

MOLECULAR ELECTROCHEMISTRY

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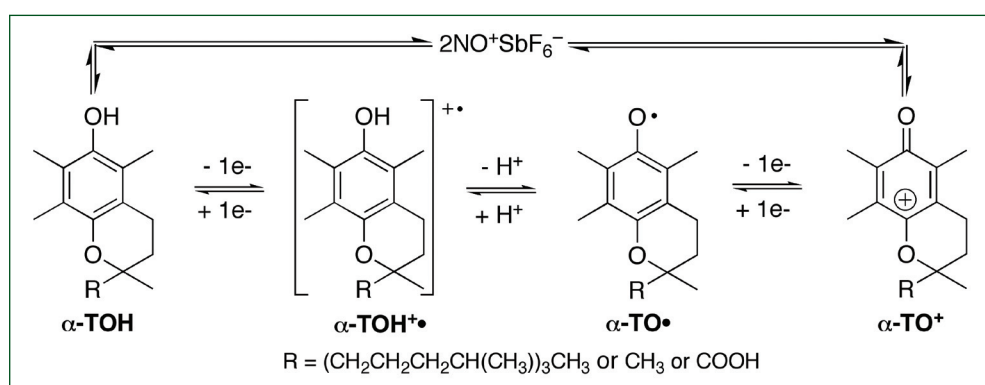


The electrochemical control of oxidation and reduction processes in organic and inorganic systems is an area of extensive research in both academia and industry. Electrochemical techniques are extremely useful in generating interesting species in unusual oxidation states, or for producing reactive intermediates (for example in the reductive dimerisation of vinyl cyanide in the Monsanto manufacture of Nylon 66), but provide little intrinsic structural information. To overcome this limitation, spectroscopic methods have frequently been used in conjunction with electrochemical methods in order to monitor the progress of a reaction and to obtain more detailed structural and mechanistic information. The *in situ* alliance of electrochemistry/spectroscopy is particularly valuable in situations where the species undergoing the redox process would not survive the transfer from an electrochemical to a spectroscopic cell, or in situations where it is essential that the spectroscopic analysis occur concurrently with the electrochemical generation, such as in kinetic studies. The focus of this research is developing and utilising spectroscopic techniques, including EPR, UV-VIS, FTIR and NMR, to study processes involving electron transfer in organic and inorganic systems.

The Redox Chemistry of Vitamin E

Vitamin E refers to a collection of naturally occurring compounds produced by plants that are based on 6-chromanol with an extended alkyl (phytyl) chain in the 2-position. α -Tocopherol (α -TOH), the fully methylated tocopherol is by far the most biologically active and abundant of all the components of vitamin E found in mammalian tissues. Work recently conducted in our laboratories has proven the existence of several intriguing and new oxidised forms of α -TOH, which are reversibly linked to the starting material through a series of proton and electron transfers. Of particular interest is the phenoxonium cation (α -TO⁺) that can be produced by chemical oxidation with NO⁺ and is remarkably stable in solution with a lifetime of at least several hours in dry organic solvents.

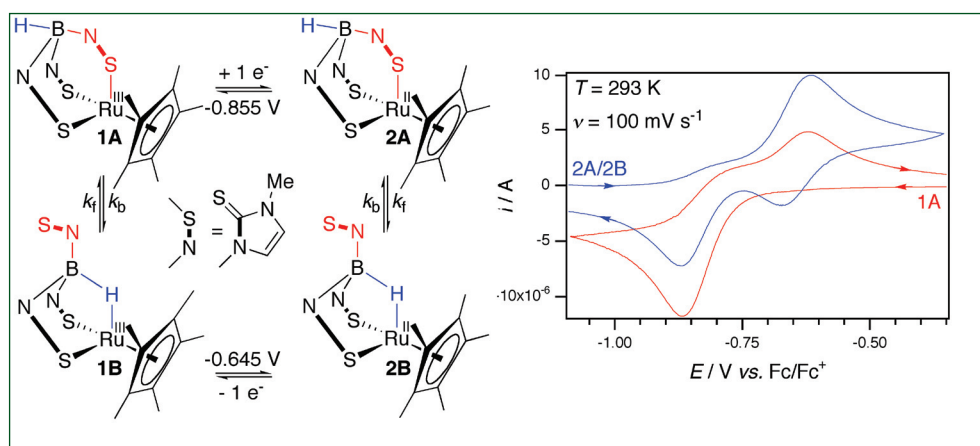
Phenoxonium cations have for a long time been postulated as intermediates produced during the oxidation of phenolic compounds, but were generally thought to be stable for only short times (<1 s). Therefore, it is an extraordinary observation that the phenoxonium cation derived from a naturally occurring compound is stable in solution. Furthermore, the stability is directly attributable to the specific molecular structure that "nature" has assigned to vitamin E. ¹³C NMR spectroscopy experiments and theoretical calculations performed on α -TO⁺ indicate that the positive charge is shared between the



carbon atoms bonded to oxygen atoms and on the quaternary carbon in the chromanol ring. While the phenoxonium cation is reactive towards nucleophiles such as water, it may be moderately stable in the hydrophobic (lipophilic) environment where vitamin E is known to occur naturally. (With S B Lee, C Y Lin, P M W Gill)

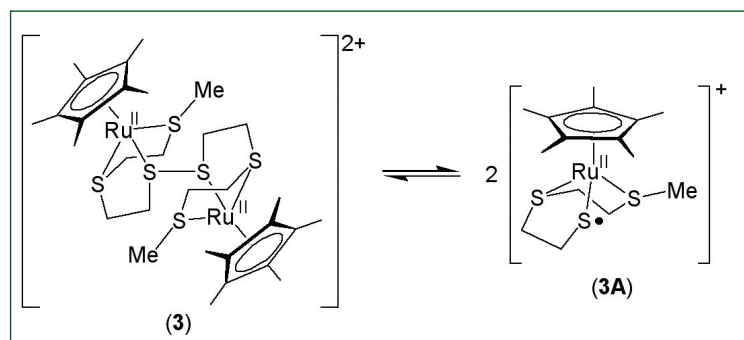
Electrochemically Induced Transformations of Organometallic Ru Compounds

$[\text{Cp}^*\text{Ru}^{\text{III}}\{\text{HB}(\text{mt})_3\}]\text{X}$ (1A) ($\text{X} = \text{Cl}, \text{PF}_6$) and $[\text{Cp}^*\text{Ru}^{\text{II}}\{\text{HB}(\text{mt})_3\}](2\text{A})$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{mt} = N$ -methyl-2-mercaptoimidazol-1-yl) were synthesised by the reactions of $\text{K}[\text{HB}(\text{mt})_3]$ with $[\text{Cp}^*\text{Ru}^{\text{III}}\text{Cl}_2]_2$ and $[\text{Cp}^*\text{Ru}^{\text{II}}(\text{OMe})_2]_2$, respectively. 1A and 2A exist in the solid state in $\kappa^3\text{-S,S',S''}$ coordination, so that the sulfur atom in each mt group coordinates to the central Ru ion producing the normal tripodal geometry of the $[\text{HB}(\text{mt})_3]$ ligand. Both compounds, however, undergo an isomerisation reaction in solution



where the sulfur on one mt group is displaced in favour of coordination to the hydrogen that is bonded to the boron (an agostic B–H–Ru interaction) resulting in $\kappa^3\text{-H,S,S'}$ coordination about the Ru (an electrochemical “square scheme” mechanism). Variable temperature NMR spectroscopic and cyclic voltammetry experiments were used to obtain the rate and equilibrium constants for the $\kappa^3\text{-S,S',S''}$ and $\kappa^3\text{-H,S,S'}$ coordination exchange.

Alkylation of $[\text{Cp}^*\text{Ru}^{\text{III}}(\text{tpdt})]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{tpdt} = \eta^3\text{-S}(\text{CH}_2\text{CH}_2\text{S})_2$) with MeI or Me_3OBF_4 resulted in the formation of a trans $\mu\text{-}\eta^1\text{-}\eta^1\text{-S}_2$ coupled species, $[\{\text{Cp}^*\text{Ru}^{\text{II}}\}_2\{\mu\text{-}\eta^6\text{-S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{SMe}_2\}]^{2+}$ (3) as the predominant product. A combination of electrochemical, EPR, UV-VIS and NMR experiments indicated that the solution phase chemistry of 3 is governed by its reversible dissociation into the mononuclear cation radical (3A).



The facile alkylation-induced S–S bond coupling and the ease of reversible homolytic S–S bond scission appear to be unique to this Ru(II) system. (With L Y Goh, [National U Singapore])

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