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Enhancement of the Rate of Addition of Free Radicals to Dicarboxylacetylene by π Acid Complexation to Ruthenium(II)–Pentaamine. A Pulse Radiolysis Study

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π-Acid metalloorganic species consisting of metal and unsaturated π-bound organic substrates have been postulated as key intermediates in various homogeneous and heterogeneous catalytic processes. Inherent to all those processes is the concept of substrate activation. Such property is, in general, measued spectroscopically and pronounced in terms of alongation or weakening of C–C bonds. It is the aim of this work to address the question of reactivity and activation as manifested by reaction rates of free radicals (•OH, $Br_2^{\overline{\bullet}}$, $(SCN)_2^{\overline{\bullet}}$) with π-acid complexed unsaturated dicarboxylic derivatives of ethylene and acetylene.

For those studies we have chosen the alkene and alkyne complexes of 'classic' pentaamine ruthenium(II), and the pulse radiolysis method by which the above mentioned radicals are formed and their reaction kinetics studied. It is the purpose of this initial communication, to show that there is a greater than 100 fold enhancement in reaction rates between $Br_2^{\overline{\bullet}}$ and $(SCN)_2^{\overline{\bullet}}$ radicals and ruthenium bound dicarboxylacetylene when compared to the equivalent reactions in the absence of ruthenium. These reactions are characterized first, by the generation of free radicals, their insertion across electron rich, π-unsaturated bonds and oxidation of ruthenium with concomitant formation of transients consistent with the postulation of their structure as Ru(III)–alkyl and –alkenyl complexes.

The previously unknown dicarboxyacetylene pentaamine ruthenium(II) dithionate salt (**1**), chosen for this study, has been synthesized following the general method used by Ludi and coworkers in the original synthesis of similar complexes containing unsaturated ligands [1]. It is also compatible with the recently reported synthesis of the methyl ester of compound **1** [2]. All manipulations were performed under an atmosphere of pure argon using Schlenk glassware unless noted otherwise. $[(NH_3)_5Ru(H_2O)](CF_3CO_2)_3$ was prepared in open air, starting from 0.33 g (1.3 mmol) of $(NH_3)_5RuCl_3$ and 0.5 g $AgCF_3CO_2$. The complex was reduced over amalgamated zinc. The aquopentaamine ruthenium(II) thus formed is added to 0.15 g (1.3 mmol) of dicarboxylacetylene in water at 40–50 °C. Addition of 0.4 g (1.65 mmol) of sodium dithionate to the deep orange–red solution caused, after cooling, the precipitation of 0.15 g (26%) of orange–red needle-shaped crystals. UV–Vis spectrum: 265(sh); 325(sh); 370nm (650 M^{-1} cm^{-1}); and 425 nm (480 M^{-1} cm^{-1}). NMR: in D_2O *trans*-NH_3, 4.2 ppm; *cis*-NH_3 (2.6 ppm) *versus* DSS. Relative intensity ratio is 4:1. Cyclic voltammetry in water and 0.5 M Na_2SO_4 as supporting electrolyte shows a reversible oxidation wave with a redox potential of 0.52 V *versus* SCE (0.76 V *versus* NHE).

The radiation chemistry of water has been studied in detail and its chemistry can be manipulated by the addition of various substrates to produce strongly reducing or oxidizing free radicals [3]. Irradiation of N_2O saturated solutions containing DMSO or tert-butanol produces $\cdot CH_3$ and $\cdot CH_2C(CH_3)_2OH$ radicals, both of which showed no significant reactivity in the presence of **1**. The result in the tert-butanol containing solution suggests that also the hydrogen atoms are unreactive towards **1** or that the product of the latter reaction has no significant absorption band in the spectral region studied.

In contrast to the above results, the •OH, $Br_2^{\overline{\bullet}}$ and $(NCS)_2^{\overline{\bullet}}$ radicals showed various degrees of reactivity in the presence of **1**. Their reaction kinetics were measured under pseudo-first order conditions: 2.2×10^{-2} M N_2O; 0.1 M bromide and thiocyanate anions; $(0.4–2) \times 10^{-4}$ M complex, pH 3.5 (see Table I). The formation and decay of transients were monitored spectroscopically by their appearance in the

TABLE I. Specific Rates of Reactions of Free Radicals (M^{-1} s^{-1})

Reactant	Free radical		
	•OH	$Br_2^{\overline{\bullet}}$	$(SCN)_2^{\overline{\bullet}}$
$(NH_3)_5RuC_4O_4$	2.7×10^{10}	5.9×10^{8}	1.8×10^{8}
$^{-}{}_2OCC{\equiv}CCO_2{}^{-}$	2.6×10^{9}	$\leq 2.0 \times 10^{6}$	1.8×10^{6}

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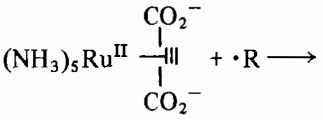
spectral region 320–630 nm immediately after the pulse. The products of reaction between **1** and ·OH or $Br_2^{\cdot -}$ are short lived transients with weak absorption bands in the visible, $\lambda_{max} \sim 460$ nm $\epsilon_{max} \sim 400$ M^{-1} cm^{-1} for the product of reaction with ·OH radicals. The kinetics of decomposition of these short lived transients are complex. The transient formed in the reaction of **1** with ·OH radicals decomposes in two consecutive reactions. The first obeys a second order rate law with $k \sim 2 \times 10^7$ M^{-1} s^{-1} and the second obeys a first order rate law with $k \sim 3 \times 10^{-3}$ s^{-1}. The final product shows a weak absorption band at 550 nm. The kinetics of decomposition in the $Br_2^{\cdot -}$ system are similar, though the specific rates of reaction differ slightly, and the final product shows absorption bands at 550 and 310 nm. The detailed kinetic study will be reported in the future.

These results clearly indicate that the free radicals react with complex **1** via attack on the ligands, probably forming the σ-alkenyl derivatives of pentaamine–ruthenium(III) (2). The reactions are most probably non-stereospecific.



$$(NH_3)_5Ru^{II} - \overset{CO_2^-}{\underset{CO_2^-}{|||}} + \cdot R \longrightarrow$$

1

$$(NH_3)_5Ru(III){-}C(CO_2^-){=}C(X)CO_2^-$$

2

(·R = ·OH, $Br_2^{\cdot -}$, $(NCS)_2^{\cdot -}$; X = OH, Br, NCS respectively.)

The arguments in favour of the reactions involving an attack on the ligand rather than an outer sphere oxidation are:

(i) The outer sphere oxidation of **1** produces a stable product with a half-live of over two minutes as can be deduced from the reversible cyclic voltammogram. On the other hand the first reaction following the formation of **2** has a half-live of several milliseconds, depending on the concentration of the transient formed.

(ii) Hydroxyl radicals are poor outer sphere oxidizing agents [4]. On the other hand they are known to react, via addition, with nearly diffusion controlled rates with unsaturated organic substrates [5]. Thus for example the β-malate free radical is formed in the reactions of fumaric or maleic acids with hydroxyl radicals [6] and pentaamine–ruthenium(III)–β-malate is formed in the corresponding reaction with the pentaamine–ruthenium(II)–fumaric acid complex [7].

(iii) The latter complex though reactive towards hydroxyl radicals is unreactive towards $Br_2^{\cdot -}$ under our experimental conditions though an outer sphere oxidation would be exothermic. This result indicates that the activation of the double bond in fumaric acid by d → π back donation is considerably smaller than that observed for complex **1**.

The results presented herein thus clearly point out that d → π back donation from the $(NH_3)_5Ru(II)$ to the $^-O_2CC{\equiv}CCO_2^-$ enhances considerably the rate of reaction of electrophilic free radicals with the ligand. This is to our knowledge the first direct quantitative measurement of such a catalysis.

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