An Autocatalytic Redox Reaction Involving Cr(II) Attack at a β-Diketonate Carbon Atom

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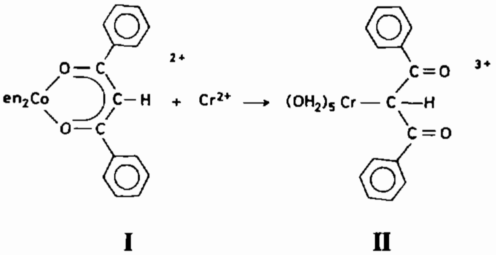
One of the earliest examples of autocatalysis in the redox chemistry of Co(III) complexes was reported in 1971 by Norris and Nordmeyer [1]. They found that the Eu^{2+} reduction of isonicotinamidepentaamminecobalt(III) proceeded by an autocatalytic mechanism. An organic radical intermediate was proposed. Since then, much work has been done by Gould *et al.* [2–8] who reported that the reductions by Eu^{2+} and V^{2+} of a number of Co(III) complexes having reducible ligands, especially those featuring pyridine ligands, exhibit autocatalysis. In these reactions, it was found that the active intermediate in the catalytic path is the ligand radical, which is derived from a one-electron reduction of the free ligand generated in a prior outer-sphere step. Gould and his co-workers were able to suppress this autocatalysis by addition of excess Eu^{3+} or V^{3+} since this reverses the act of electron transfer to the free ligand. By this technique, they were able to evaluate the specific rate for the uncatalyzed reaction. It was found that V^{3+} was the more effective suppressant, reflecting its more positive potential and the more rapid V^{2+}/V^{3+} self-exchange [8]. The ligand radical appears to be remarkably reactive for when present only in steady-state concentrations, it was capable of inducing reductions which were 100 times as rapid as those of the uncatalyzed reactions [3]. Other results from Gould's laboratory [4, 9, 10] indicated that added pyridine-substituted free ligands will also catalyze outer-sphere reactions by Eu^{2+} and V^{2+}.

Autocatalytic reactions involving Cr^{2+} are much less common. For example, it was found [4] that reductions by V^{2+} but not by Cr^{2+} of the 2,4- and 2,5-pyridinedicarboxylic acid complexes of cobalt(III) are autocatalytic. Some reactions involving Cr^{2+} are, however, known [2]. We wish, in the present work, to report an autocatalytic reaction in which the reductant is Cr^{2+}. In this process, Cr^{2+} attacks at the central carbon atom of the 1,3-diphenyl-1,3-propanedionato (DPPM) ligand to give a reaction having the overall stoichiometry of eqn. (1).



I II (1)

We are unable to determine if the Cr^{2+} directly attacks the Co(III) complex in an inner-sphere manner or if it later attacks the free ligand in solution to give **II**. Addition of free ligand accelerates the reaction only very slightly; this may be due to the extremely low solubility of the ligand in aqueous solutions.

The chromium complex (**II**) so obtained is yellow and has spectral properties $\lambda_{max}(\epsilon_{max})$ (nm (M^{-1} cm^{-1})) of 570(27), 480(240), 458(290), 378(14 000) and 286(11 000). The yellow color for a chromium(III) species is unusual and indicates the formation of a Cr–carbon bond [11]. The first example of such an organometallic complex was reported by Anet and Leblanc in 1957 [12]. They prepared the benzylpentaaquachromium(III) ion and reported that it was yellow with a low intensity maximum at 540 nm and a high intensity maximum at 358 nm. The spectra of many complexes containing a chromium–carbon bond were subsequently examined by Taube *et al.* [13]. All were found to have a characteristic yellow color and a strong absorption band at ≈390 nm. For example, the pentaaqua(diethylether)chromium(III) ion had spectral parameters 390(360) and 561(23).

Reaction (1) proceeds by an autocatalytic mechanism in which there is a considerable lag period of 10–20 min (depending on the [Cr^{2+}]) before the reaction begins. The time taken to complete the reaction is then 30–60 min. The final spectrum of the scan runs of a kinetic mixture, in all cases, corresponds to that of complex **II**.

Complex **II** may be obtained in pure form by very rapid ion-exchange on Sephadex SP-120. On the column, it decomposed quickly to a dark yellow species of high charge which would not elute from the resin, even with saturated NaCl as eluent. A possible explanation for this observation is that polymerization occurs to give complexes of the type **III**.

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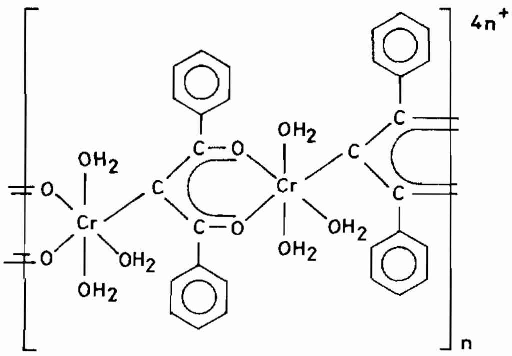

III

A highly charged green material is also produced on the column. The properties of this species are consistent with those of the green Cr(III) dimer, $[(OH_2)_4Cr(OH)_2Cr(OH_2)_4]^{4+}$. The formation of the green dimer may be expected if complex **II** decomposes homolytically to give DPPM$^{\bullet}$ radicals and Cr^{2+}. No precautions were taken on the column to exclude O_2 and a major product of the O_2 oxidation of Cr^{2+} is the formation of this dimer. Anet and Leblanc [12] reported that the benzylpentaaquachromium(III) ion tended to dissociate homolytically as well.

We were unable to suppress the autocatalysis by addition of $Cr(OH_2)_6{}^{3+}$. This may reflect a lack of reversibility of the electron transfer from $Cr(OH_2)_6{}^{3+}$ to the DPPM· radical (coordinated or free). In any case, this prevented us from directly measuring the rate of the uncatalyzed reaction using this technique which was so successfully employed by Gould *et al.* [2–8].

To the best of our knowledge, complex **II** is the first example of a carbon-bonded β-diketonate ligand on chromium, although these are known to exist in this bonding mode on other metals [14, 15]. It may also be made by direct substitution of the ligand, DPPM, on $Cr(OH_2)_6{}^{3+}$ but the reaction requires a week in an aqueous acetone solution (80% by volume acetone) to get a 20% yield. The substitution reaction is not accelerated by the addition of Cr^{2+} under anaerobic conditions. In contrast, the only product by electron transfer appears to be **II** suggesting either a direct inner-sphere attack on the cobalt(III) complex or a very efficient scavenging of the DPPM ligand by Cr(II).

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