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Photodecarboxylation and Reduction of Ethylenediaminetetraacetatocobaltate(III)*

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Irradiation of Coedta$^-$ complexes in their intense UV absorption bands was reported to result in Co(III) reduction and ligand breakdown to carbon dioxide and formaldehyde, more bulky oxidized ligand fragments being not identified with any certainty [1, 2]. At the same time [3] intermediates in the Coedta$^-$ photochemistry were detected, which were shown in subsequent studies [4, 5] to be organocobalt(III) complexes formed by the carbon dioxide elimination. The present study was undertaken to separate and more fully characterize the final photolysis products of Coedta$^-$.

Experimental

A literature method was used for the preparation of KCoedta·2H_2O [6]. Cobalt(II) was analyzed by the ammonium thiocyanate method with extraction into 2-methyl-pentan-4-one. Cobalt(III) was analyzed by the same method after photoreduction in acidic medium.

For ion-exchange separations, Sephadex DEAE-25 resins in Cl^--form and Sephadex SP-25 resins in Na^+-form were used. For desalting, the corresponding eluates were concentrated on a vacuum evaporator and passed through a Sephadex G-10 column. Irradiations were performed using a 120 W high pressure mercury lamp. Cr^{2+}-scrubbed helium gas was bubbled through the photolyte for 20 min prior to photolysis; bubbling was continued throughout the irradiation.

The 100 MHz and 360 MHz proton nuclear magnetic resonance spectra were measured in D_2O solutions relative to an internal standard, tert-butyl alcohol. All signals are referenced to tetramethylsilane with δ 1.27 for tert-butyl alcohol.

Results and Discussion

The photolyte of a 5 × 20^{-3} *M* Coedta$^-$ solution was introduced into an anion exchange column and then three main bands were eluted with 0.1 *M* NaCl, the first and third of which were grey-pink and the second purple. The second band contained the unchanged Coedta$^-$ ions, the remaining ones consisted of Co(II) complexes. The third band was identified as Coedta^{2-} because the oxidation of the corresponding eluate gave a solution indistinguishable from that of authentic Coedta$^-$. The uni-negative Co(II) complexes from the first eluate can be oxidized to uncharged Co(III) complexes and therefore they contain the tra ligand, mainly edtra as will be shown later. The quantities of Cotra$^-$ and Coedta^{2-} (the first and third bands) amounted to 0.39 and 0.31, respectively, relative to Coedta$^-$ decomposed in an experiment with 21% Coedta conversion. For 51% conversion these figures were found to be 0.49 and 0.24, respectively.

Small quantities of Co(II) complexes passing freely through the anionite (not more than 10% Coedta$^-$ decomposed even for complete reaction) were detected in the photolytes. These complexes may contain ligands with two or less carboxyl groups.

The above mentioned assignment of the first band is evident from the following experiments with extensively photolysed Coedta$^-$ solutions. Thus, the compound [Co(Hedtra)en]Cl·3H_2O has been prepared from the first eluate and its crystal and molecular structure was determined [7]. In another experiment, the Coedta$^-$ photolyte was oxidized with hydrogen peroxide and an uncharged Co(III) complex was isolated from the solution passed through the anionite and then through the cationite. The analysis of this complex corresponds closely to [Co(edtra)H_2O]·H_2O. *Anal.* Calc. for $C_8H_{15}N_2O_8Co$: C, 29.47; N, 8.59; H, 4.64. Found: C, 29.01; N, 8.45; H, 4.75.

Its 100 MHz ^1H NMR spectrum is similar to that known for Co(edtra)H_2O [8].

Next, a $CuCl_2$ solution was added to the photolyte to substitute Cu(II) for Co(II) and then Cutra$^-$ complexes were separated by ion-exchange chromatography as an eluate of the first blue band. After desalting the Cutra$^-$ complexes were destroyed by purging with H_2S gas. The 360 MHz ^1H NMR spectrum of a tra ligands solution (pH 4) thus obtained is consistent with a mixture of 7% medtra and 93% edtra. The presence of medtra is manifested by a CH_3 singlet at 3.05 ppm. Other lines in the spectrum

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*The following abbreviations are used: edta, ethylenediaminetetraacetate; tra, ligands of the ethylenediaminetriacetate type in general; edtra, ethylenediaminetriacetate; medtra, N-methyl-ethylenediaminetriacetate; en, ethylenediamine.

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belong to edtra: three singlets (3.9–4.2 ppm) due to non-equivalent acetate methylenes and two multiplets (3.75–3.8 ppm) due to ethylenediamine methylenes. These lines were also recorded for an edtra solution obtained in the same manner from specially synthesized $Cuedtra^-$ complex.

Finally, the $Cotra^-$ species were separated from the photolyte of a 2×10^{-3} M $Coedta^-$ solution after 5% conversion and then re-oxidized to $Cotra(H_2O)$. The integrated intensity of a singlet at 2.42 ppm due to $Co(medtra)H_2O$ [8] in the 360 MHz ^1H NMR spectrum of a $Co(tra)H_2O$ solution recorded after desalting indicates again 7 per cent $Co(medtra)H_2O$.

It is evident from the above results that photoreduced Co(II) ions are bound mainly to edta and edtra. Contrary to Langford's predictions [2], the medtra content in the $Coedta^-$ photolyte is negligible.

When the $Coedta^-$ photolyte is passed through the anionite and cationite, some Co(III) complexes remain in the solution. Their zero charge and d–d absorption bands at 547 and 380 nm which are characteristic of the *cis*-$Co(N)_2(O)_4$ coordination type imply tra ligands. The 360 MHz ^1H NMR spectrum of these uncharged complexes shows that they are almost exclusively $Co(edtra)H_2O$, the content of $Co(medtra)H_2O$ not exceeding one per cent. Some comments are in order here. The only $Coedtra(H_2O)$ isomer characterized in the literature by NMR spectra is the *cis*-equatorial, usually prepared by the oxidation of corresponding Co(II) complexes [8].

No lines of the *cis*-equatorial isomer of $Coedtra(H_2O)$ are seen in the NMR spectrum of the uncharged Co(III) complexes isolated from the $Coedta^-$ photolyte. To avoid difficulties of interpreting this unknown spectrum, excess of $NaNO_2$ was added to the solution of the uncharged complexes, whereby they were converted to uni-negative nitro complexes. The 360 MHz ^1H NMR spectrum of these nitro complexes after they have been separated by the ion-exchange chromatography contains only lines of the known *cis*-equatorial $Co(edtra)NO_2^-$ complex, characteristic of which are the AB quartet at 4.22 and 3.17 ppm, the AB quartet at 4.12 and 3.92 ppm and the singlet (degenerated AB pattern) at 4.10 ppm [8]. It follows that the uncharged complexes are polar and/or *trans*-equatorial isomers of $Co(edtra)H_2O$ which are converted to the *cis*-equatorial nitro complex.

The quantities of $Co(edtra)H_2O$ in the photolyte relative to Co(II) were found to be 3.17, 2.03, and 0.64 respectively for 9, 12, and 24% $Coedta^-$ conversions. It should be emphasized that the photolytes for these analyses were acidified to pH 1.7 just under helium purge at the end of irradiation to prevent the possibility of Co(II) re-oxidation by air oxygen during the photolyte work up. Reoxidation of Co(II) is also unlikely because the uncharged Co(III) complexes have no *cis*-equatorial isomer and a much lower content of medtra ligands as compared with the Co(II) complexes in the photolyte. Thus, unexpectedly one of the photochemical reaction pathways of $Coedta^-$ appears to be decarboxylation (more correctly, deacetylation) without reduction.

The charge-transfer photochemistry of the aminocarboxylate Co(III) complexes was shown to involve the contraction of the five-membered glycinato ring via the carbon dioxide elimination [9]. In the $Coedta^-$ case, the initial photochemical products contain the C-bonded N-methylene-ethylenediaminetriacetate, their geometry however being uncertain [5]. We denote these intermediates by $[CoCH_2NR_1R_2]^-$, where R_1 is $CH_2CO_2^-$ and R_2 is $(CH_2)_2N(CH_2CO_2^-)_2$. The primary process of $Coedta^-$ photolysis can thus be described by the equation:

$$Coedta^- \xrightarrow{h\nu} [CoCH_2NR_1R_2]^- + CO_2 \qquad (1)$$

Central to any mechanism of $Coedta^-$ photolysis must be the inclusion of such intermediates which are important sources of final products. Detailed discussion of a reaction sequence will be deferred until the reactivity pattern of the aminomethylene organocobalt complexes is clarified. To our knowledge, only two examples have been synthesized to date [9, 10].

The $[CoCH_2NR_1R_2]^-$ intermediates could decompose heterolytically in aqueous solutions yielding $Co(edtra)H_2O$. In strongly acidic solutions (40% $HClO_4$, for example) the only observed decay of the intermediates is one of the redox type. The attack of the intermediates by alcohols and hydrogen peroxide was shown to lead to the heterolysis, even in 40% $HClO_4$ [5]. The homolytic decay of the intermediates yields perhaps the N-methylene-ethylenediaminetriacetate radicals which could recombine or reduce $Coedta^-$ and $[CoCH_2NR_1R_2]^-$ depending on substrate concentration and light intensity. There is reason to suppose an intramolecular electron transfer between $[CoCH_2NR_1R_2]^-$ and $Coedta^-$ [5]. In 40% $HClO_4$, in the presence of $Coedta^-$, for the thermal decay of the intermediates was found to yield a CO_2 amount equal to that evolved in the primary photochemical process (1), the sum of CO_2 evolved in both processes being equal to the total $Coedta^-$ decay [5]. Since the Co(II) complexes are the only photolysis products in 40% $HClO_4$, this means that $\phi_{CO_2}/\phi_{Co(II)} = 1$. In neutral aqueous solutions, inasmuch as $Co(edtra)H_2O/Co(II)$ ratio tends to exceed 3 for $Coedta^-$ conversions approaching zero, the $\phi_{CO_2}/\phi_{Co(II)}$ ratio must also exceed 3, because the $Co(edtra)H_2O$ formation is inevitably coupled with the CO_2 evolution. This is inconsistent with the findings of Natarajan *et al.* [1] that the $\phi_{CO_2}/\phi_{Co(II)}$ ratio is close to 1.0 for the pH in the range $1 \leqslant pH \leqslant 6$. If the thermal redox reactions of the intermediates are accompanied by the CO_2 evolution in neutral solutions also, then a CO_2 source is not the intermediate since only small quantities of Co(II) complexes with the ethylenediaminediacetate type ligands were detected (not more than 10% $Coedta^-$ decomposed).

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