

Ag(II)-Bipyridyl Complex—Development as a Redox Titrant

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An acidic solution (1.0 M HNO₃) of silver(II) bipyridyl nitrate is found to be suitable as a titrant for oxalic acid. Like potassium permanganate, it is a self-indicator and an advantage over permanganate is that oxidation of oxalic acid by silver(II) bipyridyl is very fast and the titration can be performed at room temperature and also in the cases where permanganate ions interfere. Results yield almost a 2% higher concentration but it being a regular feature, can be adjusted by giving a proper allowance.

INTRODUCTION

Higher valent silver, *i.e.*, silver(II) and silver(III) are not much stable in the form of their simple compounds even in the solid state but many of their complexes are quite stable, Silver(II)-bipyridyl complex [Ag(bipy)₂]²⁺ is one of such stable complexes¹, 2,2'-bipyridine being a donor nitrogen containing ligand.

The +2 and +3 states of silver are among the strongest oxidants known² in aqueous solution. The silver(II) complexes are also potent oxidants. The redox potential of Ag(bipy)₂²⁺/Ag(bipy)₂⁺ is 1.453 V in 1.0 M HNO₃ at 25°C³. Solutions of Ag(bipy)₂²⁺ salts bring about quantitative oxidation⁴ of nitrous acid, oxalic acid, and vanadyl ions. This complex may find use as an oxidant in some redox titrations if proper conditions are set. Some initial efforts in this direction were made by Barbieri *et al.*⁴. We have been successful in deciding the proper conditions and also in bringing out a little economy.

EXPERIMENTAL

Silver(II) bipyridyl nitrate was prepared by the oxidation of silver(I) bipyridyl nitrate with peroxydisulphate. Light yellow coloured [Ag(bipy)₂]NO₃ (prepared by the reaction of hot 50% ethanolic solution of AnalaR silver nitrate with hot 50% ethanolic solution of AnalaR 2,2'-bipyridine) was dissolved in a concentrated aqueous solution of GR grade K₂S₂O₈ with constant stirring¹. A time of 1 h was allowed for the complete reaction. Red-brown crystals of silver(II) bipyridyl nitrate are separated. The complex is in fact in the form of its monohydrate⁵, *i.e.*, [Ag(bipy)₂](NO₃)₂·H₂O. It was filtered, washed with water and dried. Solution of silver(II) bipyridyl nitrate was prepared in 1.0 M aqueous AnalaR nitric acid. Red-brown clear transparent solution was obtained. Since silver(II) bipyridyl nitrate oxidises water and its concentration decreases rapidly, the

solution was first stored in dark for 24 h and filtered. The solution was now standardised with a standard solution of hydrogen peroxide (GR) and used for titration. The decrease in concentration of silver(II) bipyridyl nitrate was negligible in a 24 h old solution and the formed silver(I) bipyridyl nitrate did not interfere in titration.

Other reagents used were also of AnalaR of GR grade. Volumetric titrations were conveniently performed at room temperature using the usual procedure. Like potassium permanganate, the silver(II) bipyridyl nitrate is a self-indicator and disappearance of red-brown colour indicated the equivalence point. Titration between oxalic acid and potassium permanganate was also performed by the usual procedure.

Water was distilled once in an all-glass still; subsequent purification is not very effective⁶.

Faint red-brown titrated solutions were not thrown. Instead they were collected and stored in air-tight flasks in dark.

RESULTS AND DISCUSSION

Three different aqueous solutions of oxalic acid (0.001 N, 0.002 N and 0.005 N) were used for testing the usefulness of acidic (1.0 M HNO₃) silver(II) bipyridyl nitrate solution as a redox titrant. Comparison was made by titrating the same oxalic acid solutions with standardised potassium permanganate solutions. Results are given in Table-1.

TABLE-1

(COOH) ₂ ·2H ₂ O		[Ag(bipy) ₂](NO ₃) ₂ ·H ₂ O		KMnO ₄	
Normality N	Volume mL	Normality N	Volume mL	Normality N	Volume mL
0.001	10.0	0.001	10.2	0.001	10.0
0.001	10.0	0.002	5.1	0.002	5.0
0.002	10.0	0.001	20.5	0.001	20.0
0.002	10.0	0.002	10.2	0.002	10.0
0.005	10.0	0.001	51.0	0.001	50.0
0.005	10.0	0.002	25.6	0.002	25.0

More concentrated solutions of silver(II)-bipyridyl nitrate were not used for titration since more salt dissolved only with difficulty and also the concentrated solutions were found to be comparatively less stable. The most suitable concentration of nitric acid was found to be 1.0 M to prepare the solutions of silver(II) bipyridyl nitrate. Below 1.0 M HNO₃ the [H⁺] has an inverse order⁷ (in the reaction in which silver(II) bipyridyl nitrate oxidises water). Above 1.0 M HNO₃ we found a catalytic effect of [H⁺] in the reaction involving the oxidation of water by silver(II) bipyridyl nitrate.

Silver(II) bipyridyl nitrate solution in 1.0 M nitric acid seems to be a good titrant for oxalic acid. As evident, only about 2% higher concentration of oxalic acid is indicated by this reagent. However, since it seems to be a regular feature, this much adjustment can always be made while calculating the results. A big advantage of silver(II)-bipyridyl solution over permanganate solution is the fact that the titration with the former can be performed at room temperature because the reaction is sufficiently fast whereas in latter case the heating is required. The reagent can be used as an alternative when for one reason or other the heating is to be avoided or where the permanganate ions interfere.

The development of silver(II) bipyridyl as a redox titrant is not a replacement to the potassium permanganate which is very economic but a little economy can be made in the case of former also by regenerating the silver(II) bipyridyl in the titrated solutions by the addition of calculated quantities of $K_2S_2O_8$ wherein the formed silver(I) bipyridyl nitrate is converted back to silver(II) state. Solutions so obtained are filtered and standardised again for reuse.

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