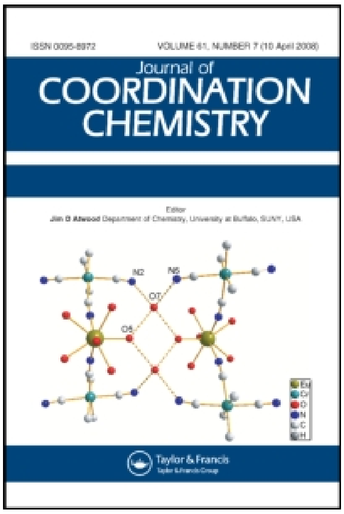

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On the mechanism of reduction of maleate by a Co(I) complex with a macrocylic ligand in aqueous solutions

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On the mechanism of reduction of maleate by a Co(I) complex with a macrocylic ligand in aqueous solutions[#]

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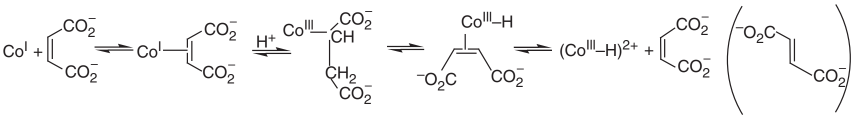
Recently, it was shown that a Ni(I) complex with a tetraazamacrocyclic ligand (Ni^I(1, 4, 8, 11-tetraazacyclotetradecane)$^+$, Ni(I)L_2^+, cyclam), reduces maleate in aqueous solutions. It was decided to investigate whether this is a general reaction of low valent transition metal complexes. In this study, the reactions of Co^IL^+ ($L = $5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) with maleate were investigated. The effect of the addition of maleate to aqueous solutions containing this low valent metal complex, prepared *via* the pulse radiolysis technique, was studied. The $d \rightarrow \pi^*$ complexes formed between the monovalent cobalt complex and maleate were detected and characterized by UV-Vis spectroscopy. The nature of the final products formed was studied and detailed mechanisms of the reduction processes are proposed. The mechanism and kinetics of the reaction of Co(I)L^+ with maleate was studied applying pulse-radiolysis and analysis of the final products.



Keywords: Maleate; Cobalt macrocyclic complex; Kinetics and mechanism; Reduction

1. Introduction

A range of transition metal complexes acts as catalysts or electrocatalysts for various reduction processes, due to the ability of these cations to exist in a variety of oxidation states, stabilized by suitable ligands [1–7]. $Ni^{II}L^i$ and $Co^{II}L^i$ complexes, with suitable macrocyclic ligands, are reduced reversibly to relatively stable nickel(I) and cobalt(I) species, respectively, in aqueous solutions [8–10]. Nickel(I) macrocyclic complexes have attracted considerable attention because they enable the electrocatalytic reduction of

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[#] This article is dedicated to Prof. Rudi vanEldik on the occasion of his 65th birthday.

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alkyl halides [3, 11–19]. Furthermore, nickel complexes have recently increasingly been utilized as catalysts for ethylene polymerizations and oligomerizations [20]. Cobalt(I) complexes are used in catalytic reductions including those analogous to B12 [21, 22], of N_2 to ammonia and acetylene to ethylene [23], CO_2 to CO [24–31], and reduction of water [32].

Alkenes are known to form d → π^* complexes with low valent transition metal ions. In a previous paper, it was reported that Ni^I (1,4,8,11-tetraazacyclotetradecane)$^+$, $Ni(I)L_1^+$, reduces ethylene quantitatively to ethane plus butane (and hexane traces) in neutral aqueous solutions [33]. A radical mechanism of reduction of ethylene was proposed. The first step probably involves the formation of a d → π^* complex between the low valent $Ni(I)L_2^+$ complex and the ethylene:

$$\mathrm{Ni(I)L_1(H_2O)_2^+} + \mathrm{C_2H_4} \overset{K_1}{\rightleftarrows} ((\mathrm{H_2O})\mathrm{L_1Ni}-||)^+ \tag{1}$$

Studying the effect of electron withdrawing groups, e.g. CO_2^-, on the mechanism of reduction of alkenes by $Ni(I)L^+$ yielded the following results [34]. The mechanisms of reduction of maleate and fumarate by $[Ni(I)L_1]^+$ differ significantly from each other in spite of the similarity of the two substrates. The difference is probably mainly due to the fact that the radical anions formed in the reduction of both substrates have different characteristics due to the strength of the hydrogen bond in the radical anion of the maleic acid [35–38]. The first reaction observed is attributed to the equilibrium reaction between radiolytically produced NiL_1^+ and maleate or fumarate in the solution to produce the Ni-alkene d → π complex in analogy to the Ni(I)-ethylene system.

It seemed of interest to investigate whether the reduction of alkenes is a general reaction of low valent transition metal complexes. In this study, the reactions of the macrocyclic complex Co^IL^+ (L = 5, 7, 7, 12, 14, 14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) with maleate is investigated. The effect of the addition of maleate to aqueous solutions containing this low valent metal complex, prepared *via* the pulse radiolysis technique, is studied.

2. Experimental

2.1. *Materials*

All the organic and inorganic chemicals and solvents were purchased from Fluka, Sigma–Aldrich, were of AR grade, and were used as received. The water used was deionized water which was further purified by passing through a Millipore Milli-Q setup with a final resistivity of $>10\,\mathrm{mol\,L^{-1}\,\Omega^{-1}\,cm^{-1}}$. The pH was adjusted with NaOH or $HClO_4$. He, Ar, and N_2O were purchased from Maxima, Israel. Solutions were saturated with Ar or He using the syringe technique.

The complex N-rac-$(Co^{II}L)(ClO_4)$ [39, 40], was synthesized according to literature procedures and characterized by NMR and UV-Vis and IR spectroscopy. $(Co^{II}L)^{2+}$ exists in the meso and rac forms and undergoes pH dependent isomerization in solution. The amounts of the meso and rac forms can be quantified by UV-Vis and NMR spectroscopy [41].

2.2. *Irradiations*

A Noratom 3500 ^{60}Co γ-source with dose rates of 2.0–3.3 Gy min^{-1} was used for low-dose-rate experiments and product analysis. Pulse radiolysis experiments were performed at the electron LINAC of the Hebrew University, Jerusalem, using the same setup and procedures described earlier in detail [42, 43]. 0.1–1.5 µs 5 MeV 200 mA mp pulses were used yielding 1–30 Gy pulse^{-1}. For kinetic determinations, at least three independent experiments were performed, and each set of data was analyzed both for first- and second-order kinetic fits.

2.3. *Analysis of final products*

Analysis was performed using a Waters HPLC model Delta 600 equipped with a Waters 996 Photodiode array detector. A RP-18 Ultrasphere column by Beckman 250 mm × 4.6 mm × 5 µm was used. Elution solution 1% CH_3OH, pH 2.8 (H_3PO_4), 0.8 mL min^{-1} was used. The retention times and spectra of all the peaks were recorded and compared with blank solutions. The peaks were detected at 210 nm (the peak maxima of maleic and fumaric acid).

The samples were acidified to pH 2.0 with H_3PO_4 before injection. In cases where the complex prevented a good separation, the samples were further purified from the complex by passing through a Dowex 50W-X8 column (0–39–1.00 mm particle size).

Hydrogen analysis was undertaken by GC on a Hewlett Packard 5890 Series II Gas chromatograph with a Poropaq QS Supelco column and a TCD detector.

2.4. *Production of Co(I)L$^+$ and of radicals*

2.4.1. Ionizing radiation as a source of reducing radicals. When neutral dilute aqueous solutions are irradiated by ionizing radiations, the following primary products are formed [44]:

$$H_2O \xrightarrow{\gamma, e^-} \cdot OH\ (2.65), e^-_{aq}\ (2.65), \cdot H\ (0.60), H_2\ (0.45), H_2O_2\ (0.75), H_3O^+\ (2.65). \quad (2)$$

The yield of the products is reported as *G* values, which are the number of product molecules (species) formed per 100 eV of radiation absorbed in the sample. The values in parentheses in equation (1) are the *G* values for the different primary products in dilute aqueous solutions [44]. In concentrated solutions, the "radical" (·OH, e^-_{aq}) yields are somewhat higher and the "molecular" (H_2, H_2O_2, and H·) are somewhat lower [44].

When formate is added to the irradiated solutions, it reacts with the ·OH radicals and the H atoms *via* [45]

$$\begin{aligned} &HCO_2^- + \cdot OH/\cdot H \rightarrow CO_2^{\cdot -} + H_2O/H_2, \quad k_{\cdot OH} = 3.2 \times 10^9\ (\text{mol L}^{-1})^{-1}\ \text{s}^{-1}[45] \\ &k_{\cdot H} = 2.1 \times 10^8\ (\text{mol L}^{-1})^{-1} \text{s}^{-1}[45] \end{aligned} \quad (3)$$

transforming the strong oxidizing agent, ·OH radicals, into a reducing agent, $CO_2^{\cdot -}$ anion radicals. Thus, in these solutions only two strong reducing radicals remain e^-_{aq}, $E^\circ = -2.87$ V *versus* SHE [46] and $CO_2^{\cdot -}$, $E^\circ = -1.9$ V *versus* SHE [46].

Table 1. Important rate constants for the formation of the Co(I) complex.

M/L	$M(II)L^{2+} + e^-_{aq} \rightarrow M(I)L^+_{aq}$ k $(mol\,L^{-1})^{-1}\,s^{-1}$	$M(II)L^{2+} + CO_2^{\cdot-} \rightarrow M(I)L^+_{aq} + CO_2$ k $(mol\,L^{-1})^{-1}\,s^{-1}$
Co/L	$k_{rac} = 4.4 \times 10^{10}$ $k_{meso} = 4.7 \times 10^{10}$	$k_{rac} = 8.5 \times 10^8$[47] $k_{meso} = 3.0 \times 10^9$
Maleate		1.0×10^8 (pH 6.0) this study and [36]

Co(I) is produced in irradiated aqueous solutions containing formate. In these solutions, the $CO_2^{\cdot-}$ and e^-_{aq} radical anions reduce the $Co(II)L^{2+}$ *via* [8] (table 1):

$$Co(II)L^{2+} + e^-_{aq} \rightarrow Co(I)L^+_{aq}, \tag{4}$$

$$Co(II)L^{2+} + CO_2^{\cdot-} \rightarrow Co(I)L^+_{aq} + CO_2. \tag{5}$$

The yield of $Co(I)L^+$ is lower than $G(\cdot OH + \cdot H + e^-_{aq})$ as formed $M(I)L^+$ is oxidized by the H_2O_2 produced in irradiated solutions, a relatively fast reaction that proceeds over several millisecond. $G(Co(I)L^+ = G(\cdot OH + \cdot H + e^-_{aq}) - 2G(H_2O_2) = 4.5$.

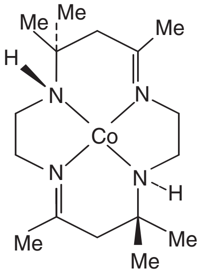
We could not use N_2O saturated solutions, in which all the primary radicals are transformed into $CO_2^{\cdot-}$ anion radicals, as $Co(I)L^+$ reacts in a fast reaction with N_2O [8, 47].

In weak acidic solutions, Co(I)L is transformed into the hydride complex, $(LCo^{III}\text{–}H)^{2+}$, which has a stability constant of $3.0 \times 10^9\,(mol\,L^{-1})^{-1}$ [48]. The rate of the reaction $Co^I + H\text{-}A \rightarrow [Co^I\text{–}H^{\delta+}\text{–}A^{\delta-}] \rightarrow (Co^{III}\text{–}(H^-))^{2+} + A^-$ increases with the decrease in the pKa of HA and has for $H_2PO_4^-$ a value of $k = 0.98 \times 10^8\,(mol\,L^{-1})^{-1}\,s^{-1}$ [49].

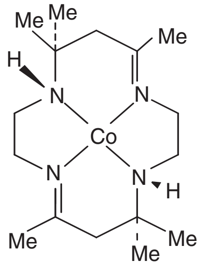
3. Results and discussion

3.1. *Reactions of N-rac-Co(I)L$^+$ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) with maleate*

The complex $Co(II)L^{2+}$ is extensively used as catalyst [10, 28, 29, 31, 47, 50, 51]. The complex exists in the meso and rac forms. In alkaline aqueous solutions, isomerization proceeds and the N-rac isomer predominates ($K = 10$). In acidic aqueous solutions, no stereo isomerization occurs even during the course of a week. The reduced complex $Co(I)L^+$ retains the isomeric form of the initial Co(II) complex [47].



Meso



Rac

All the experiments in this study were performed in neutral or slightly acidic solutions to prevent isomerization. In this study, two buffer systems were employed: In the presence of 0.1 mol L^{-1} phosphate buffer at pH 6.0 ($H_2PO_4^-/HPO_4^{2-}$) the complex $(LCo^{III}–H)^{2+}$ is formed in a relatively fast reaction, while, when using 0.1 mmol L^{-1} of the same buffer, the Co(I)L$^+$ intermediate is stable enough to interact with the substrates present in the solution [47, 49, 52, 53].

3.2. *Formation of the Co(I) complex and its reaction with maleate*

Co(I)L^+_{aq} is produced by irradiation (short electron pulse) of dilute aqueous solutions (He saturated) containing Co(II)L^{2+} (3×10^{-4} mol L^{-1}) in the presence of 0.03 mol L^{-1} $NaHCO_2$, 0.1 mmol L^{-1} phosphate buffer at pH 6.0. The spectrum of the derived intermediate corresponds to that reported for the Co(I)L^+_{aq} complex in the literature, which has a maximum at 630 nm [47]. The complex disappears in a first-order process with $k_f = (3.2 \pm 0.4) \times 10^4$ s^{-1} under the experimental conditions.

The addition of maleate (1–8)$\times 10^{-4}$ mol L^{-1} to the solution accelerates the disappearance of Co(I)L$^+$. At the observation wavelengths, three additional distinct time-resolved reactions are observed (figure 1a–c). The decomposition reactions occur over timescales of a few microseconds, up to about 100 s.

The spectra of the derived intermediates in the reaction of Co(I)L$^+$ with maleate were recorded at different times (4 µs, 80 µs, and 4 s) of the reaction and are shown in figure 2.

The first decomposition reaction observed, the disappearance of the initially formed Co(I)L$^+$ (see spectrum observed after 4 µs in figure 2) takes place in the µs time range and obeys a first-order rate law, see figure 1. From a plot of k_{obs} *versus* the concentration of the maleic acid, (figure 3) its rate constant was determined as $k_1 = (5.7 \pm 1.2) \times 10^8$ mol L^{-1} s^{-1}. The graph shows a relatively large intercept, corresponding to a $k_{-1} = (4.6 \pm 1.0) \times 10^4$ s^{-1} and a $K_1 = (1.2 \pm 0.3) \times 10^4$ mol L^{-1}, indicating that the reaction of Co(I)L$^+$ with maleate to form the π-complex is an equilibrium reaction, according to

$$Co^IL^+_{(aq)} + {}^-O_2CCH = CHCO_2^- \rightleftharpoons LCo^I - ({}^-O_2CCH = CHCO_2^-)^-. \quad (6)$$

Under the experimental conditions, nearly all of the Co(I)L$^+$ is converted into the Co(I)-maleate complex.

The second distinct reaction observed (figure 1b), follows a first-order rate law. The measured rate is independent of cobalt complex or maleate concentration and independent of the concentrations of other components of the solution, or wavelength of observation. The third reaction follows a second-order rate law and the fourth a first-order rate law, both independent of any solution components. Table 2 summarizes the rate constants derived for the different steps in the reaction between Co(I)L$^+$ and maleate. The first and second reactions are affected by the pH of the solution (in the range pH 5.0–7.0), whereas reactions 3 and 4 show no pH effect. Those results are shown in table 3. The pH effect in the first reaction can be explained by the fact that the COOH groups in the acidic form of maleic acid (pK_a 6.2) are stronger electron acceptors than the COO$^-$ groups, and therefore the acid form is the stronger π acid and leads to a stronger bond and faster bond formation between maleic acid and Co(I)L$^+$.

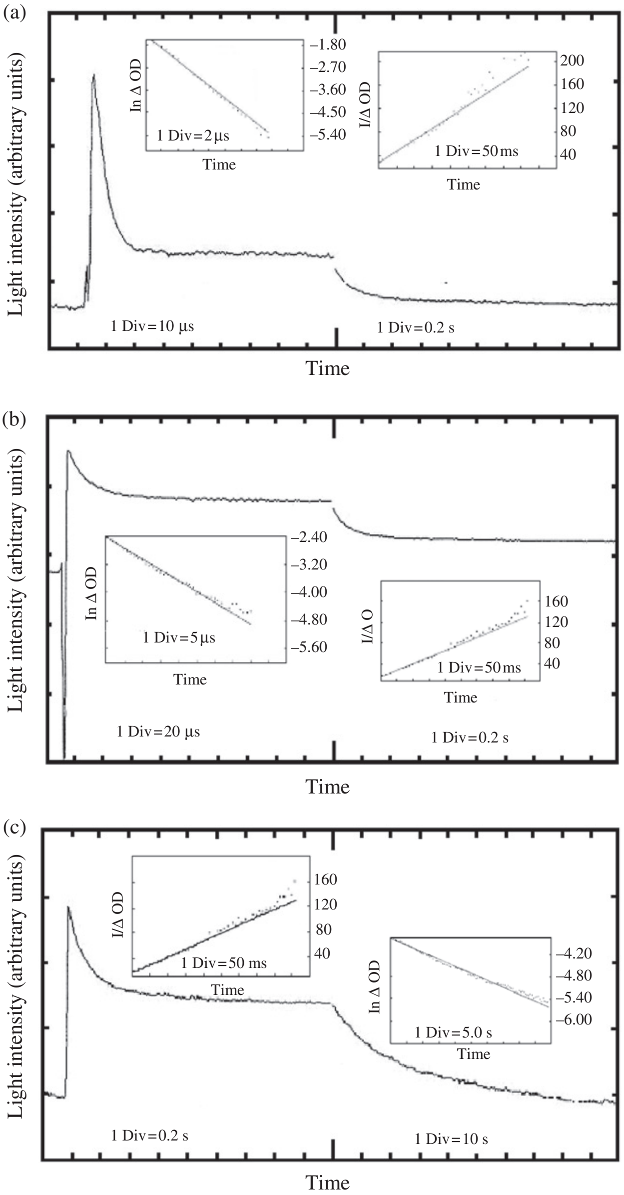


Figure 1. (a) Fast formation and first two decomposition processes observed at 575 nm in the $(Co^{II}L)^{2+}$/maleate system. (b) First two decomposition processes observed at 400 nm in the $(Co^{II}L)^{2+}$/maleate system. (c) Longer decomposition processes observed at 400 nm in the $(Co^{II}L)^{2+}$/maleate system.
Insets show the kinetic fits. Solution composition: $[CoL]^{2+} = 3 \times 10^{-4}\,mol\,L^{-1}$, $[HCOO^-] = 0.03\,mol\,L^{-1}$, [phosphate]=$0.1\,mmol\,L^{-1}$, pH 6.0, [maleate]=$3.0 \times 10^{-4}\,mol\,L^{-1}$, He saturated, irradiations at 3.0 Gy, $\lambda = 400$ nm.

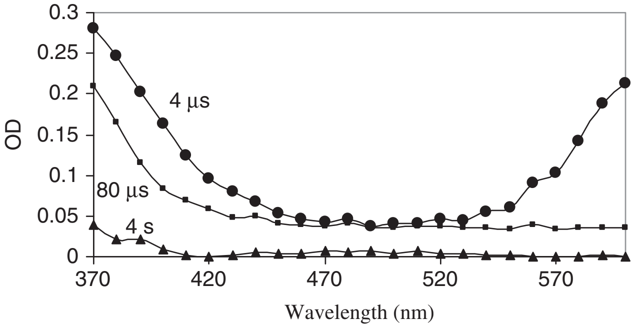


Figure 2. Spectra of the intermediates during the disappearance of Co(I)L^+ and its maleate complex at different times. Solution composition: $[CoL]^{2+} = 3 \times 10^{-4}\,mol\,L^{-1}$, $[maleic] = 5 \times 10^{-4}\,mol\,L^{-1}$, $[formate] = 0.01\,mol\,L^{-1}$, $[phosphate] = 0.1\,mmol\,L^{-1}$, pH 6.0, He saturated solution; measured 4, 80 µs and 4 s after the pulse; irradiations at 3.0 Gy.

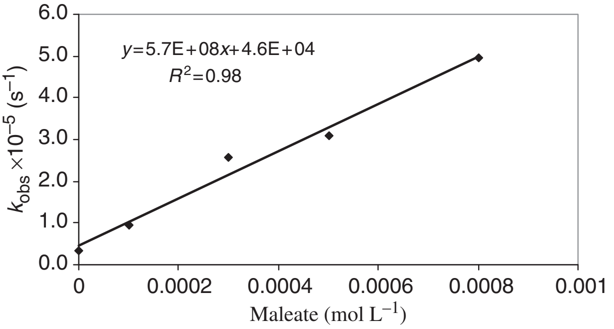


Figure 3. The linear dependence of the rate constant of formation of reaction (6) on the maleate concentration. Solution composition: $[CoL]^{2+} = 3 \times 10^{-4}\,mol\,L^{-1}$, $[HCOO^-] = 0.03\,mol\,L^{-1}$, $[phosphate] = 0.1\,mmol\,L^{-1}$, pH 6.0, $[maleate] = (1\text{–}10) \times 10^{-4}\,mol\,L^{-1}$, He saturated, irradiations 3.0 Gy.

Table 2. Rate constants of the distinct reactions observed in the Co(I)L^+/maleate system and Co(III)–H^{2+}/maleate system (alternating rows respectively).

Number of reaction	Timescale	Wavelength (nm)	Rate constant of the reaction
1	20 µs	575	$k = (5.7 \pm 1.2) \times 10^8\,(mol\,L^{-1})^{-1}\,s^{-1a}$
	<40 µs	470	$K = (1.2 \pm 0.3) \times 10^4\,(mol\,L^{-1})^{-1a}$
			$K = 3000 \pm 600\,(mol\,L^{-1})^{-1b}$
2	200 µs	400	$k = (5.3 \pm 1.2) \times 104\,s^{-1a}$
	400 µs	400	$k = (3.4 \pm 0.5) \times 10^4\,s^{-1b}$
3	2 s	400	$2k = (9.3 \pm 2.3) \times 10^5\,(mol\,L^{-1})^{-1}\,s^{-1a}$
	100 ms	400	Probably second order but difficult to judge[b]
4	100 s	400	$k = (0.12 \pm 0.04)\,s^{-1a}$
	40 s	400	$*k = (0.43 \pm 0.05)\,s^{-1b}$

[a] Solution composition Co(I)L^+/maleate system: $[CoL]^{2+} = 3 \times 10^{-4}\,mol\,L^{-1}$, $[maleic] = 3 \times 10^{-4}\,mol\,L^{-1}$, $[formate] = 0.03\,mol\,L^{-1}$, $[phosphate] = 0.1\,mmol\,L^{-1}$, pH 6.0, He saturated solution, Irradiations at 3.0 Gy.

[b] Solution composition Co(III)–H^{2+}/maleate system: $[CoL]^{2+} = 3 \times 10^{-4}\,mol\,L^{-1}$, $[maleic] = 5 \times 10^{-4}\,mol\,L^{-1}$, [formate] = 0.03 M, $[phosphate] = 0.1\,mol\,L^{-1}$, pH 5.8, He saturated solution, irradiations at 3.0 Gy.

*After exclusion of photochemical contribution.

Table 3. Influence of pH on the rates of reactions 1 and 2.

pH	Rate constant of reaction 1	Rate constant of reaction 2 (s^{-1})
5.0	Too fast to be measured	1.9×10^4
6.0	5.8×10^8 $(mol\,L^{-1})^{-1}\,s^{-1}$	2.5×10^4
7.0	1.8×10^8 $(mol\,L^{-1})^{-1}s^{-1}$	6.0×10^4

Solution composition: $[CoL]^{2+} = 3 \times 10^{-4}\,mol\,L^{-1}$, $[maleic] = 8 \times 10^{-4}\,mol\,L^{-1}$, $[formate] = 0.03\,mol\,L^{-1}$, $[phosphate] = 0.1\,mmol\,L^{-1}$, pH 5.0–7.0, He saturated solution, irradiations at 3.0 Gy.

3.3. *Final products analysis*

Samples containing $[CoL]^{2+} = 2 \times 10^{-3}\,mol\,L^{-1}$, $[maleic] = 3 \times 10^{-4}\,mol\,L^{-1}$, $[formate] = 0.1\,mol\,L^{-1}$, $[phosphate] = 0.1\,mol\,L^{-1}$, pH 6.0, He saturated solution, were irradiated in a ^{60}Co γ-source and analyzed by HPLC and GC. The following results were obtained:

1. Only 23%, relative to formed Co(I), of maleate disappeared *versus* an expected 50%.
2. Relative to Co(I), 8% of fumarate formed.
3. Relative to Co(I), 20% of molecular dihydrogen formed.

Under the experimental conditions, no formation of succinic acid could be observed due to the low concentrations and its low extinction coefficient.

3.4. *Proposed reaction mechanism*

The first decomposition reaction observed visibly at 575 nm (absorption peak of $Co(I)L^+$) [47, 54] evidently corresponds to the reaction of the radiolytically formed $Co(I)L^+$ with maleate to form a π-complex. The first spectrum that can be measured directly following the pulse (4 µs, see figure 2) corresponds to a mixture of $Co(I)L^+$ and its maleate complex, which forms in an equilibrium reaction according to reaction (6), vide *supra*.

In the following the ligand L and water ligands on the central cobalt ion are not depicted for simplification purposes.

(6′)

At 400 nm, an additional reaction can be observed which apparently does not affect considerably the light absorption at 575 nm. This reaction is apparently due to an isomerization reaction of the formed complex facilitated by proton addition. The size of the measured rate constant indicates that the proton source is abstraction from water molecules and not reaction with H_3O^+ or $H_2PO_4^-$ and as the rate increases slightly with increasing pH (table 3).

(7)

Thus spectrum 2 is attributed to Co^{III}–$CH(CO_2^-)CH_2CO_2$.

The third reaction observed in the time range of 2 s after the pulse is a second-order reaction independent of the Co(II)L^{2+} concentration. The latter indicates that the reaction is not due to homolysis of the Co^{III}–C bond. The fact that maleate concentration has only a very slight effect on the rate constant of reaction 3 implies that the following reaction plays a role:

(8)

Apparently, the second equilibrium reaction is slower than the first and isomer B reacts faster with isomer A, according to

(9)

before it can decompose to (Co^{III}—H)$^{2+}$ and maleate in the previous reaction (8). The contribution of both reactions explains the second-order characteristics of the third observed reaction.

The fourth reaction, observed over 100 s under the experimental conditions as a first-order reaction, yields succinate and LCo^{II} according to the following equation:

(10)

We propose that the relatively small yield of organic products and disappearance of maleic acid are due to a reaction parallel to the last, in which the Co^{II}–C bond breaks forming Co^{II}, hydrogen, and maleate, according to the following reaction

(11)

This mechanism is in agreement with the experimental observations, mainly the observed rate constants and their order of reaction and the final products of the reaction.

It can be summed up that Co(I)L^{+} indeed reduces maleate in aqueous solutions. The yield is smaller than expected and several parallel reactions ensue during the process.

The mechanism established in this case agrees with that found by Wang *et al.* [55] for a completely different Co(I) complex, an initially formed Co(I) complex reacts to bind an alkene, further forming a Co(III) intermediate. Shukla *et al.* [56] reported that during the reaction of Co(I) with alkylhalide an intermediate of the form R–Co(III)-X is formed, which then further reacts with alkene. In this study, we observed different follow-up reactions, which cannot be consolidated with the addition of a second alkene to form a dimer. Furthermore, a dimer was not observed in significant amounts as a final product. One should point out that our experimental conditions differ from those of Wang *et al.* and Shukla *et al.* [55, 56] who worked in organic solvents and produced a constant high yield of Co(I).

3.5. *Reactions of N-rac-(LCo^{III}–H)$^{2+}$ with maleate*

Under experimental conditions of 0.1 mol L^{-1} of phosphate buffer, Co(I)L^{+} reacts in a fast reaction to yield (LCo^{III}–H)$^{2+}$ [47, 49], vide *supra*, experimental part.

Solutions (He saturated) containing $0.03\,\mathrm{mol\,L^{-1}}$ $NaHCO_2$, $0.1\,\mathrm{mol\,L^{-1}}$ phosphate buffer at pH 6.0, and maleate in the presence of $Co(II)L^{2+}$ ($3 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) were irradiated by a short electron pulse. At the observation wavelength of 400 nm, three distinct time-resolved reactions are observed (figure 4; table 1), plus an additional initial fast reaction for which only its equilibrium constant could be measured under the experimental conditions (figure 6). All reactions are independent of complex concentration, in the range $0.1\text{–}0.1\,\mathrm{mol\,L^{-1}}$, and buffer concentration, in the range $0.05\text{–}0.2\,\mathrm{mol\,L^{-1}}$.

The first process observed is the formation of H–Co(III)maleate in an equilibrium process. The spectrum of the first intermediate observed is clearly different from that formed in the Co(I)/maleate system were Co(I)-maleate is formed. The absorbance of the first intermediate observed is dependent on the maleate concentration and plotting 1/[maleate] *versus* 1/OD (figure 6) yields the equilibrium constant as $K = 3000 \pm 600\,\mathrm{mol\,L^{-1}}$.

Thus, the first intermediate observed at 400 nm is the H–Co(III)maleate complex. Neither $Co(I)L^{+}$ nor $(LCo^{III}\text{–}H)^{2+}$ can be observed prior under the experimental conditions, probably due to the very fast reaction of $(LCo^{III}\text{–}H)^{2+}$ with maleate. At 470 nm, one can differentiate a very fast reaction over a few µs; its rate constant cannot be measured as the reaction is too fast.

The H–Co(III)maleate complex decomposes in a first-order reaction followed by two further reactions (table 2). The second of these two reactions showed a photochemical influence. This reaction was therefore studied while placing a filter before the optical cell in order to filter all shorter wavelengths light below 380 nm.

3.6. *Final products analysis*

Samples containing $[CoL]^{2+} = 2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$, $[\text{maleic}] = 3 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$, $[\text{formate}] = 0.1\,\mathrm{mol\,L^{-1}}$, $[\text{phosphate}] = 0.1\,\mathrm{mol\,L^{-1}}$, pH 6.0, He saturated solution, were irradiated in the ^{60}Co γ-source (for 150, 230, and 300 min) and analyzed by HPLC. The following results were obtained: Only a small amount of maleate disappeared ($G = -1.0$) while only a small amount of succinate is formed ($G = 0.5$), whereas in blank solutions not containing the Co(II)-complex only a negligible amount of maleate remained after 150 min irradiation.

3.7. *Proposed mechanism*

The first reaction observed is attributed to the reaction of $(LCo^{III}\text{–}H)^{2+}$ with maleate to form the H–Co(III)maleate π-complex according to

(12)

The second reaction observed, which follows a first-order rate law is assigned to an isomerization reaction of the formed maleate complex

(13)

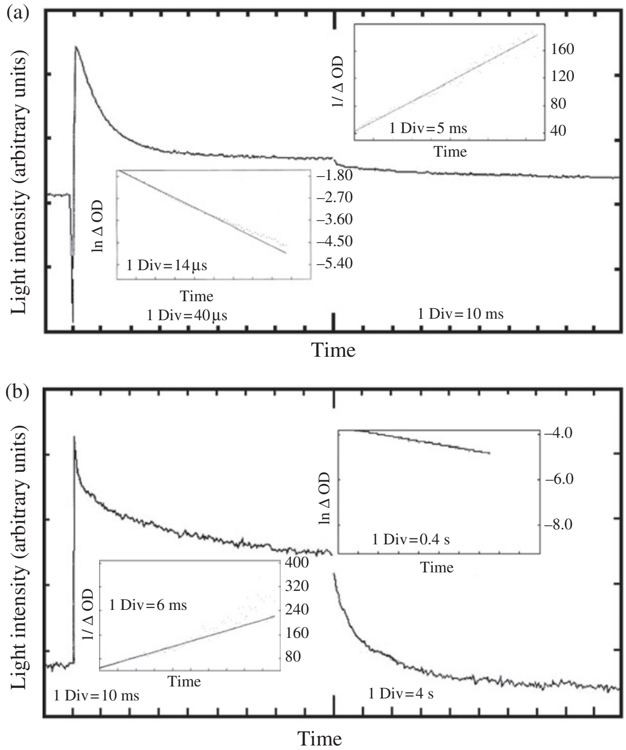


Figure 4. (a) The formation and first two decomposition processes observed at 400 nm in the $(LCo^{III}–H)^{2+}$/maleate system. (b) Two decomposition processes observed at 400 nm in the $(LCo^{III}\text{-}H)^{2+}$/maleate system. Insets show the kinetic fits. Solution composition: $[CoL]^{2+} = 3 \times 10^{-4}\,mol\,L^{-1}$, $[HCOO^-] = 0.03\,mol\,L^{-1}$, $[phosphate] = 0.1\,mol\,L^{-1}$, pH 5.8, $[maleate] = 8.0 \times 10^{-4}\,mol\,L^{-1}$, He saturated, irradiations at 3.0 Gy, $\lambda = 400\,nm$. The spectra of the observed intermediates are shown in figure 5.

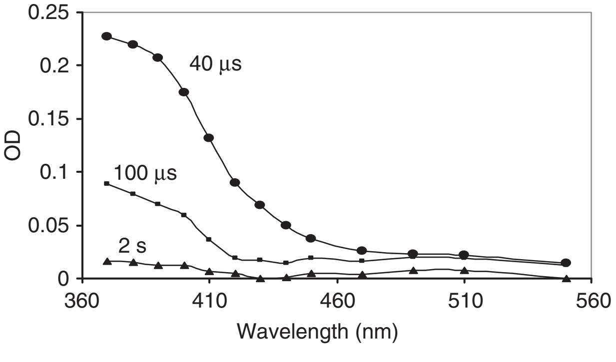


Figure 5. Spectra of the intermediates in the $(LCo^{III}–H)^{2+}$/maleate system at different times. Solution composition: $[CoL]^{2+} = 3 \times 10^{-4}\,mol\,L^{-1}$, $[maleic] = 3 \times 10^{-4}\,mol\,L^{-1}$, $[formate] = 0.03\,mol\,L^{-1}$, [phosphate] = 0.1 M, pH 5.9, He saturated solution; measured 40, 400 µs and 2 s after the pulse; irradiations at 3.0 Gy.

It should be noted that the rate constant measured for this reaction is similar to that of the second reaction during the reaction of Co(I)L$^+$ with maleate, where it was proposed that the formed Co(I)-maleate intermediate isomerizes according to Equation 7 (vide *supra*).

The third reaction observed in this system is proposed to be reaction (14)

(14)

In accordance with the proposed mechanism, this reaction follows a second-order rate law. The rate constant measured in this system though is higher than that in the previous one, which seems to indicate that in the (LCo^{III}–H)$^{2+}$/maleate system the concentration of the intermediates (LCo^{III}–H)$^{2+}$ or ($^{-}$O2CCHCHCO$_2^-$)–Co^{III}–H are higher than the analogue intermediates in the Co(I)L$^+$/maleate system.

The last reaction observed is attributed to the decomposition of the Co(II) maleate complex to yield fumaric and maleic acid.

(15)

To sum up, in the two systems studied, which differ only in the amount of phosphate buffer employed (0.1 mmol L^{-1} *versus* 0.1 mol L^{-1}) two different intermediates are formed initially (as can be seen by the difference of the initial spectra obtained), a Co(I)maleate or a H–Co(III)-maleate π-complex. Both intermediates decompose in similar processes (table 2) with similar rate constants and mechanisms. The first decomposition reaction of the initially formed π-complexes is proposed to be an isomerization reaction to form the corresponding σ-complexes, which then decompose further by a reaction with another intermediate, eventually yielding maleate and fumarate.

The source of the slight, though significant, differences in the rates of reaction (9) and (11), table 2, in the two systems is not clear. A reasonable explanation is that reaction (12), or even the reaction of Co(I)L$^+$ + H$_2$PO$_4^-$ → LCo(III)–H^{2+}, is accompanied by an isomerization of the complex, from trans-III to another isomer, which affects the rates of the follow-up reactions.

The mechanism observed in the CoL-maleate systems is similar to that observed in the NiL$_2$ system [34] in that initially maleate forms a π-complex with the central metal cation. It differs from that observed for the NiL$_2$ system in that the yield of succinate is

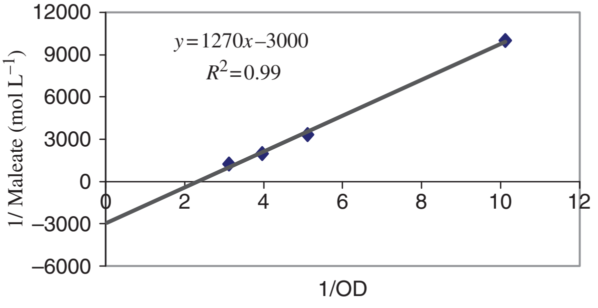


Figure 6. Determination of the equilibrium constant of the first observed process in the (LCo^{III}–H)$^{2+}$/maleate system. Solution composition: [CoL]$^{2+}$ = 3 × 10^{-4} mol L^{-1}, [HCOO$^-$] = 0.03 mol L^{-1}, [phosphate] = 0.1 mmol L^{-1}, pH 6.0, [maleate] = (1–8) × 10^{-4} mol L^{-1}, He saturated, irradiations at 3.0 Gy, 400 nm, 4 μs after the pulse.

considerably lower in the cobalt system. This is expected due to the differences in redox potentials of the M(II/I) couples of the NiL_2 (−1.34 V *versus* NHE) [9] and CoL (−1.34 V *versus* SCE) [10] complexes.

The results point out that the monovalent complexes investigated, formed by the pulse radiolysis method or by γ radiation, react with maleate to form the complex M(I)-maleate (M=Ni or Co) in an equilibrium reaction. The observed rate constants of the complexes formation depend on the maleate concentration. After two additional equilibrium reactions in the presence of H^+, the M^{III}–$CHXCH_2Y$ complex is formed. From this intermediate, there are different pathways and different end products depending on the central metal cation and the different ligands of the complexes. The Co^IL^+ complex reduces less maleate than the Ni(I) complexes as several side reactions occur producing molecular hydrogen. This observation is attributed to the electronic structure of the cobalt. This is the reason why cobalt has a tendency to form cobalt hydride more than nickel and give different end products.

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