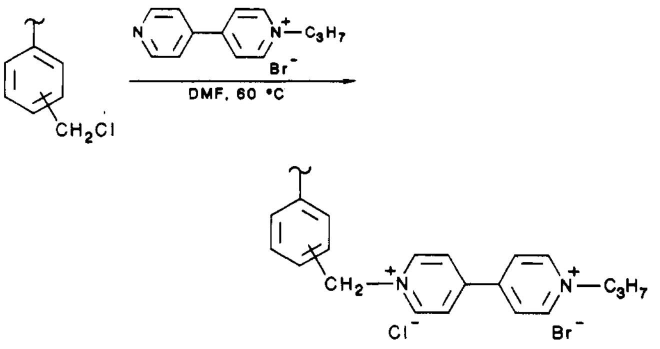


In this article the role of MV^{2+} and P-V^{2+} as ETC is examined in the reduction of acrylonitrile with Zn powder and sodium dithionite.

Experimental Section

Materials. The soluble polymer (P-1) containing viologen moiety was synthesized from poly(chloromethylstyrene–styrene) (CH_2Cl; 33 mol %) and 1-propyl(4-pyridyl)pyridinium bromide in dimethylformamide (DMF) at 60 °C for 48 h. After the reaction, P-1 was obtained by reprecipitating with excess acetone (yield 95%, V^{2+} content = 31 mol %). 1-Propyl-4-pyridylpyridinium bromide was prepared according to a reported method.[9]

The cross-linked polymer (P-2 V^{2+} content; 12 mol %) carrying V^{2+} moiety was also obtained from cross-linked chloromethylated polystyrene (DVB = 2 mol %, CH_2Cl = 15 mol %, 50 mesh) by the same method described above (V^{2+} content = 12 mol %). The content of V^{2+} in the polymers was estimated by elemental analysis. (P-1; N, 4.36. P-2; N, 2.90.) 1,1′-Dihydrodipyridyl (Q) was prepared according to the reported procedure.[10]

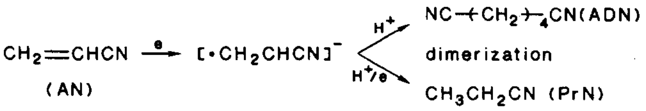


Reduction of Acrylonitrile by Zinc in the Presence of V^{2+}. A typical procedure for the reduction of acrylonitrile (AN) is as follows: A solution AN (50 mmol) in $MeOH$–H_2O (5:1 = 5 mL) was added to zinc (Zn, 60 mmol) as a reducing agent and methyl viologen (MV^{2+}) or P-1, P-2. (V^{2+}/AN = 2–20 mol %). The reaction mixture was stirred at 50 °C for 4 days in sealed tube. After removing Zn with titration, the yield of adiponitrile (ADN) was estimated from the ratio of peak area of AN and ADN by GLC analysis of the solution.

Reduction of Acrylonitrile by Sodium Dithionite in the Presence of V^{2+}. To an aqueous solution (50 mL) of $Na_2S_2O_4$ (50 mmol), K_2CO_3 (100 mmol), and viologens (V^{2+}/AN = 2–10 mol %) was added an MeOH solution (50 mL) of AN (50 mmol). The reaction mixture was stirred at room temperature for 4 days under an argon atmosphere. After extracting with either, the solvent was removed in vacuo. The yield of products (ADN and propionitrile) was determined by GLC analysis in same manner as described before. Further, the reduction of fumaronitrile was also carried out by the same method.

Results and Discussion

Reduction of Acrylonitrile with Zn/V^{2+} System. The adiponitrile (ADN) has been industrially produced by the electrochemical reduction of acrylonitrile (AN). As byproducts, propionitrile (PrN) and some oligomers are obtained.[11]



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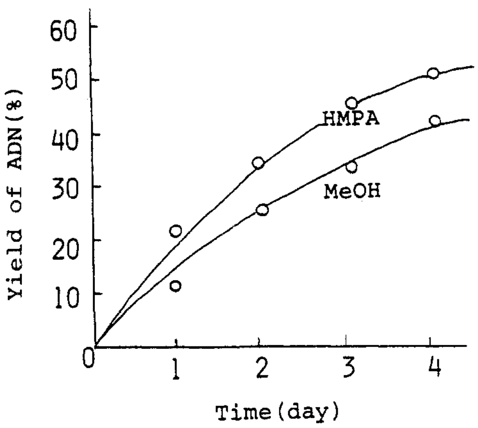


Figure 1. Effect of time on the reduction of acrylonitrile by Zn in the presence of MV^{2+} (20 mol %).

Table I. Reduction of Acrylonitrile (AN) by Zn[a] in the Presence of V^{2+}

V^{2+} [b]	V^{2+}/AN[c] (mol ratio)	recovered AN (%)	yield (%)	
			ADN	PrN
MV^{2+} [d]	0.10	64	34	0
	0.05	87.7	12.3	0
	0.02	95	5	0
P-1	0.02	85	15	0
P-2	0.02	88	12	0

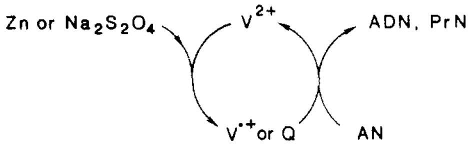
[a] Zn = 60 mmol, AN = 50 mmol, MeOH/H_2O = 5/1, 4 days, 50 °C. Zn/Zn^{2+} ($E°$ = −0.762 vs. SHE). [b] N,N′-Dialkyl-4,4′-dipyridinium (V^{2+}). [c] $E_{1/2}$ = −1.94 vs. SCE. [d] $E°$ = −0.44 (pH 7, 30 °C).

Table II. Solvent Effect on Reduction of Acrylonitrile (AN)[a]

solvent	V^{2+}/AN	recovered AN (%)	yield of ADN (%)
MeOH–H_2O	0.20	57	43
CH_3CN–H_2O	0.20	77	23
DMF–H_2O	0.20	65	35
HMPA[a]–H_2O	0.20	48	52

[a] Zn = 30 mmol, AN = 25 mmol, org. sol./H_2O = 5/1, 4 days, 50 °C. [b] Hexamethylphosphoramide.

We attempted to reduce AN in an electron-transfer system containing the reducing agents (Zn, $Na_2S_2O_4$) and V^{2+} as ETC.



The reduction of AN with zinc powder in the presence of V^{2+} as a catalyst proceeded smoothly to obtain ADN selectively which is afforded by one-electron reduction of AN, although the reduction could not occur at all in the absence of V^{2+} due to a large difference of redox potential between V^{2+} and AN. The results are summarized in Table I. As the amount of MV^{2+} as ETC increased, the yield of ADN increased. The soluble viologen polymer (P-1) and cross-linked polymer (P-2) acted as ETC effectively. The solvent effect in the reduction of AN with zinc by use of MV^{2+} (20 mol %) as ETC was examined, as shown in Table II. The cosolvent such as CH_3CN and DMF lowered the yield of ADN. The effect of time on the yield of ADN is shown in Figure 1. The viologen radical cation obtained by the reduction with Zn acted as active species in the reduction to give ADN.

Table III. Reduction of Acrylonitrile (AN) by $Na_2S_2O_4$ in the Presence of V^{2+} [a]

V^{2+}	V^{2+}/AN (mol ratio)	recovered AN (%)	yield (%)	
			ADN	PrN
MV^{2+}	0.10	15	62.5	12.5
	0.05	54.5	30	15.5
	0.02	92.7	2.1	5.2
P-1	0.02	18.6	33.7	47.7
P-2	0.02	34.1	29.3	36.6
quinoid	2.20[b]	5	49.0	46.0

[a] AN = 50 mmol, $Na_2S_2O_4$ = 60 mmol, K_2CO_3 = 100 mmol, MeOH/H_2O = 1/1, 4 days, rt, under argon. [b] Quinoid as reducing agent.

Reduction of Acrylonitrile with $Na_2S_2O_4$/V^{2+} System. It has been reported[8,10] that viologen derivatives give the quinoid form (Q) by two-electron reduction with sodium dithionite ($Na_2S_2O_4$) in alkaline solution. It was found that AN was reduced with $Na_2S_2O_4$ in the presence of V^{2+} as an ETC to ADN and PrN. Both radical cation and quinoid form were active species in the reduction, and 1,1′-dihydrodipyridyl (Q), which was obtained by the reduction of MV^{2+} with $Na_2S_2O_4$, could easily reduce AN to give ADN and PrN as shown in Table III. Further, fumaronitrile as a substrate could be also reduced by Zn or $Na_2S_2O_4$ with MV^{2+} to obtain succinonitrile quantitatively. Our results suggest that V^{2+} such as MV^{2+} and polymeric viologen have played the role of catalysts for the reduction of active olefines, and especially AN is reduced to ADN or PrN by the difference of reducing agents.

Registry No. Q, 25128-26-1; MV^{2+}, 1910-42-5; AN, 107-13-1; ADN, 111-69-3; PrN, 107-12-0; Zn, 7440-66-6; sodium dithionite, 7775-14-6.

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The Structure of Two Isomeric 1,3,2-Dioxaphosphorinanes

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Previously,[1] we have reported the synthesis of 5-(benzyloxy)-2-chloro-1,3,2-dioxaphosphacyclohexane 2-oxide (1) which was used to prepare 2′-deoxy-5-fluoro-5″-hydroxy-5′-O-1″,3″,2″-dioxaphosphacyclohex-2″-yluridine 2″-dioxide (2). At the time, we commented on the fact that these compounds could exist in two isomeric forms, depending upon the orientation of the substituent in the 1,3,2-dioxaphosphacyclohexane ring, but we could not establish the orientation or indeed whether they were mixtures. We subsequently became aware of a paper by Denney and Varga[2] in which they reported the synthesis of 5-hydroxy-2-methoxy-1,3,2-dioxaphosphacyclohexane 2-oxide (3), but again the configuration was not established, although they suspected that the isomer with the methoxyl and hydroxyl groups in the axial positions was the most likely one to be present.

Our interest in the synthesis of 2 was a part of a project to prepare metabolically labile[3] and acid-labile dioxap-

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