Inorganica Chimica Acta, *155* (1989) 1–3

Kinetics of the Formation of a Cobalt(III)–alkyl Complex by the Intramolecular Oxidation of Cobalt(II) by the Coordinated Free Radical

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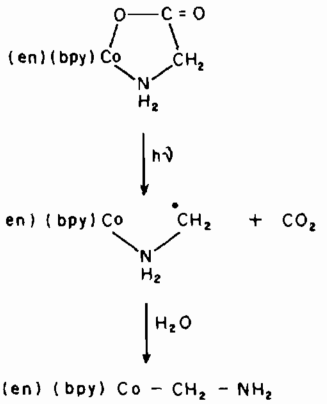
(Received March 22, 1988)

The chemistry of alkyl metal complexes is of interest since several biological reactions are known to involve metal–carbon bond formation [1]. Cobalt–alkyl complexes are of particular concern in the understanding of the metabolic pathways of vitamin B_{12} [2]. There have been quite extensive studies on the synthesis and reactivity of cobalt–alkyl complexes [3]. However, there does not seem to be much information available on the mechanism of formation of cobalt–alkyl complexes and the kinetics of these reactions. We report here the kinetics of the formation of the cobalt–alkyl complexes investigated by flash photolysis of the cobalt(III)–amino acid complex (glycinato)(ethylenediamine)(2,2′-bipyridine)cobalt(III) perchlorate, [Co(en)(bpy)(gly)]$(ClO_4)_2$ (**1**).

The cobalt(III)–amino acid complex **1** was prepared by the method described in the literature [4] and the purity of the complex was ascertained by comparing the absorption maxima and the intensities of the ligand field and charge-transfer bands. Flash photolysis of the complex in acidic aqueous medium (pH = 3) using an Applied Photophysics Excimer laser flash photolysis system, revealed the formation of a transient species (growth of absorbance) and decay at 410 nm (Figs. 1, 2). The observed rate constant for the formation of the transient species was determined to be $8.6 \pm 0.9 \times 10^4$ s^{-1}. The observed rate constant for the formation of the transient species was found to be independent of the hydrogen ion concentration in the pH range 1–7. The transient species decays in acidic solution with a faster rate constant and the decay of the transient species was also monitored.

The absorption spectrum of the transient species has been obtained and is shown in Fig. 3.

Cobalt(III)–amine complexes have been extensively studied in order to understand the properties of the ground state and the excited state [5]. Photolysis of cobalt(III)–amine complexes leads to substitution and redox reactions. However, in all the cases known so far, studies are limited to the determination of quantum yields for the products. Except in the case of oxalato complexes of cobalt(III) [6], transient species are not observed since the cobalt(II) complexes produced are rapidly hydrolysed in acidic aqueous solution. We report here for the first time the spectrum and further reaction of the transient species observed from the charge-transfer excited state of a cobalt(III)–amino acid complex. It was known earlier [7] that photoproduced methyl radicals react with $[Co^{II}[14]\text{-}4,11\text{-}dieneN_4(H_2O)]^{2+}$ to give a cobalt(III)–methyl bonded product. On steady photolysis in aqueous solution, **1** produces carbon dioxide and the cobalt(III)–carbon bonded complex $[Co(en)(bpy)(CH_2{-}NH_2)(H_2O)]^{2+}$. The formation of this product in the steady photolysis reaction has been reported earlier [8]. The spectrum of the transient species is very similar to the spectrum reported for the photo product on steady irradiation in neutral medium. In acid medium the cobalt(III)–alkyl complex is converted to the cobalt(II) aqueous ion and other products. In the case of the acetatopentaamminecobalt(III) complex [9], a methyl radical is formed along with the cobalt(II) ion and this methyl radical does not react with the cobalt(II) ion, presumably because of the rapid breakdown of the cobalt(II)–amine complex in acid medium. The cobalt(II)–amine complex is oxidised by the coordinated methylamine radical intramolecularly before the cobalt(II)–amine complex undergoes the hydrolysis reaction. It is known that carboxylate free radicals lose carbon dioxide in a very short time [10] ($t_{1/2} \simeq 10^{-9}$ s) and the still-coordinated amino methyl radical oxidises the cobalt(II)–amine to give a cobalt(III)–carbon bonded complex. In fact it is resonable that carbon dioxide is lost in the geminate radical pair itself ($-Co^{\bullet}OOC{-}CH_2{-}NH_2$) to give the $NH_2{-}CH_2^{\bullet}$ radical. Similar reactions have been observed for a number of different amino acid complexes of cobalt(III)–amines [11]. The reactions are shown in Scheme 1.



Scheme 1.

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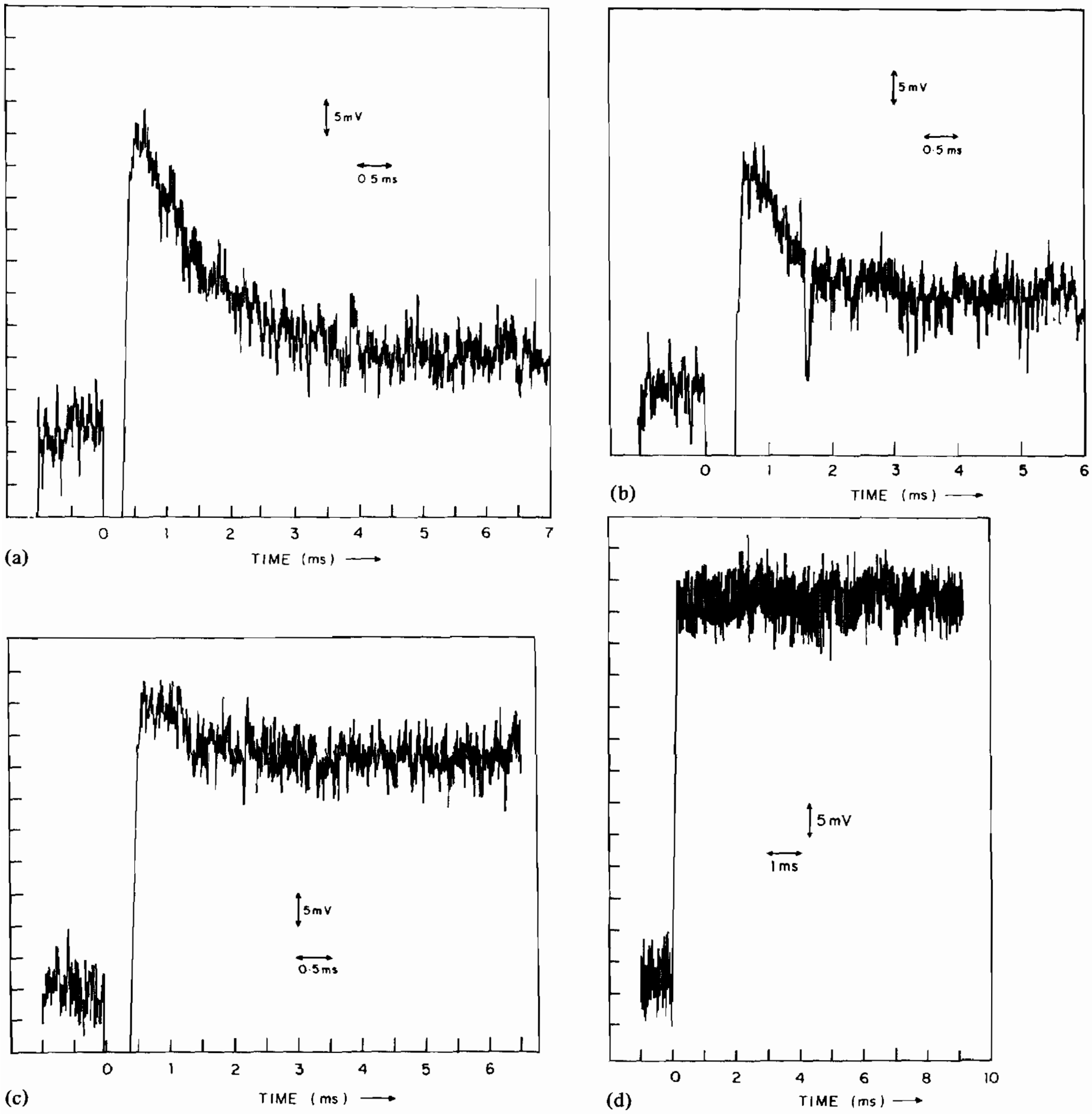

Fig. 1.. Flash photolysis of [Co(en)(bpy)(gly)](ClO$_4$)$_2$ at 410 nm showing decay of the transient species in: (a) 0.1 M HClO$_4$; (b) 0.05 M HClO$_4$; (c) 0.01 M HClO$_4$; (d) water.

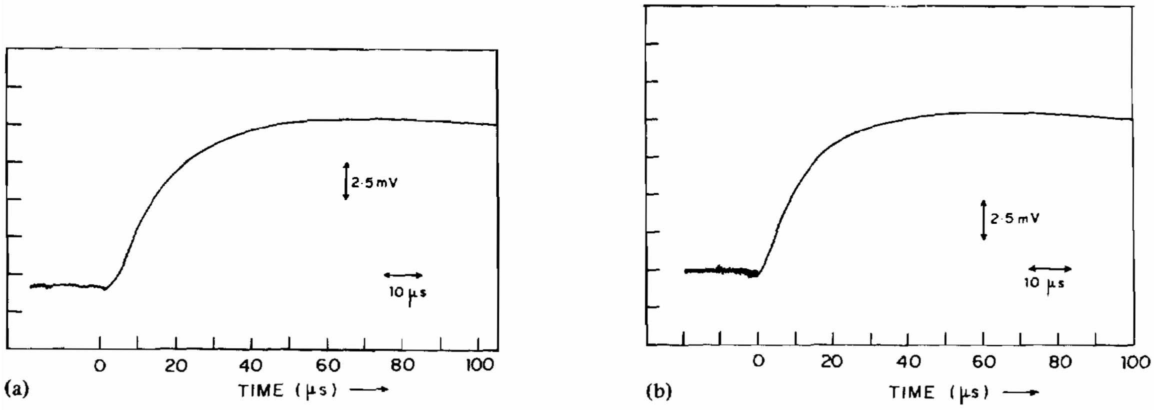

Fig. 2. Laser flash photolysis of [Co(en)(bpy)(gly)](ClO$_4$)$_2$ at 410 nm showing growth of the transient species in: (a) water; (b) pH = 3, (HClO$_4$).

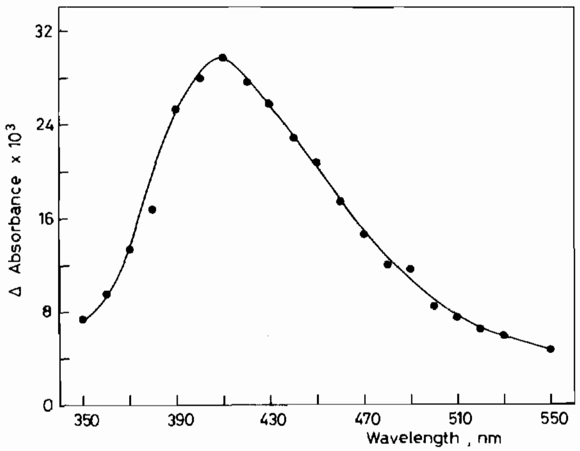

Fig. 3. Absorption spectrum of the transient species on flash photolysis of $[Co(en)(bpy)(gly)](ClO_4)_2$ in water.

The absorption spectra of the transient species for the cobalt(III)–alkyl complexes are similar to those reported for such complexes. Although several reactions involving cobalt(II) complexes with free radicals have been reported, this appears to be the first report on the intramolecular oxidation of a cobalt(II)–amine complex by a coordinated free radical.

Acknowledgements

This investigation was supported in part by the UGC COSIST programme and by a DST SERC Thrust Area Programme.

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