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Photoinduced electron transfer in pentaamminecobalt(III) complexes of α-hydroxy acids

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The rates of photoreduction of pentaamminecobalt(III) complexes of α-hydroxy acids at 254 nm are comparable to the rates of formation of cobalt(II) and the corresponding carbonyl product. This is suggestive of electron transfer to cobalt(III) and C—C bond cleavage in an almost concerted manner. The charge transfer to metal ion has an excited state as $t_2^5e^*$ facilitating photoreduction of cobalt(III). The $d\rightarrow\pi$ back bonding is ligand-centered, favouring C—C bond cleavage. In all these reactions, the quantum yield of Co^{2+} is nearly 0.24.

Photoinduced electron transfer in cobalt(III) complexes has been studied in detail[1]. However, not much work is reported on irradiation of pentaamminecobalt(III) complexes of α-hydroxy acids, such as lactic, mandelic, benzilic acids. As the alcoholic group of the ligands is separated from the Co(III) centre by a saturated fragment, we envisage that irradiation of these complexes may result in the reduction of the cobalt(III) centre and C—C bond cleavage, probably, in a synchronous manner. Evidence for such a reaction can be provided if one studies the rates of disappearance of cobalt(III) coupled with rates of formation of cobalt(II) and organic products. The results of such an investigation are reported in this paper. Results of photolysis of pentaamminecobalt(III) complexes of glycine, malonic, oxaloacetic and pyruvic acids, are also included for comparison.

Materials and Methods

The pentaamminecobalt(III) complexes of lactic, mandelic, benzilic, malonic, 2-hydroxy-2-ethylbutyric (HEBA), pyruvic and oxaloacetic acids and glycine were prepared by literature procedure[2] and their purity checked by elemental analyses. For photolysis studies, continuous reaction apparatus, model MLV 18 (Photophysics, London, England) was used. Photolysis of pentaamminecobalt(III) complexes was carried out at 254 nm in 0.10 mol dm^{-3} $HClO_4$ at $30 \pm 5°C$ so that ligand to metal charge transfer excitation could be performed. The 254 nm radiation was generated by low pressure mercury resonance lamps. Solutions were deoxygenated before irradiation. During continuous photolysis, gas bubbling and stirring ensured the homogeneity of the solution. Samples were removed after exposure to a desired time and concentration of Co(III) at any time interval was determined spectrophotometrically (using a Carl-Zeiss VSU 2-P spectrophotometer) at 502 nm. The initial rate of the reaction was determined from linear zero order plots of change in absorbance versus time and the specific rates obtained from such zero order plots agreed well (within ± 7%) with k_0 values calculated from the integrated rate equation (for the initial 30-40% of reaction). Cobalt(II) was determined as soon as possible by making up 2.5 ml of the irradiated solution to 25 ml with conc. HCl and measuring its absorbance at 692 nm ($\varepsilon \simeq 560$ $dm^3mol^{-1}cm^{-1}$). From such measurements the specific rates for the formation of cobalt(II) were calculated. The specific rate determined by either procedure was only approximate as there was an increase in temperature (by 5°C) during photolysis. The specific rates reported were calculated for first 30-40% reaction and during this time interval change in temperature was 2-3°C. The fluctuations in specific rates were not much during this time interval; a similar observation was made by Endicott and Hoffmann[3].

For all the determination of quantum yield (ϕ) of Co^{2+} from continuous photolysis, the yield of Co^{2+} as a function of exposure, was generally linear with rate decreasing with decrease in [substrate] and intensity of absorbed radiation. The values of $\phi(Co^{2+})$ for the complexes, $[(NH_3)_5Co\ O_2C\ CH_3]^{2+}$ and $[(NH_3)_5\ Co(H_2O)]^{3+}$, are 0.19 (ref. 3) and 0.23 (ref. 4). These form the basis for $\phi(Co^{2+})$ calculations in the present work. The values of $\phi(Co^{2+})$ determined in this way are known at least to be within ± 10%. Table 1 summarises the yields of products in the 254 nm photolysis of some pentaamminecobalt(III) complexes and the quantum yield of Co^{2+}.

Table 1—Yields of products during photolysis of some pentaamminecobalt(III) complexes[a] at 254 nm and quantum yields of Co^{2+}

$[(NH_3)_5Co^{III}\text{-}L]^{2+}$ (L=)	[Co(III)] % reduced (mmol)	[Co(II)] % formed (mmol)	[Carbonyl product] % (mmol)	$\phi(Co^{2+})$
Lactato	2.0 (100)	1.90(95)	1.60[b](80)	0.28
Mandelato	1.96(98)	1.94(97)	1.80[c](90)	0.26[d]
Benzilato	1.92(96)	1.92(96)	1.86[e](93)	0.21
2-Hydroxy-2-ethyl-butyrato	1.90(95)	1.90(95)	—	0.25
Pyruvato	1.98(99)	1.94(97)	—	0.20
Glycinato	1.86(93)	1.86(93)	1.66[f](83)	0.19
Acetato	2.0 (100)	2.0(100)	—	0.20
Propionato	1.96(98)	1.94(97)	—	0.18
Małonato	1.98(99)	1.94(97)	—	0.21
Dimethylmalonate	1.90(95)	1.82(91)	—	—
Oxalacetato	2.0 (100)	1.86(93)	—	0.22
Aquo	1.98(100)	1.86(93)	—	0.14

[a] The percentage yields of Co(II), carbonyl product and percentage of reduction of Co(III) are calculated on the basis of initial concentration of Co(III) complex. $[Co^{III}]_{initial} = 2.0 \times 10^{-3}$ mol dm^{-3} in 0.10 mol dm^{-3} $HClO_4$.

[b] The product is acetaldehyde.

[c] The product is benzaldehyde.

[d] In the presence of [benzaldehyde] 2.0×10^{-4} mol dm^{-3} or [biacetyl] $= 2.0 \times 10^{-4}$ mol dm^{-3} or $[Cu^{II}\text{-glycinato}] = 2.0 \times 10^{-4}$ mol dm^{-3}, the quantum yield of Co^{2+} is 0.24 or 0.23 respectively.

[e] The product is benzophenone.

[f] The product is formaldehyde.

Results and Discussion

The rates of photoinduced electron transfer at different concentrations of pentaamminecobalt(III) complexes are summarised in Table 2. The rate of disappearance of cobalt(III) is given by Eq. (1).

$$\frac{-d[Co^{III}]}{dt} = \text{constant} = k_0 \quad \ldots(1)$$

This is further corroborated by the linear plot of change in [Co(III)] versus time and the slope furnishes k_0 value which agrees with that calculated from integrated zero order equation. Though the photoreduction of these Co(III) complexes exhibits zero order kinetics, there seems to be some dependence on structure of these ligands, and photoexcitation possibly depends on the electronic influence of ligands. With increasing $[HClO_4]$, the rate increases considerably and similar *p*H-dependent photoreductions are reported by Endicott[5].

Table 2—Kinetic data for photoinduced electron transfer in some pentaamminecobalt(III) complexes[a]

$10^3[(NH_3)_5Co^{III}\text{-}L]^{2+}$ (mol dm^{-3}) (L=)	$10^7 k_0$ (mol $dm^{-3} s^{-1}$)
Lactato	
2.0	1.87
10.0	2.0
Mandelato	
0.50	2.3
1.00	2.2
8.0	2.7[b,c]
20	2.8
Benzilato[d]	
2.0	0.80
5.0	0.90
2-Hydroxy-2-ethyl-butyrato	
2.0	1.59
10.0	2.0
Pyruvato	
2.0	1.50
10.0	1.70
Glycinato	
2.8	1.13
10.0	1.17
Oxaloacetato	
2.0	1.42
10.0	1.56
Acetato	
2.0	0.83
10.0	0.85
Propionato	
2.0	0.93
10.0	0.95
Aquo	
2.0	0.82
10.0	0.89

[a] Photolysis was carried out at 254 nm in 0.10 mol dm^{-3} $HClO_4$

[b] The specific rates ($10^7 k_0$) in the photolysis of mandelatopentaamminecobalt(III) perchlorate at 0.010 and 0.050 mol dm^{-3} $HClO_4$ at an ionic strength of 0.10 mol dm^{-3} are 0.27 and 1.02 respectively.

[d] In 25% methanol + 75% H_2O (v/v)

Though the addition of benzaldehyde or benzophenone to mandelato- or benzilato pentaamminecobalt(III) perchlorate does not affect the rate of photoreduction, the addition of photosensitizer, viz., biacetyl, enhances the rate of photoreduction, possibly due to the interaction of excited biacetyl with cobalt(III) complex (Table 3). As the primary photo-

Table 3—Rate of photoreduction of pentaamminecobalt(III) complexes of mandelic and benzilic acids in presence of added product, biacetyl and Cu(II)-glycinato complex[a]

$[(NH_3)_5Co^{III}-L]^+$ L=	$10^7 k_o$ (mol $dm^{-3} s^{-1}$)
1. Mandelato	
2.0×10^{-3} (mol dm^{-3})	
i. 10^4[Benzaldehyde] (mol dm^{-3})	
—	1.71
1.0	2.0
10	2.2
ii. 10^4 [biacetyl] (mol dm^{-3})	
—	1.71
2.0	3.4
5.0	11.3
iii. 10^4[Cu(II)-glycinato] (mol dm^{-3})	
—	1.71
2.0	33
10	91
2. Benzilato[b]	
2.0×10^{-3} (mol dm^{-3})	
10^4[Cu(II)-glycinato] (mol dm^{-3})	
—	0.80
1.0	5.6
2.0	6.5

[a] Irradiation at 254 nm in 0.10 mol dm^{-3} $HClO_4$

[b] in 25% methanol + 75/H_2O (v/v)

Table 4—Comparative rates of disappearance of Co(III) and appearance of products[a]

$10^3[(NH_3)_5Co^{III}-L]$ (mol dm^{-3}) (L=)	$10^7 k_o$ (mol $dm^{-3} s^{-1}$) for Co(III)	Co(II)	Carbonyl product
Mandelato			
0.50	2.1	1.98	—
1.0	1.82	1.93	—
2.0	1.71	2.0	1.90
4.0	1.98	1.75	1.87
8.0	1.84	1.80	1.88
Benzilato[b]			
1.0	0.84	0.72	0.89
2.0	0.83	0.80	0.87
4.0	0.88	0.85	0.95

[a] 254 nm irradiation in 0.10 mol dm^{-3} $HClO_4$

[b] in 25% methanol + 75% H_2O (v/v)

chemical reaction during flash photolysis of Cu(II)-α-amino acid complexes involves formation of Cu(I) coordinated to the free radicals[6,7], the effect of added copper(II) glycinato complex on the photoreduction of mandelatopentaamminecobalt(III) complex was attempted. With increase in [Cu(II)-glycinato], the rate of photoreduction of mandelatocobalt(III) complex increases, possibly due to interaction of Co(III) centre with free radicals formed from Cu(II)-glycinato complex during irradiation at 254 nm. Such an outer-sphere reduction of Co(III) by radical intermediates, in a way, evidence the presence of radical intermediates.

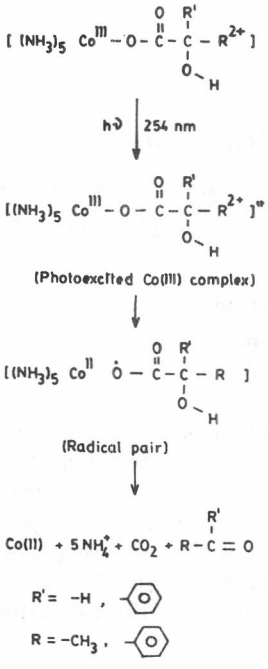
In the cases of pentaamminecobalt(III) complexes of mandelic and benzilic acids, the rate of disappearance of Co(III) is nearly the same as the rate of formation of Co(II) or the corresponding carbonyl product (Table 4). Possibly the reduction at Co(III) centre and C—C bond cleavage leading to the formation of carbonyl product, occurs nearly in a synchronous manner.

Mechanism

The quantum yield of Co(II) is close to 0.24 in all these cases (Table 1) and the yield of Co(II) and C—C cleavage product are nearly 100% (Table 1). The above results are suggestive of a common mechanistic pathway. Since the ground state species has low spin $3d^6$ configuration in Co(III) complexes, excitations populating σ-antibonding orbitals (e^*) are more likely to produce photoredox products than excitations populating π-nonbonding metal orbitals (t_2). In low-spin cobalt(III) complexes, spin allowed ligand- to- metal charge transfer (CTTM) excitations will produce a metal-centred electronic configuration such as $t_2^6 e^*$ and hence the vibrationally relaxed excited state is labilised along metal-radical ligand axis. This labilisation should occur within the life-time of excited state which is less than 10^{-6}s. As excited states, such as $t_2^6 e^*$ with electron density in antibonding orbitals, should resemble $3d^7$ system in lability, photoexcitations producting excited states with such metal centred electronic configuration would be expected to undergo higher photoreduction.

Though such a metal-centred excited state can explain photoreduction at Co(III) centre, the C—C bond cleavage occurring in Co(III) complexes of α-hydroxy acids employed presently can be explained by considering low energy antibonding orbitals available on these ligands. In such cases photochemical reaction will be influenced by $d \rightarrow \pi$ back bonding in the excited state. Thus the bond cleavage reaction in the ligand due to $d \rightarrow \pi$ back bonding may accompany the metal-ligand bond cleavage due to CTTM excitation. This, in a way, explains the almost comparable rate of reduction of Co(III) centre and rate of formation of carbonyl product.

Alternatively the photoexcited Co(III) complex may form a radical-pair[8,9] in which intramolecular electron transfer leads to C—C bond cleavage (Scheme 1).



SCHEME 1

As the life-time of the photoexcited state is of the order of 10^{-6}s, it may not be possible to distinguish between the two mechanistic pathways from the time scale in which the present work has been carried out.

During irradiation of pentaamminecobalt(III) complexes of α-hydroxy acids in the presence of acrylonitrile, polymerisation did not occur. Possibly reactive, long-lived, radicals are not formed during this irradiation process.

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