

Slow Electron Exchange at Tetrahedral Copper

A. GRAHAM LAPPIN and ROBERT D. PEACOCK

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

Received March 4, 1980

Introduction

The differing geometric requirements of copper(II) and copper(I) have a profound effect on the dynamics of electron transfer between the two oxidation states in aqueous solution. Thus, for copper complexes of 1,10-phenanthroline (phen) [1, 2] and its substituted derivatives [2, 3], conflicting reports of the Marcus self-exchange rate constants evaluated using the rates of different cross reactions, can be rationalised in terms of a concomitant structural change which may participate in the rate determining step of the cross reaction. Kinetic evidence for such a change has been presented [4] for the reduction of $\text{Cu}(\text{dmsphen})_2^{2+}$ where dmsphen^{2+} is 2,9-dimethyl-4,7-di(phenylsulphonate)1,10-phenanthroline, even though the steric requirements of the ligand are thought [5] to distort the geometry of the copper(II) complex towards the tetrahedral arrangement favoured by copper(I). This structural barrier to electron transfer is apparently minimised in the blue copper electron transport proteins such as plastocyanine and azurin where both oxidation states share a similar distorted tetrahedral geometry imposed by the folding of the amino acid chain [6]. Therefore, direct comparisons of the proteins with simpler copper complexes are not straightforward. The central metal ion coordination site in the 12-tungstometallate (Keggin) anions is a tetrahedral arrangement of oxide ligands which is retained on redox and is buried about 5 Å inside a polytungstate shell. This distance is similar to the distance of closest approach of the copper site to the surface of the blue protein plastocyanine. Previous studies [7] of the redox properties of $\text{CuW}_{12}\text{O}_{40}^{6-}$ indicate that the couple is reversible though the copper(I) complex may involve some $\text{Cu}^{\text{I}}-\text{W}^{\text{VI}} \leftrightarrow \text{Cu}^{\text{II}}-\text{W}^{\text{V}}$ intervalence charge transfer. It is of interest to investigate the electron transfer kinetic behaviour of this complex as it should be free from substantial structural rearrangement and should provide an interesting comparison with the blue copper proteins. Kinetic investigations of electron transfer properties of 12-tungstometallate complexes have hitherto been restricted [8, 9] to $\text{CoW}_{12}\text{O}_{40}^{5-}$. We present here a kinetic study of the oxidation of $\text{CuW}_{12}\text{O}_{40}^{7-}$ by

$\text{Fe}(\text{CN})_6^{3-}$ and evidence for slow electron transfer at tetrahedral copper.

Experimental

The cesium salt of 12-tungstocuprate(II), $\text{Cs}_6\text{CuW}_{12}\text{O}_{40}\cdot 10\text{H}_2\text{O}$, was prepared in low yield by methods outlined in the literature [10]. All measurements were made at 25 °C, in 0.01 M acetate buffer, pH 4.50 and ionic strength 0.1 M (NaClO_4). Cesium ion in these solutions was precipitated as CsClO_4 and was removed by millipore filtration.

The reduction potential of $\text{CuW}_{12}\text{O}_{40}^{6-}$ was determined under the above conditions using a three electrode system consisting of a platinum wire working electrode, a platinum wire auxiliary electrode and a Ag/AgCl reference electrode. Voltammograms were generated using a Bioanalytical Systems Inc CV-1A instrument and were recorded on a JJ Instruments PL51 X-Y recorder. Results indicate a reversible reduction potential of -230 mV (vs. Ag/AgCl) with a peak-to-peak ratio of 80 mV. Further reductions at more negative potentials were interpreted [7] in terms of heteropolyblue formation.

Solutions of $\text{CuW}_{12}\text{O}_{40}^{7-}$ were prepared by reduction of solutions of the copper(II) complex with a few crystals of dithionite. The products of dithionite oxidation had no effect on the subsequent reaction kinetics. The copper(I) complex has a broad absorption maximum at 485 nm (ϵ 2400 $\text{M}^{-1}\text{cm}^{-1}$) and is sensitive to aerial oxidation.

The kinetics of oxidation of $\text{CuW}_{12}\text{O}_{40}^{7-}$ by $\text{Fe}(\text{CN})_6^{3-}$ were monitored at the absorption maximum of the copper(I) complex using an Applied Photophysics Ltd. 1705P stopped-flow spectrophotometer. Reaction traces were recorded on a Tektronix 5111 storage oscilloscope and were analysed using a Data General Nova 2 minicomputer. Under conditions of excess $[\text{Fe}(\text{CN})_6^{3-}]$, the observed kinetics followed a first-order rate law.

$$\frac{-d[\text{Cu(I)}]}{dt} = k_{\text{obs}}[\text{Cu(I)}]$$

Excellent first-order plots were obtained and gave the pseudo-first order rate constant, k_{obs} . Rate constants are the average of at least three determinations.

Results and Discussion

The reduction potential of $\text{CuW}_{12}\text{O}_{40}^{6-}$ is -0.02 V relative to N.H.E. and is in good agreement with a value determined previously under conditions of

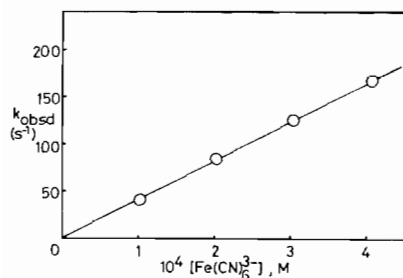
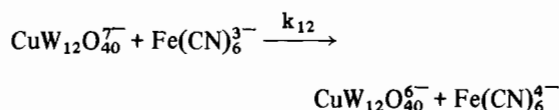


Fig. 1. Plot of k_{obs} against $[\text{Fe}(\text{CN})_6^{3-}]$ for reaction of $\text{CuW}_{12}\text{O}_{40}^{7-}$ with $\text{Fe}(\text{CN})_6^{3-}$ at 25 °C, 0.1 M NaClO_4 and pH 4.5. $[\text{CuW}_{12}\text{O}_{40}^{7-}] = 2.3 \times 10^{-5}$ M.

higher ionic strength [7]. The negative shift in the reduction potential compared with the aquo ion is not surprising in view of the charge on the polytungstate ligand. However, it does serve to illustrate the relative importance of the ligand donor compared to ligand geometry in stabilising copper(I) relative to copper(II).

Convenient preparation of the copper(I) complex allows examination of the kinetics of oxidation by $\text{Fe}(\text{CN})_6^{3-}$.



Pseudo first-order rate constants, k_{obs} , show a linear dependence on $[\text{Fe}(\text{CN})_6^{3-}]$ (Fig. 1), from which a second-order rate constant, k_{12} , of $4.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ was evaluated. While this value is of similar magnitude to the rate of oxidation of reduced parsley plastocyanin [11] by $\text{Fe}(\text{CN})_6^{3-}$ at pH 7.5, $9.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ no direct comparisons can be made since the driving forces for the reactions are very different.

The second-order cross-reaction rate constant can be related to the self-exchange rate constants k_{11} and k_{22} for the two reacting complexes by Marcus theory [12].

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$

where

$$\log_e f_{12} = \frac{(\log_e K_{12})^2}{4 \log_e(k_{11}k_{22}Z^{-2})}$$

and K_{12} is the overall equilibrium constant for the cross reaction and Z is the collision frequency, $10^{11} \text{ M}^{-1} \text{ s}^{-1}$. Electron transfer properties of $\text{Fe}(\text{CN})_6^{3-/4-}$ are well known with $E^\circ = 0.41 \text{ V}$ and $k_{11} = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ from which, by using an iterative method, a value for k_{22} , the self-exchange rate

constant for $\text{CuW}_{12}\text{O}_{40}^{6-/7-}$ of $2.61 \text{ M}^{-1} \text{ s}^{-1}$ was calculated. Marcus theory is not generally applicable to protein reactions when electron transfer proceeds by a protein-substrate complex [13], but for comparison, a self exchange rate around $10^5 \text{ M}^{-1} \text{ s}^{-1}$ can be calculated for plastocyanin using the above data.

The small value for the self-exchange rate constant of $\text{CuW}_{12}\text{O}_{40}^{6-/7-}$ is somewhat surprising in view of the limited structural change possible during redox and may indicate that the nature of the polytungstate medium through which the electron must pass has a controlling influence on the reaction. Evidence in support of this postulate comes from comparison of the exchange rates of $\text{CuW}_{12}\text{O}_{40}^{6-/7-}$ ($2.61 \text{ M}^{-1} \text{ s}^{-1}$) and $\text{CoW}_{12}\text{O}_{40}^{5-/6-}$ ($0.45 \text{ M}^{-1} \text{ s}^{-1}$, LiCl) [8] at 25 °C and 0.1 M ionic strength. In view of the differences in experimental conditions and the inaccuracies involved in determining the former parameter by Marcus theory, the agreement is very close, suggesting that the rate limiting step in both reactions is the same. A hop mechanism involving rate determining electron transfer within the tungstate shell is proposed.

Further studies on these and similar complexes are in progress.

Acknowledgement

The authors wish to thank the S.R.C. for support in the purchase of the stopped-flow apparatus.

References

- 1 G. S. Yoneda, G. L. Blackmer and R. A. Holwerda, *Inorg. Chem.*, **16**, 3376 (1977).
- 2 M. A. Augustin and J. K. Yandell, *J. Chem. Soc. Chem. Comm.*, 370 (1978); *Inorg. Chem.*, **18**, 577 (1979).
- 3 A. G. Lappin, M. P. Youngblood and D. W. Margerum, *Inorg. Chem.*, in press.
- 4 N. Al-Shatti, A. G. Lappin and A. G. Sykes, to be submitted.
- 5 B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961).
- 6 P. M. Colmann, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw and M. P. Vekatappa, *Nature*, **272**, 319 (1978).
- 7 D. R. Wexell and M. T. Pope, *J. Chem. Soc. Chem. Comm.*, 886 (1971).
- 8 P. G. Rasmussen and C. H. Brubaker, *Inorg. Chem.*, **3**, 977 (1964).
- 9 Z. Amjad, J.-C. Brodovitch and A. McAuley, *Canad. J. Chem.*, **55**, 3581 (1977).
- 10 D. H. Brown and J. A. Mair, *J. Chem. Soc.*, 3946 (1962).
- 11 M. G. Segal and A. G. Sykes, *J. Am. Chem. Soc.*, **100**, 4585 (1978).
- 12 R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).
- 13 A. G. Lappin, M. G. Segal, D. C. Weatherburn and A. G. Sykes, *J. Am. Chem. Soc.*, **101**, 2297 (1979).