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ELECTROCHEMISTRY AND SPECTROELECTROCHEMISTRY OF AN α -IMINOXIME IRON(II) MACROCYCLIC COMPLEX

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Herein we report on the electrochemistry and spectroelectrochemistry of the complex $[\text{Fe}(\text{imox})(\text{Nmin})_2]^+$, **1**, where imox = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundecane-3,8,10-tetraen-11-ol-1-olate, and Nmin = N-methyl imidazole. In aqueous solution, **1** undergoes aquation producing $[\text{Fe}(\text{imox})(\text{Nmim})(\text{H}_2\text{O})]^+$, which under one-electron oxidation leads to formation of a μ -hydroxo iron(III) dimer with an estimated K_{dim} value of 1.0×10^4 . The forward and reverse rate constants for the dimerization reaction are $k_1 = 1.8 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ and $k_{-1} = 0.18 \text{ s}^{-1}$, respectively.

KEYWORDS: iron-macrocyclic complex, iron-iminoxime electrochemistry dimerization equilibrium

INTRODUCTION

The iron-oxo-hydroxo interactions in chemistry and biochemistry have inspired an intensive study in this area.¹ Oxo-hydroxo diiron complexes are well known and have been reported as models for a variety of non-heme iron proteins such as ferritin,² purple acid phosphatase and uteroferrin.³ Synthetic iron(III) dimers have been extensively reported^{4–7} and the subject was recently reviewed by Kurtz.⁸ Spectroscopic and electrochemical investigations of oxo-hydroxo-diiron dimers have been widely carried out with metalloprophyrins^{9,10} and related macrocyclic ligands.^{11,12}

In this work we report on the electrochemistry and spectroelectrochemistry of the iron bis(iminoxime) macrocyclic complex, (**1**). Spectroscopic¹³ and ligand substitution kinetic¹⁴ studies have previously been reported for this complex. Here, we concentrate on the dynamics of the equilibrium reactions because of their relevance to better understanding of the biological oxidation processes.¹⁵

Glossary of Numbered Species: $[\text{Fe}(\text{imox})(\text{Nmim})_2]^+$ (**1**), $[\text{Fe}(\text{imox})(\text{Nmim})(\text{H}_2\text{O})]^+$ (**2**), $[\{(\text{Nmim})(\text{imox})\text{Fe}\}_2-\mu\text{-OH}]^{n+}$ (**3**) ($n = 1, 2, 3$). The numbers refer to

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the cations and can also be applied to different oxidation states. For example, 2^{II} means species **2** in the 2+ oxidation state.

EXPERIMENTAL

The α -iminooxime ligand and the tetrafluoroborate salt of (**1**) were prepared according to procedures previously published in the literature.^{13,16}

Electrochemical measurements were performed under argon by using a Princeton Applied Research Model 173 potentiostat and a model 175 Universal Programmer. Cyclic voltammograms were recorded by use of a glassy carbon working electrode, a platinum wire counter electrode and a Ag/AgCl (1 M KCl, 0.222 V *versus* SHE) reference electrode with the conventional Luggin capillary. Spectroelectrochemical experiments were carried out with the potentiostat attached to a Hewlett-Packard 8452A diode-array spectrophotometer. A three electrode system was designed for a thin layer cell of 0.025 cm internal optical pathlength. A gold minigrid was used as a transparent working electrode, in the presence of a small Ag/AgCl (1 M KCl) reference electrode and a platinum auxiliary electrode. The measurements were carried out at 25°C under semi-infinite diffusion conditions. Ionic strength was kept constant using KCl. All potentials are reported *versus* the standard hydrogen electrode, SHE.

RESULTS AND DISCUSSION

The spectroelectrochemical behavior of **1** is illustrated in Figure 1. The electronic spectrum of **1** at 0 V features a strong absorption band at 600 nm ($\epsilon = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) assigned to an Fe(II)-to-diimine charge transfer transition.¹³ As the applied potential is increased from 0 to 0.82 V, the charge transfer band loses its intensity and undergoes a bathochromic shift. The band shape is also changed, becoming symmetric, with no definition of the vibronic side band which is typical of iron(II)-diimine complexes.¹⁷ At the same time, a new band emerged at *ca.* 500 nm ($\epsilon = 1.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). This behaviour is completely different from that observed in the oxidation of the related iron-macrocyclic complexes $[\text{Fe}(\text{DMGH})_2(\text{Im})_2]^{18}$ and $[\text{Fe}(\text{tetraen})(\text{Nmin})_2]^{2+}$,¹⁹ where no band shift was observed (DMGH⁻ = dimethylglyoximate, tetraen = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene).

The assignment of the band at 500 nm has been subject to discussion in the literature. For several diiron(III) dimers⁴ it has been assigned as an oxygen bridge-to-iron(III) charge transfer transition. However, this band has also been assigned as a ligand field transition, whose unusually high intensity is due in part to relaxation of spin restrictions upon antiferromagnetic coupling of the two iron atoms.²⁰ Nevertheless, resonance Raman excitation profiles performed for various diiron complexes have demonstrated that the vibrations of the Fe-O-Fe moiety is strongly enhanced when excited in the visible region (400–500 nm) implying that the electronic transitions in this range indeed have a large charge transfer character.²¹ Furthermore, Lippard and Armstrong²² have noticed that oxo-bridged diiron(III) complexes tend to have several visible absorption bands arising from

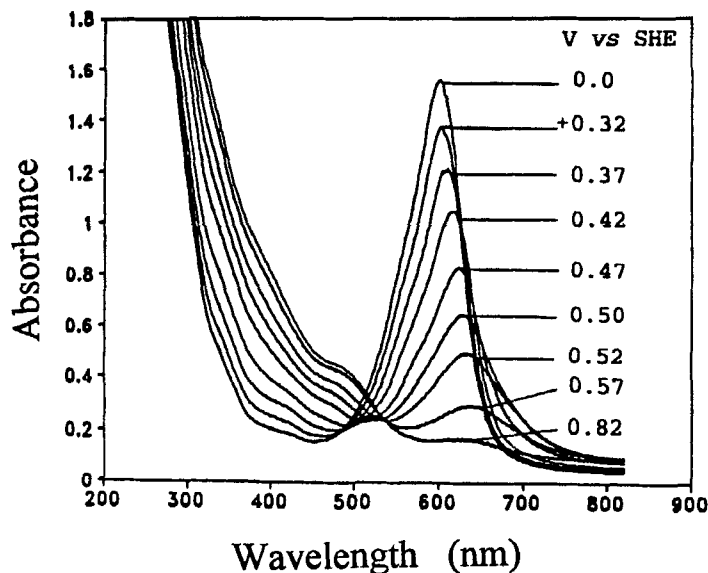
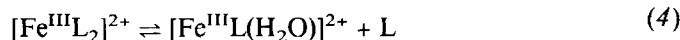
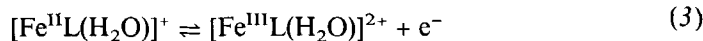
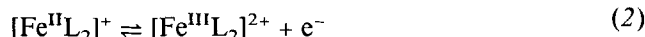
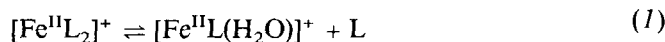


Figure 1 Spectroelectrochemistry (A) of **1** (1×10^{-2} M); Conditions: [Nmim] = 3.8×10^{-2} M; KCl 0.10 M; pH 6.86; 25°C, starting measurements at 0.0 V vs SHE.

charge transfer and ligand field transitions, while μ -hydroxo diiron(III) dimers such as $[\text{Fe}_2(\mu\text{-OH})(\text{O}_2\text{CCH}_3)_2(\text{HBpz}_3)_2](\text{ClO}_4)$ have no visible absorption bands ($\text{HBpz}_3 = \text{hydrotris}(1\text{-pyrazolyl})\text{borate}$), because the ligand field transitions are forbidden by orbital and spin rules.³ On the other hand, $[\text{Fe}(\mu\text{-OH})(\text{O}_2\text{CCH}_3)_2(\text{TMIP})_2]^{3+}$ (TMIP = tris(*N*-methylimidazol-2-yl)phosphine)³ and $[\text{Fe}_3(\text{OH})_2(\text{O}_2\text{CC}_6\text{H}_5)_4(\text{N}_3)_2](\text{PF}_6)_3$ ²³ do have absorption bands at 440–480 nm ($\epsilon = 225\text{--}260 \text{ M}^{-1}\text{cm}^{-1}$) similar to the ligand field bands observed in oxo-bridged complexes.^{20,24}

The spectral changes observed for **1** in Figure 1 indicate that the intermediate oxidized species still have an Fe(II) chromophore. This suggests formation of the mixed valence complex $\{[(\text{Nmim})(\text{imox})\text{Fe}]_2\text{-}\mu\text{-OH}\}^{2+}$, $3^{\text{III/II}}$. Disagreement appears in the literature^{5,9,11,25,26} concerning the nature of the bridging group, *i.e.*, μ -oxo, hydroxo or even dihydroxo. Even though the electrochemical data alone may not be able to distinguish between the various groups, our results can be explained by the reactions shown in Scheme 1.

Scheme 1. L = Nmim; the imox ligand is not shown for simplicity.



Precedence for a μ -hydroxo group bridging the metal centers of a mixed-valence diiron complex is known, for example, the proposed model for the dinuclear site of uteroferrin.²⁷ Stynes *et al.*¹¹ have also reported the electrochemical formation of a mixed-valence diiron complex of the bis(difluoro)(dimethylglyoximate)borate ligand.

Above 0.6 V oxidation of the second iron atom is complete as seen by disappearance of the charge-transfer band at 600 nm in Figure 1. The electrochemical oxidation was shown to be 90% reversible, **1** being regenerated within minutes.

Cyclic Voltammetry

The typical cyclic voltammogram of **1** measured at high concentration of the axial ligand, Nmim, to prevent dissociation ($[\text{Nmim}]/[\text{Fe}^{\text{II}}] = 100$), at 0.10 M KCl and 25°C, exhibits only one reversible wave with a formal redox potential $E_{\text{Nmim}}^f = 0.35$ V. This is assigned to the one-electron transfer reaction: $\mathbf{1}^{\text{III}} + e^- \rightarrow \mathbf{1}^{\text{II}}$. On the other hand, a different electrochemical response is observed when a low concentration of Nmim is used, as shown in Figure 2. E_{pa} is slightly shifted to more positive potentials as well as the formal redox potential, here denoted $E_{\text{H}_2\text{O}}^f = 0.38$ V, and a new cathodic peak appears at -0.1 V (wave C, Figure 2A). The intensity of wave C is much higher when an initial cathodic scanning is made (compare with Fig. 2B), however only one anodic peak is observed for either cathodic or anodic initial scanning. This means that the new species associated with wave C is unstable in the fully reduced form. We propose that upon oxidation **2** undergoes a rapid dimerization reaction producing $\mathbf{3}^{\text{III/III}}$. When **3** is completely reduced, the dimer immediately breaks up explaining the missing anodic peak in the range of 0.01 to 1 V s^{-1} . The amplitude dependence of the waves B and C with respect to the scan rate is also consistent with this hypothesis. At low scan rates, the wave C is barely noticeable due to the fact that $\mathbf{2}^{\text{III}}$ is consumed at lower potential shifting the equilibrium: $2[\mathbf{2}^{\text{III}}]^{2+} \rightarrow [\mathbf{3}^{\text{III/III}}]^{3+} + \text{H}^+ + \text{H}_2\text{O}$, and causing a significant decrease in the concentration of $\mathbf{3}^{\text{III/III}}$. On the other hand, at fast scan rates, both species, $\mathbf{2}^{\text{III}}$ and $\mathbf{3}^{\text{III/III}}$, can be detected in a “frozen” state. Cyclic voltammograms of $[\{\text{Fe}^{\text{III}}\text{TMPyP}(\text{H}_2\text{O})\}_2\text{O}]^{8+}$ (TmPyP^{2+} = meso-tetra-N-methylpyridiniumporphyrinate)⁹ and $[\text{Fe}_2(\mu\text{-OH})(\text{O}_2\text{CCH}_3)_2(\text{HBpz}_3)_2](\text{ClO}_4)_3$ also showed similar electrochemical behavior, illustrating the general tendency of dinuclear ferric complexes to dissociate upon reduction. The fact that wave C is broad suggests that the reduction of $\mathbf{3}^{\text{III/III}}$ occurs in two successive steps with potentials very close but not identical, indicating small communication between the two metal atoms, as expected considering the nature of the bridging group involved.

Reaction of $\mathbf{1}^{\text{II}}$ with Oxygen

Interesting behavior was observed when we promoted the chemical oxidation of $\mathbf{1}^{\text{II}}$ with molecular oxygen, as illustrated in Figure 3. Contrary to the electrochemical oxidation, no band shift was observed in the electronic spectra, indicating that under aerobic conditions, the mixed-valence species, $\mathbf{3}^{\text{III/II}}$ is not formed; the most probable pathway being an oxygenation reaction, producing a μ -peroxo dimer of iron(III) as reported for iron porphyrins^{6,7} and related complexes.^{4,28} μ -peroxo species tend to be unstable at room temperature, undergoing decomposition to

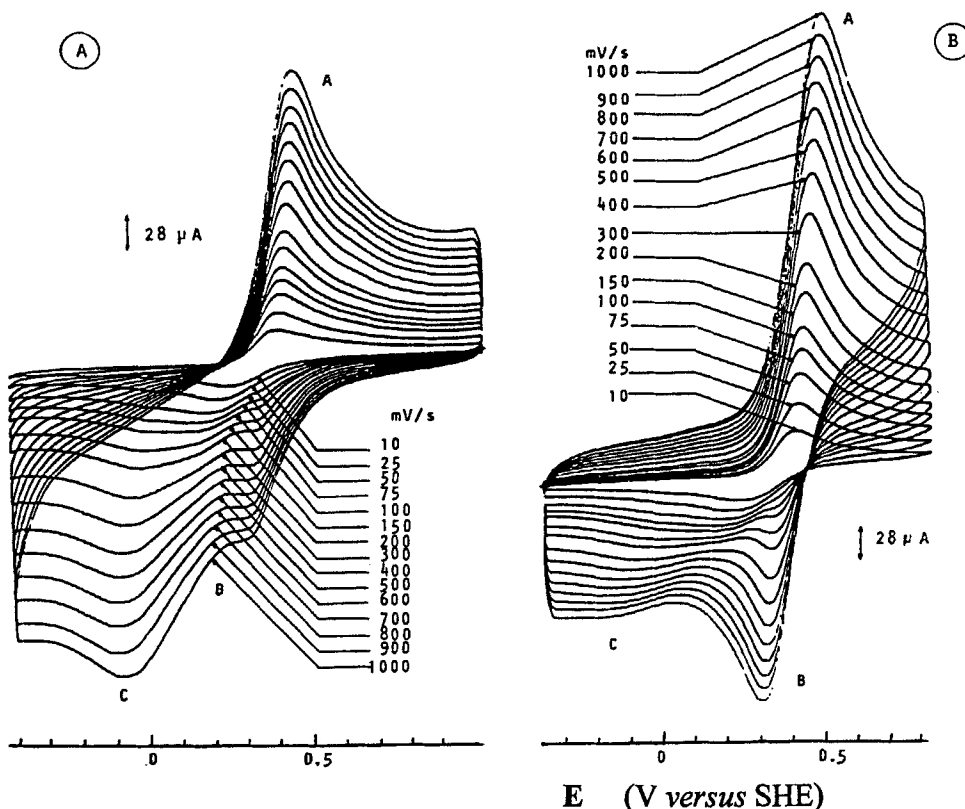
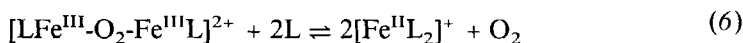


Figure 2 Cyclic voltammograms of **1** (4.6×10^{-3} M); (A) initial cathodic scan, and (B) initial anodic scan. Conditions: [Nmim] = 24×10^{-3} M; KCl 0.10 M; pH = 6.86; 25°C.

μ-oxo complexes as reported by Chin *et al.*⁶ Nevertheless, our data exhibit a remarkable spectral resemblance to that reported for the μ-peroxo complex, $[\{\text{Fe}(\text{TIM})(\text{H}_2\text{O})\}_2\text{-}\mu\text{-O}_2]^{4+}$ (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene), known to be stable at room temperature²⁷ (band at 448 nm, $\epsilon = 1.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$; compared to 425 nm, $\epsilon = 2.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in our case). We emphasize that the chemical oxidation of I^{II} is 70% reversible, being achieved by adding an excess of Nmim, but unlike the electrochemical reaction which is complete within minutes, it takes *ca.* 3 h and can be rationalized by equilibrium (6),



where L = Nmim.

The reversible reduction of $[\text{LFe}^{\text{III}}\text{-O}_2\text{-Fe}^{\text{III}}\text{L}]^{2+}$ by Nmim strongly supports the formation of μ-peroxo species, being consistent with similar behavior reported for $[\text{Fe}(\text{TIM})(\text{H}_2\text{O})_2\text{-}\mu\text{-O}_2]^{4+}$.²⁸

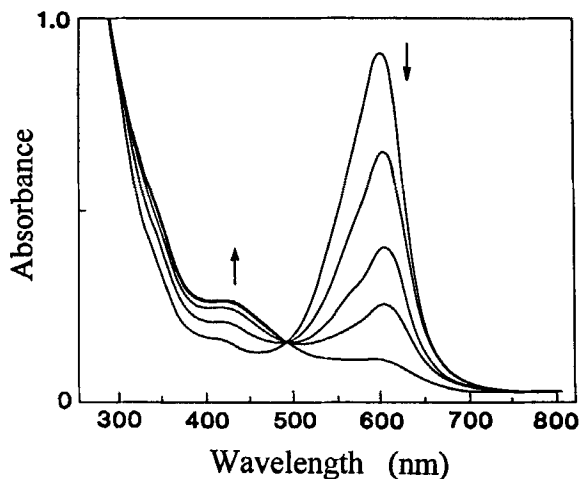


Figure 3 Spectra changes for the reaction of **1** (1×10^{-4} M) and molecular oxygen (saturated solution). Conditions: $[\text{Nmim}] = 1.3 \times 10^{-3}$ M; pH = 6.86; KCl = 0.10 M; 25°C.

Thermodynamic Stability of $3^{\text{III/III}}$

The equilibrium constant, K_{dim} , for reaction (7) (the imox ligand is missing for clarity) can be evaluated from eq. (8), considering that $[\text{Fe}_{\text{total}}] = [1^{\text{III}}] + [2^{\text{III}}] + 2[3^{\text{III/III}}]$, and $K_{\text{d}}^{\text{III}} = [2^{\text{III}}][\text{Nmim}]/[1^{\text{III}}]$.

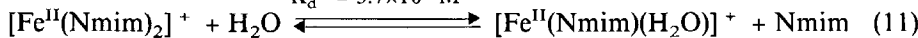
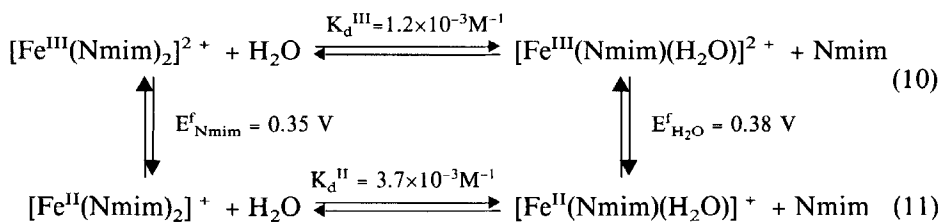


$$K_{\text{dim}} = \frac{[3^{\text{III/III}}][\text{H}^+]}{[2^{\text{III}}]^{22}} = \frac{[3^{\text{III/III}}][\text{H}^+](K_{\text{d}}^{\text{III}} + [\text{Nmim}])^2}{\{K_{\text{d}}^{\text{III}}([1^{\text{III}}] + [2^{\text{III}}])\}^2} \quad (8)$$

$K_{\text{d}}^{\text{III}}$ was calculated as $1.2 \times 10^{-3} \text{ M}^{-1}$ using eq. (8), the formal reduction potentials, $E_{\text{Nmim}}^{\text{f}} = 0.35 \text{ V}$, $E_{\text{H}_2\text{O}}^{\text{f}} = 0.38 \text{ V}$ and $K_{\text{d}}^{\text{II}} = 3.7 \times 10^{-3} \text{ M}^{-1}$.¹⁴ These values are related together in the thermodynamic cycle shown in Scheme 2.

$$(RT/F) \ln K_{\text{d}}^{\text{III}} = E_{\text{Nmim}}^{\text{f}} - E_{\text{H}_2\text{O}}^{\text{f}} + (RT/F) \ln K_{\text{d}}^{\text{II}} \quad (9)$$

Scheme 2



In Figure 2B, i_{pA} is proportional to $[\text{Fe}_{\text{total}}]$, and in Figure 2A, i_{pB} is proportional to $[2^{III}] + [1^{III}]$. From mass balance, $(i_{pA} - i_{pB})$ is proportional to $2[3^{III/III}]$. In other words, $i_{pA} = \alpha[\text{Fe}_{\text{total}}]$, $(i_{pA} - i_{pB})/2 = \alpha[3^{III/III}]$ can be expressed as

$$[3^{III/III}] = (i_{pA} - i_{pB})[\text{Fe}_{\text{total}}]/2i_{pA} \quad (12)$$

In this way, $[3^{III/III}]$ was calculated as 1.6×10^{-3} M. $[\text{Nmim}]$ was calculated based on the expression for K_{d}^{III} . Substituting these values into eq. (9), K_{dim} was calculated as $(10 \pm 0.3) \times 10^4$.

Comparisons with the literature values of K_{dim} are often difficult, because of the different stoichiometries reported, as discussed by Miller *et al.*⁷ However, for illustration purposes, we reproduce the dimerization constant of 2.2×10^3 reported by Kuwana and Forshey⁹ for the $\{[\text{Fe}^{III}\text{TMPyP}(\text{H}_2\text{O})_2\text{O}]\}_2^{8+}$ dimer.

Kinetic behavior of $3^{III/III}$

Second order reactions occupy a significant role in electrochemistry. Nevertheless, only a very few general mathematical treatments have been published.²⁹ Among the various second-order coupled reactions, the case of electrochemically initiated dimerization is of interest particularly because of the occurrence of radical coupling reactions.

The rate at which 2^{III} spontaneously dimerizes to $3^{III/III}$ is governed by the rate constant k_1 in eq. (8) and was evaluated by cyclic voltammetry measurements using the theoretical method offered by Nicholson, *et al.*²⁹ To be consistent with Nicholson's schemes, cyclic voltammograms were recorded making an initial anodic scan from solutions of 2^{II} . The ratios of the currents, i_{pA}/i_{pB} were measured as a function of the scan rate to evaluate k_1 . The procedure involves the use of a working curve³⁰ that relates i_{pA}/i_{pB} to $\omega = [2^{III}]T k_1$, where $T = (E_{\gamma} - E_{\text{H}_2\text{O}}^f)/v$. A plot of ω vs T is shown in Figure 4, from which $k_1 = (1.8 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ resulted. Together with the value of K_{dim} , we can evaluate the reverse rate constant of dimerization, $k_{-1} = (1.8 \pm 0.6) \times 10^{-1} \text{ s}^{-1}$, and consider reaction (7) reasonably characterized.

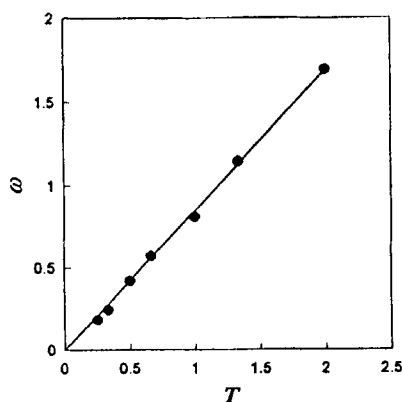


Figure 4 Correlation between ω and T for determination of the bimolecular forward rate constant, k_1 , for the dimerization reaction of 2^{III} (see text for details).

Acknowledgements

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