Effect of Some Macrocyclic Ligands on the Rate of Reduction of Perchlorate Ion by Titanium(III)*

*Giulio A. Amadei and Joseph E. Earley, Sr.***

Department of Chemistry, Georgetown University, Washington DC 20057, USA

Complexation with cyclam increases the rate of reduction of perchlorate ion by Ti^{III} (in acidic, aqueous, 4 mol dm^{-3} LiCl solutions at 25 °C) relative to the rate of the corresponding reduction of Ti^{3+}. A modified cyclam with pendant amine and *p*-aminobenzyl functional groups is more effective in this regard than is cyclam itself. Both redox reactions are acid catalyzed. The data is consistent with involvement of an intermediate containing two Ti^{III} centers.

Key words: titanium(III), perchlorate, perchlorate-reduction, cyclam, catalysis, kinetics, dinuclear intermediate, macrocyclic ligands, titanous ion.

INTRODUCTION

In aqueous media, perchlorate ion has an exceedingly low tendency to participate in either substitution or oxidation-reduction reactions and therefore is widely used as the anionic component of inert supporting electrolytes in studies of inorganic solution chemistry. Powerful inorganic reductants such as stannous ion or chromous ion display no detectable reactivity with perchlorate ion under usual conditions. In contrast to the lack of reactivity of aqueous solutions of perchlorates, solid perchlorate salts are powerful oxidants, and have been extensively used in rocket propulsion systems. Large quantities of perchlorates have been discarded in connection with military and industrial activities. Advances in analytical techniques have made it possible to detect low concentrations of perchlorate ion in water supplies. In

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regions of heavy perchlorate use, perchlorate levels in ground water have been found to be high enough to raise serious concern. Prolonged ingestion of water contaminated by low concentrations of perchlorate may interfere with thyroid function. There is a need to devise efficient and cost-effective ways to destroy perchlorates.[1]

A few inorganic reductants do react with perchlorate ion more or less rapidly[2] – among them is titanous ion, $[Ti(H_2O)_6]^{3+}$ (hereafter designated Ti^{3+}). Since the oxidation products of Ti^{III} are titania (TiO_2) and related materials – widely used as nontoxic white pigments – Ti^{III} would be a highly favorable choice for use in destruction of perchlorate, if a catalyst could be found to increase the rate of that reaction.

This paper reports that the macrocyclic ligand »cyclam«, **I**, increases the rate of reduction of perchlorate ion by Ti^{III} and a related ligand, **II**, that we have recently synthesized, does so even more effectively.
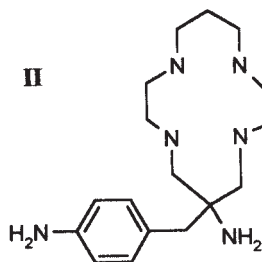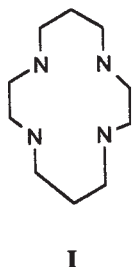
EXPERIMENTAL

Synthesis and characterization of **II**, 6-amino-6-(4-aminobenzyl)-1,4,8,11-tetraaza-cyclotetradecane, CYCAPAB, and its Co^{III} complexes have been published elsewhere.[3] Stock solutions of Ti^{III} were prepared by dissolving titanium metal sponge (Aldrich 99.9%+) in deareated HCl (12 mol dm^{-3}) under an atmosphere of deoxygenated nitrogen (aqueous chromous sulfate scrubbing towers). The preparation was stirred at room temperature for 48 hours and filtered through a glass frit under deoxygenated nitrogen to remove unreacted Ti and TiO_2. Solutions for kinetic studies were prepared by diluting aliquots of stock solution to final volume in a deoxygenated nitrogen atmosphere. Ti^{III} solutions were standardized by oxidimetric titration with potassium dichromate under nitrogen using barium diphenylamine sulfonate as indicator.[4] The molar extinction coefficient of Ti^{3+} at λ = 504 nm was found to be 3.95 ± 0.05 mol^{-1} dm^3 cm^{-1} ([H$^+$]: 100–2500 mmol dm^{-3}; μ = 4 mol dm^{-3} (LiCl)) in good agreement with the literature.[5] The hydrogen ion concentration of Ti^{III} solutions was determined by potentiometric titration with NaOH while the solution was magnetically stirred in air to promote oxidation of Ti^{III}. A white deposit of TiO_2 was observed at pH > 3.9. Hydrogen ion concentration was calculated assuming complete conversion of Ti^{III} to TiO_2.[6]

Kinetics was studied using a Hewlett-Packard 8451A diode array spectrophotometer at 24.8 ± 0.1 °C. Calculated volumes of LiCl and HCl solutions were placed in a 10 cm cylindrical quartz cell immersed in a thermostated water bath, while deoxygenated nitrogen was passed through the solution. A weighed amount of the solid ligand was added. After 10 minutes, the cell was sealed with rubber septa held in place by copper wire. Calculated volumes of Ti^{3+} were injected into the sealed cell using a glass syringe (Perfectum®, Popper & Sons Inc.). To allow for complete formation of the Ti^{III} complex, 8–12 minutes were allowed to elapse before $LiClO_4$ solution was injected to start the redox reaction.

RESULTS AND DISCUSSION

Both ligands of interest form Ti^{III} complexes that absorb more strongly in the UV-Vis than does Ti^{3+} (Figure 1). The shoulder on the long wavelength side of the absorption peak in the Ti^{3+} spectrum is shifted to longer wavelengths in the spectra of the complexes. That band is more prominent for the complex of **II** than for the complex of **I**.

When excess perchlorate was added, absorption bleached over several hours. Experiments using excess Ti^{III} showed that, at relatively short reactions times (tens of hours), 2.0 ± 0.2 moles of Ti^{III} were consumed for each
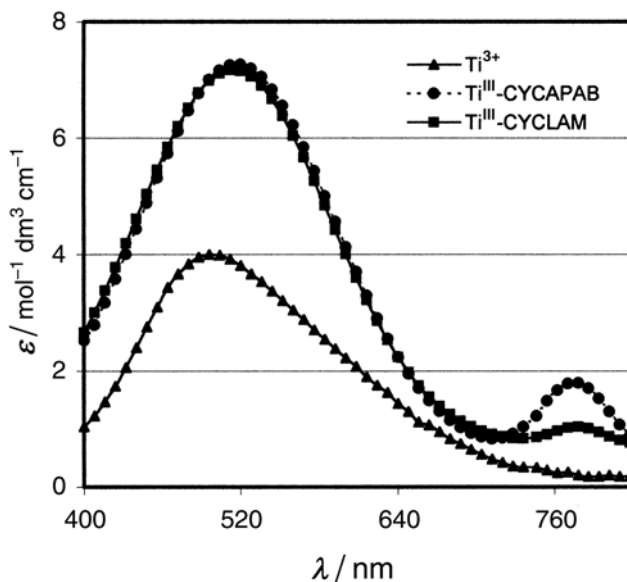

Figure 1. UV/Vis absorption spectra (at 25 °C, in 3.7 mol dm^{-3} LiCl) of Ti^{3+} and Ti^{III} complexes with ligands **I** and **II**. Triangles: [Ti^{3+}] = 62 mmol dm^{-3}, [H^+] = 65 mmol dm^{-3}. Squares: [$Ti^{III}L(\mathbf{I})$] = 34.8 mmol dm^{-3} (1:1), [H^+] = 68 mmol dm^{-3}. Circles: [$Ti^{III}L(\mathbf{II})$] = 36.5 mmol dm^{-3} (1:1), [H^+] = 68 mmol dm^{-3}.

mole of perchlorate destroyed. If the reaction was allowed to proceed for several days ([Ti^{III}] being in excess), 7.8 ± 0.3 moles of Ti^{III} were consumed.

In excess perchlorate, a slow rise in absorbance followed the initial relatively rapid absorbance decrease. After correction for the subsequent absorbance increase, the initial absorbance decrease was adequately fitted by a single exponential, and yielded a psuedo-first-order rate constant, k_{obs}. Table I shows kinetic data obtained. In all kinetic experiments, the ligand concentration was somewhat less than [Ti^{III}]. Under the conditions of the experiments, the ligand would be expected to be completely complexed. Since a single exponential fitted the absorbance-time data throughout the reaction, catalytic recycling of ligand occurred.

The results of experiments using excess Ti^{III} show that chlorate is the initial chlorine-containing reduction product, but that further reduction to chloride eventually occurs. (Because, when [Ti^{III}] is in excess, the concentration of chlorate is quite low, this second reaction occurs slowly). Kinetic modeling indicates that the results we obtain would be expected if the rate constant for reduction of chlorate by the reductants studied is at least two orders of magnitude larger than the corresponding rate constant for reduction of perchlorate by the same reductants.

For both ligands, observed rates of the initial reduction in excess perchlorate are proportional to the concentration of perchlorate ion, and in-

TABLE I

Observed rate constants for the reduction of perchlorate ions by titanous complexes.
$T = 24.8 \pm 0.1$ °C, $\mu = 4.40 \pm 0.05$ mol dm^{-3} (LiCl)

Ligand	[Ti^{III}] mmol dm^{-3}	[H$^+$] mmol dm^{-3}	[L] mmol dm^{-3}	$10^4 \, k_{obs}$ s^{-1}
II	8.82	52	6.15	17.0
II	8.99	110	6.20	18.5
II	8.81	230	6.13	25.7
II	8.84	347	6.09	35.0
II	9.07	418	6.03	41.0
I	8.96	104	6.00	1.00
I	9.10	208	6.32	1.28
I	9.04	406	6.01	2.12
NONE	8.86	65	–	0.127
NONE	8.91	189	–	0.200
NONE	8.86	316	–	0.400
NONE	8.90	420	–	0.511

crease as acid concentration increases. When observed rates at constant perchlorate concentration are plotted against [H$^+$], concave plots are obtained. This indicates some contribution from rate law terms with second order dependence on [H$^+$]. This has been observed in earlier studies of related reactions.[7] At [H$^+$] = 420 ± 10 mmol dm^{-3}, presence of the macrocyclic ligand **I** increases the rate of the perchlorate reduction by a factor of 5. The presence of pendant groups on **II** still further increases the rate of reaction to a factor of 80 with respect to the rate observed for Ti^{3+} at the same acidity.

Our present data is consistent with the suggestion that we have made elsewhere[8] that the mechanism of the reaction-type of interest involves an intermediate or transition state that involves two Ti^{III} centers, as well as ligands and a perchlorate ion coordinated to both metal centers. A significant piece of evidence that supports this suggestion is the observation that reactions of the kind being studied here show psuedo first order kinetics, but display rate constants that are proportional to the initial Ti^{III} concentration. This unusual behavior is also generated (for appropriate parameter values) by dynamic system modeling of mechanisms involving dinuclear reductants.[9] Cyclam and related ligands are known to form dinuclear complexes involving divalent cations,[10] and also[11] involving Fe^{III}. The enhanced long wavelength absorption associated with the Ti^{III} complex of **II** appears to be associated with an increased tendency of this ligand to form dinuclear complexes. This also accounts for the greater catalytic effectiveness of this ligand. The efficiency of a dimetallic complex as an intermediate in this reaction derives from its ability to facilitate a two-electron change (perchlorate to chlorate) even though Ti^{III} is a one-electron reductant.

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SAŽETAK

Učinak nekih makrocikličkih liganada na brzinu redukcije perkloratnih iona titanijem(III)

Giulio A Amadei i Joseph E. Earley, Sr.

Brzina redukcije perkloratnih iona s makrocikličkim ciklamskim kompleksom titanija(III) povećava se (u kiseloj vodenoj otopini LiCl, 4 mol dm^{-3}, pri 25 °C) u odnosu na istu reakciju s ionima Ti^{3+}. Ciklam s amino- i *p*-aminobenzilnim funkcionalnim skupinama mnogo je aktivniji od nesupstituiranog liganda. Obje redoks-reakcije katalizirane su H^{+}-ionima. Dobiveni podatci u skladu su s pretpostavkom da nastaje intermedijar koji sadržava dva iona titanija(III).