Inorganica Chimica Acta, 133 (1987) 21–22

Formation of Metal–Alkyl Intermediates in Reactions of C-centered Radicals with Macrocyclic Complexes of Cu(I) and Ag(I)*

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(Received April 2, 1987)

Although there are a number of studies concerned with the formation of copper–alkyl intermediates in reactions between carbon-centered radicals and copper(I) species [1–3], the generation of such intermediates with macrocyclic complexes has not been reported. In this work we have investigated the formation of metal–alkyl intermediates when macrocyclic complexes of d^{10}-metal ions, e.g. Cu(I) and Ag(I), react with 2-methyl-2-hydroxy-1-propyl radicals.

Results and Discussion

Pulse radiolysis of $Ag([14]aneN_4)^{2+}$, deaerated solutions containing 2 10^{-4} M $Ag([14]aneN_4)^{2+}$ in 0.1 M $(CH_3)_3COH$, resulted in spectral transformations which signaled the reduction of the Ag(II) complex. No transient species were observed when the accumulation of the Ag(I) product was prevented by promptly refreshing the solution after each irradiation and by limiting irradiation by the monitoring light to a minimum. Transient spectra, Fig. 1, were recorded, however, when the concentration of $Ag([14]aneN_4)^+$ reached a steady state value larger than 5 μM. The transient spectra have been assigned to a silver–alkyl species that is generated, eqn. (1), in competition with the radical dimerization, eqn. (2).

Related metal–alkyl intermediates were generated in similar experiments when $Ag(bipy)_2{}^+$ or $Cu(Me_6\text{-}[14]aneN_4)^+$ reacted with $\dot{C}H_2C(CH_3)(OH)CH_3$ radicals, Figs. 2 and 3. In these experiments with micromolar concentrations of the Cu(I) and Ag(I) complexes, the formation of the intermediates takes place with a diffusion controlled rate and the disappearance with rates that showed a first order dependence on the concentrations of the intermediate has been observed in a microsecond time domain.

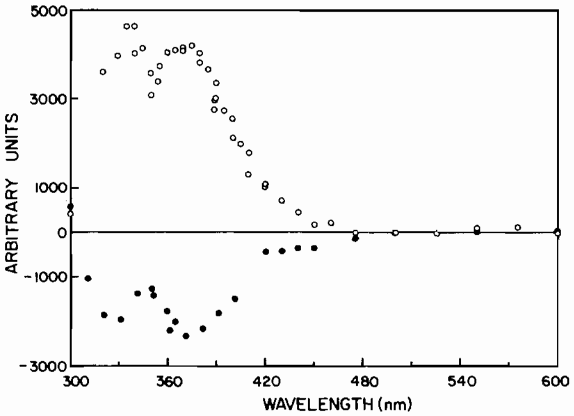


Fig. 1. Transient spectra determined in the reaction of $Ag([14]aneN_4)^+$ with $\dot{C}H_2C(CH_3)(OH)CH_3$ at $t = 0.3$ μs (○) and $t = 20$ μs (●) in aqueous acidic, pH 5, solutions.

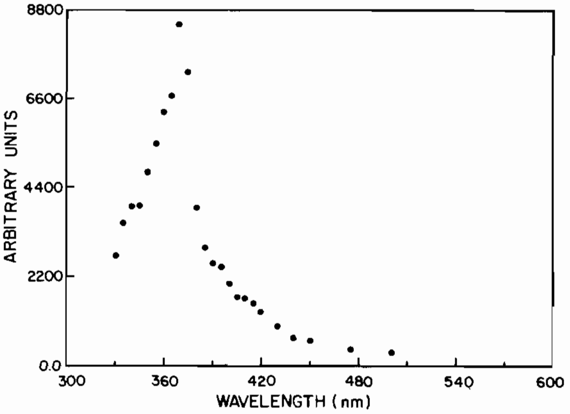
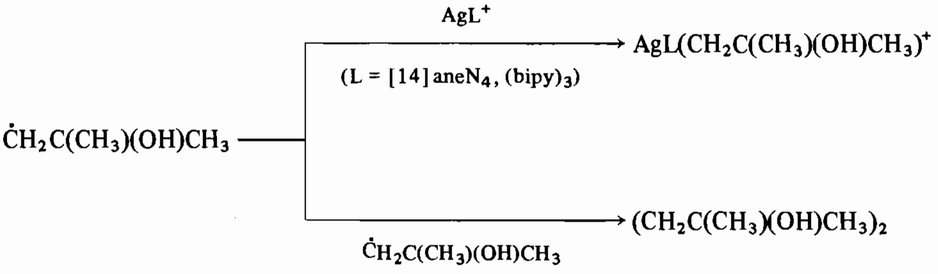


Fig. 2. Transient spectrum assigned to $Ag(bipy)_3(\dot{C}H_2)C(CH_3)(OH)CH_3{}^+$. The spectrum was recorded at $t = 0.5$ μs in the reaction of $Ag(bipy)_2{}^+$ with $\dot{C}H_2C(CH_3)(OH)CH_3$ radicals at pH 5.



$$\dot{C}H_2C(CH_3)(OH)CH_3 \xrightarrow[(L\,=\,[14]aneN_4,\ (bipy)_3)]{AgL^+} AgL(CH_2C(CH_3)(OH)CH_3)^+ \tag{1}$$

$$\dot{C}H_2C(CH_3)(OH)CH_3 \xrightarrow[\dot{C}H_2C(CH_3)(OH)CH_3]{} (CH_2C(CH_3)(OH)CH_3)_2 \tag{2}$$

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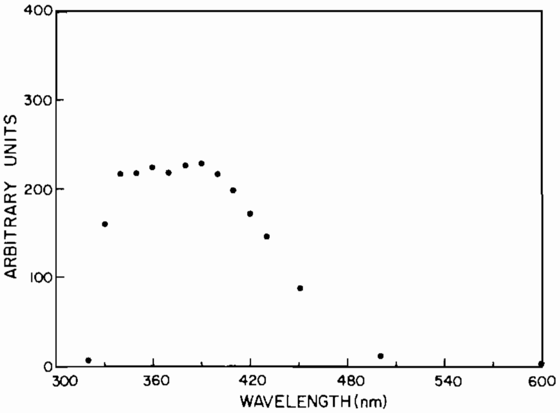

Fig. 3. Spectrum of the transient Cu–alkyl intermediate generated when Cu([14]aneN$_4$)$^+$ reacts with $\dot{C}H_2C(CH_3)(OH)CH_3$ radicals at pH 6.7. The spectrum was determined with delays corresponding to a complete reaction of the solvated electron with the Cu(II) macrocycle.

Experimental

Pulse radiolysis experiments were carried out with an apparatus previously described in the literature [4]. The solutions were deaerated with streams of ultrahigh purity N_2 and kept in the dark in order to prevent photolysis of the silver complexes. In experiments where photolysis of the silver(II) compounds had to be prevented, a broad band pass filter was placed between the source of monitoring light and the reaction cell.

The silver complexes, (Ag([14]aneN$_4$))(ClO$_4$)$_2$ and (Ag(bipy)$_2$)(ClO$_4$)$_2$, and the copper complex, (Cu(Me$_6$[14]aneN$_4$))(ClO$_4$)$_2$, were prepared and purified according to literature procedures [5–7]. The elemental analysis and spectral properties of these compounds agreed with those reported elsewhere. Other chemicals were reagent grade and used without further purification.

Acknowledgement

The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy.

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