Mechanisms of Acid Catalyzed Dissociation of Trisbenzoyl-acetonatocobalt(III) in Acetone-Water

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Acid-catalyzed dissociation of trisbenzoylacetonatocobalt(III) complex has been investigated in acetone-water medium (70% v/v) between 40° and 60°C in the presence of 1.0 to 3.0 mol dm^{-3} HNO$_3$. Protonation of one of the bound ligands at the carbonyl oxygen facilitates chelate ring opening. This results in the loss of its quasi-aromatic character leading to a fast rupture of the other metal-ligand bond. Further protonation of a second ligand results in the decomposition of the complex. Rate of dissociation of the benzoylacetonato complex is smaller than that of the corresponding acetylacetonato complex.

Numerous mechanistic studies on the reactions of β-diketonates of metal ions are available in the literature[1-4]. These reactions follow various mechanistic paths. Acid catalysed dissociation of trisacetylacetonatochromium(III) and cobalt(III) proceed by the protonation of one of the bound ligands, leading to its rupture from the metal centre. Chromium(III) complex successively dissociates to bis- and mono-acetylacetonato complexes and then to hexaaquo complex. However, the cobalt(III) complex gives oxidation products of acetylacetone along with free acetylacetone and a reduced state (Co^{2+}) of the metal ion[2,3].

Acetylacetone in its metal complexes forms a pseudo-aromatic ring and it is known that a substituent on a pseudo-aromatic ring influences the rate of dissociation of the complex[5,6]. In the present investigation, we have studied the acid-catalyzed reaction of trisbenzoylacetonatocobalt(III) complex to assess the plausible mechanisms of the reactions of β-diketonato complexes. As this complex is insoluble in water, the present study has been made in 70% acetone-water (v/v).

Materials and Methods

Trisbenzoylacetonatocobalt(III) was prepared by the method of Bauer and Drinkard[7], and recrystallized twice from acetone-water (Found, Co, 16.83; C, 65.72; H, 5.1. Co(C$_{10}$H$_9$O$_2$)$_3$ requires Co, 16.56; C, 66.4; H, 4.98%).

Trisacetylacetonatocobalt(III) was also prepared by the literature[7,8] method and its purity checked (Found, Co, 16.37; C, 50.1; H, 5.86. Calc. for Co(C$_5$H$_7$O$_3$): Co, 16.56; C, 50.5; H, 5.90%).

Sodium diaquobisacetylacetonatocobalt(III) was obtained by the solvolysis of sodium *trans*-dinitrobisacetylacetonatocobalt(III) in basic aqueous solution[12]. (Found: Co, 18.92; C, 38.3; H, 5.90. Na[Co(acac)$_2$ (H$_2$O)$_2$] requires Co, 18.67; C, 37.98; H, 5.70%).

Methyl methacrylate (MMA) (AR, BDH) was used as such. All other chemicals and reagents used were of AR grade. A 70% (v/v) mixture of acetone (GR, E. Merck) with triply distilled water was used for the preparation of the solutions. Since the complex decomposed in HClO$_4$ medium the reaction was followed spectrophotometrically using a Beckman DU-2 spectrophotometer in nitric acid medium (1-3 mol dm^{-3}) at 590 nm, corresponding to the absorption maximum of the complex. The reaction was followed at 550 and 630 nm, with negligible change in results. Ionic strength was maintained with sodium nitrate. Although the first order rate plots were linear, the pseudo-first order rate constants were evaluated graphically by Guggenheim's method[9], to avoid dependence of the rate constant on the single value measured for final absorbance (A_∞).

The absorption spectrum of the reaction mixture kept at 40° for 48 hr indicated complete dissociation of the complex. After completion of the reaction, the reaction mixture was evaporated, neutralized with sodium bicarbonate, cooled, filtered, the filtrate treated with a slight excess of copper(II) acetate solution, pH adjusted to ~5.5, and then extracted with chloroform to remove all the benzoylacetone as Cu(Bzac)$_2$ (ref. 10). The formation of benzoylacetonatocopper(II) complex indicated that free benzoylacetone was released as a product of the reaction. The aqueous phase was then passed through a cation exchange resin (Amberlite. IR 120) in the H$^+$-form to remove excess of copper(II) and cobalt(II) from the solution. The effluent solution was then tested for the absence of benzoylacetone and copper(II). This effluent was evaporated for some time over a steam-bath and tested with 2, 4-dinitrophenylhydrazine for the presence of a ketone[14]. The test was positive and the ketone was identified as acetophenone.

Formation of free radicals in the reaction was confirmed as follows: A 70% acetone-water solution of

Table 1—Dissociation of Trisbenzoylacetonatocobalt(III) in 70% Acetone-Water

$(I=3\ \text{moldm}^{-3})$

Temp (°C)	$k_{obs}\times10^5(s^{-1})$ in [HNO₃], moldm⁻³					
	1.0	1.5	2.0	2.3	2.7	3.0
40	1.3	2.1	2.8	3.4	4.2	4.8
45	1.7	2.7	3.8	4.6	5.25	6.2
50	2.1	3.6	5.3	5.75	6.5	8.7
52.5	2.4	4.0	5.6	6.9	8.55	9.6
55	2.7	4.6	6.9	8.3	11.0	13.0
60	3.6	6.2	9.3	11.3	14.5	17.4

the complex $(1\times10^{-3}\ \text{moldm}^{-3})$ in 2 moldm⁻³ HNO₃ was treated with methyl methacrylate (1 ml), the mixture thoroughly flushed with pure nitrogen and maintained at room temperature (31°) for 2-3 days. The appearance of the white turbidity indicated that the reaction proceeded by a free radical mechanism.

Formation of intermediate complex $Co(Bzac)_2$ $(H_2O)_2^+$ could not be identified at the end of the reaction by chromatographic or other means. However, during the reaction (about 1 hr after the start of the reaction) a portion of the reaction mixture was neutralized with sodium bicarbonate and subjected to chromatography over silica column. The unreacted complex moved first followed by a green effluent which exhibited an absorption spectrum similar to that of $Co(acac)_2$ $(H_2O)_2^+$ (ref. 12) indicating that probably the diaquo complex was formed at this stage.
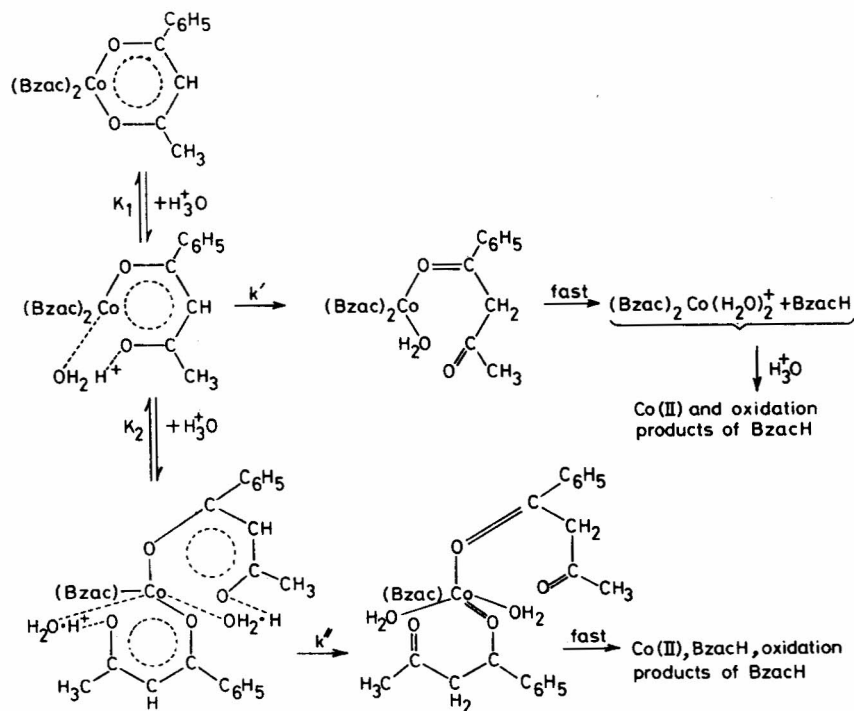
Although the study was made in acetone-water, no evidence for solvolysis of the complex by acetone was observed.

Results and Discussion

Good first order plots were obtained at all acid concentrations and experimental temperatures. Observed rate constants (k_{obs}) are given in Table 1. The influence of [H⁺] on the reaction rate was studied over the [acid] range of 1.0-3.0 moldm⁻³ at various temperatures. A plot of $k_{obs}/[\text{H}^+]$ versus [H⁺] was linear leading to an acid dependence of k_{obs} in accordance with Eq.(1)

$$k_{obs}=k_1[\text{H}^+]+k_2[\text{H}^+]^2 \qquad \ldots (1)$$

The values of k_1 and k_2 at various temperatures obtained from intercepts and slopes of such plots (Fig. 1) are presented in Table 2. The activation parameters were obtained by Eyring's treatment, i.e. from plots of $\log(k_1/T)$ versus $1/T$ and $\log(k_2/T)$ versus $1/T$. The values $\Delta H_1^{\ddagger}$ and $\Delta H_2^{\ddagger}$ were determined as 37.7 ± 1 and 92 ± 2 kJmol⁻¹ respectively. The entropies of activation $\Delta S_1^{\ddagger}$ and $\Delta S_2^{\ddagger}$ for the two paths were found to be -217.6 ± 4.7 and -67 ± 8.4 kJK⁻¹mol⁻¹ respectively. From the reaction products and the rate equation given by Eq.(1), the possible mechanism may be represented as shown in Scheme 1 (BzacH = benzoylacetone)

Scheme 1 leads to the rate law (2)

$$\text{Rate}=K_1k'[\text{complex}][\text{H}^+]+K_1K_2k''[\text{complex}][\text{H}^+]^2$$
$$=k_1[\text{complex}][\text{H}^+]+k_2[\text{complex}][\text{H}^+]^2\ldots (2)$$

Scheme 1

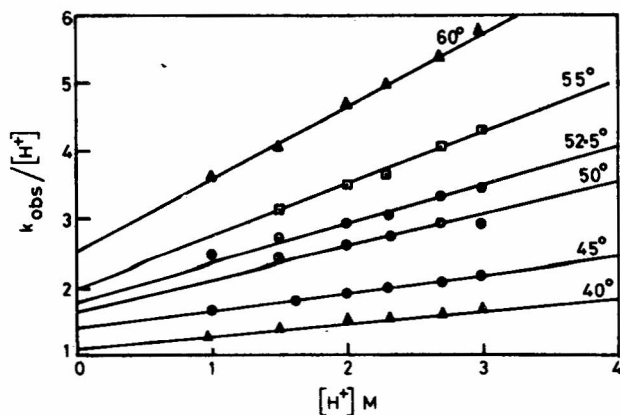Fig. 1—Plot of $k_{obs}/[H^+]$ versus $[H^+]$

Table 2—Variation of k_1 and k_2 with Temperature

$[HNO_3] = 1\cdot3$ moldm^{-3}; [complex] $= 2 \times 10^{-3}$ moldm^{-3}

Temp (°C)	$k_1 \times 10^5$ (dm^{3}mol^{-1}s^{-1})	$k_2 \times 10^6$ dm^{6}mol^{-2}s^{-1})
40	1.10	1.83
45	1.35	2.7
50	1.65	4.66
52.5	1.82	5.67
55	2.01	7.65
60	2.53	10.55
$\Delta H\ddagger$, kJmol^{-1}	37.7 ± 1	92 ± 2
$\Delta S\ddagger$, JK^{-1}mol^{-1}	217.6 ± 4.7	-67 ± 8.4

Protonation of the bound ligand at the carbonyl oxygen facilitates the chelate ring-opening leading to a loss in the quasi-aromatic character of the ring and hence to a faster rate of the rupture of the remaining metal-ligand bond. Protonation of two ligands as shown in the second path leads to complete decomposition of the complex. Cobalt(III) undergoes reduction to cobalt(II) and oxidises benzoylacetonate to various products. Formation of free radicals and acetophenone can reasonably be accounted for by considering the degradation of the BzacH radical as shown in Scheme 2.

Scheme 2
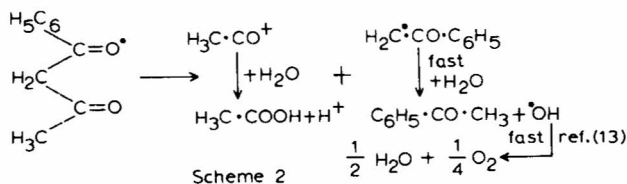
The rate of dissociation of the trisacetylacetonato complex was also investigated in 70% acetone-water solvent for comparison. The k_{obs} ($\times 10^5$) values of the two complexes in the presence of 2 moldm^{-3} nitric acid ($I = 3$ moldm^{-3}) are as follows:

For Co(acac)$_3$, 9.0 ± 0.1, 16.6 ± 0.2, 19.0 ± 0.2, 29.4 ± 0.2 and for Co(Bzac)$_3$, 3.8 ± 0.12, 5.3 ± 0.1, $5 6 \pm 0.3$ and 6.9 ± 0.2 s^{-1} at 45°, 50°, 52.5° and 55° respectively.

The base strength of the coordinated benzoylacetone is greater than that of the acetylacetone (acid

ionization constants of benzoylacetone and acetylacetone are 4×10^{-10} and 1.17×10^{-9} respectively[11]). In the coordinated form although the basicity of these ligands are different as compared to their noncoordinated forms, the changes are expected to be of the same order. So, protonation of benzoylacetonato· ligand takes place more easily than that of the acetylacetonato ligand. In an acid catalyzed dissociative reaction, both these factors, i.e. the substitution of bulky phenyl group on the chelate ring and the easy protonation of the bonded ligand, should give a higher reaction rate for the benzoylacetonato complex.

However, the observed rate order is just the reverse. The observed lower rate constants of the benzoylacetonato complex can be explained as follows: β-Diketonates form pseudo-aromatic six-membered chelate rings with delocalized π electron system spread over the whole molecule. The π-π interaction between the pseudo-aromatic diketonate ring and the phenyl group of the benzoylacetonato chelate increases the stability of the complex by resonance. The basicity of the benzoylacetonate is also higher than that of the acetylacetonate and this factor also increases the stability of the complex. The slow rate of dissociation of benzoylacetonatocobalt(III) is because of the increased overall stability of the complex by a combination of these two factors. Apart from these two factors, it is likely that the formation of the reaction intermediate is also influenced somehow. Of course the nature of the reaction intermediate is difficult to predict at this stage.

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