

Gluconate Complex of Yttrium (III)

C. PANDA and R. K. PATNAIK*

Department of Chemistry, Regional Engineering College, Rourkela-8

Manuscript received 7 May 1977, accepted 20 May 1977

Gluconate complex of yttrium has been studied by pH titration method. Yttrium forms a doubly charged cationic complex below pH 4.4 which dissociates subsequently to a cationic complex C^+ in the pH range 4.4 to 6.0 and finally to a neutral complex C in the pH range 6.0 to 8.4. The equilibrium constants of the reactions $Y^{3+} + HGl \rightleftharpoons C^{2+} + H^+$, $C^{2+} \rightleftharpoons C^+ + H^+$, $C^+ \rightleftharpoons C + H^+$ and $Y^{3+} + Gl^- \rightleftharpoons C^+ + H^+$ are 7.92×10^{-2} , 1.41×10^{-4} , 3.29×10^{-6} and 3.52×10^{-4} respectively.

N.A.KOSTROMINA^{1,2} determined the instability constants of rare earth gluconate complexes in the pH range 2-3 by potentiometric and ion exchange methods.

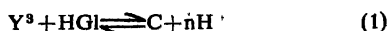
The present paper presents the determination of stability constants of the formation of doubly charged cationic gluconate complex of yttrium at low pH and its dissociation to other complexes at higher pH.

Experimental

All chemicals used were of B. D. H. Analar grade. pH titrations were carried out with a Marconi pH meter at $32 \pm 1^\circ$. The ionic strength has been maintained at 0.1M by the addition of suitable amount of potassium nitrate. The reaction of $Y(NO_3)_3$ with gluconic acid was found to be slow. So the solutions were stored for 48 hrs. in glass-stoppered bottles before the pH measurement.

Results and Discussion

The number of protons liberated during the complex formation between yttrium ion and gluconic acid remains same when the metal-ligand ratio is increased from 1 : 1.25 to 1 : 5. This indicates the formation of a 1 : 1 type of complex. The reaction taking place in experiment-1 may be represented as



where HGl is represented by gluconic acid.

The charge of the complex C in the reaction (1) depends on the value of n, the number of protons liberated.

As derived in the cadmium citrate complex³ and earlier investigations⁴⁻⁵, it can be shown that

$$\frac{\Delta[NaOH] - a/b \Delta[IGl]}{[C]} = n - a/b \quad (2)$$

where $a = \frac{k}{[H^+]}$; $b = 1 + \frac{k}{[H^+]}$, $\Delta[NaOH] = [NaOH]_B - [NaOH]_A$, $\Delta[IGl] = [IGl]_B - [IGl]_A$; $[NaOH]_B$, $[NaOH]_A$, $[IGl]_B$, $[IGl]_A$, and $[C]$

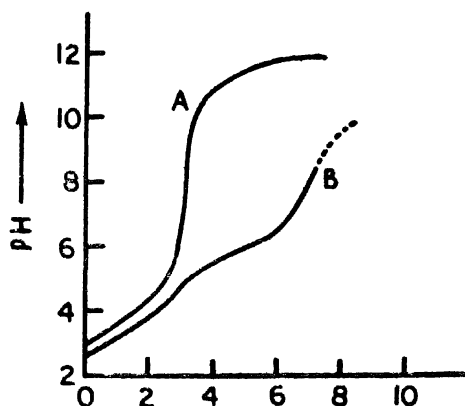


FIG. 1

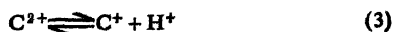
0.1 M NaOH added ml.

Fig. 1. pH titration of 50.0 ml of solution containing 5.0×10^{-3} g. mole of potassium nitrate and 3.125×10^{-4} g. mole of gluconic acid (curve A) and that of the same volume of another solution containing the same quantities of the above constituents with 2.5×10^{-4} g. mole of yttrium nitrate (curve B, Experiment 1) against 0.1 M sodium hydroxide.

are represented by the molar concentration of Sodium hydroxide at B, sodium hydroxide at A, total gluconate at B, total gluconate at A and the complex at B respectively where B and A are two points on the curves B and A on the same pH axis. k, the dissociation constant of gluconic acid⁹ is 2.75×10^{-4} . When the formation of the complex is complete, $[C] = [Y(NO_3)_3]$. The value of n, calculated at different pH, are recorded in table 1. It is >1 between pH 4.6 and 6.0 and >2 between

pH 5.0 and 8.4. Assuming n to be one below pH 4.60, the value of $[C^{2+}]$ is calculated. The value of the equilibrium constant K of the reaction (1) calculated by the method followed in the cadmium citrate complex³ is found to be 7.92×10^{-2} against a value of 6.68×10^{-2} reported earlier² after proper conversion.

In the pH range of 4.6–6.0, n is >1 but <2 which indicates the dissociation of the complex C^{2+} by the equation



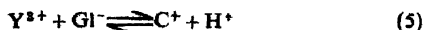
The equilibrium constant, K_1 of the reaction (3) is calculated as followed in the citrate complex of cadmium³ and is found to be 1.41×10^{-6} (Table-1).

In the pH range of 6.0–8.4, n is >2 but <3 . So the complex C^+ dissociates by the equation



The equilibrium constant, K_2 of the reaction (4) calculated as before is found to be 3.29×10^{-8} and recorded in table 1. A precipitate of yttrium hydroxide is formed at pH 8.4.

In the experiment-2, (Fig 2), the reaction taking place may be represented as



where Gl^- is represented by gluconate ion.

The complexes C^+ and C^{2+} exist in the pH range 4.6–6.0 as observed in experiment 1. When the pH is decreased, the complex C^+ combines with a proton to form the complex C^{2+} . Beyond the 1 : 1 metal-ligand ratio, the pH increases due to the addition of excess sodium-gluconate and the complex C^{2+} dissociates to

C^+ and H^+ . It can be shown as in the earlier investigations^{4–8} that

$$[TGl] - [Y(NO_3)_3] = b[HG] \quad (6)$$

$$[C^+] = [H^+] + [HG] \quad (7)$$

$$\text{and } [C^{2+}] = [Y(NO_3)_3] - [C^+] \quad (8)$$

The equilibrium constant, K_1 of the reaction (3) is calculated as before and the mean value of K_1 is 1.04×10^{-6} (Table 2). This value agrees with those recorded in Table-1.

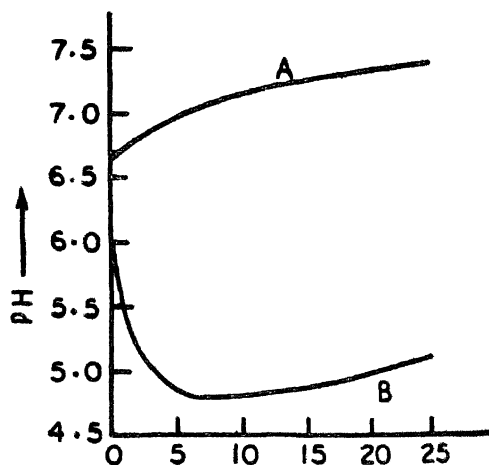


FIG. 2

0.05 M Sodium gluconate added ml.

Fig. 2. pH titration of 50.0 ml of solution containing 5.0×10^{-4} g. mole of potassium nitrate (curve A) and that of the same volume of another solution containing the same quantities of the above constituents and 2.5×10^{-4} g. mole of yttrium nitrate (curve B, Experiment 2) against 0.05 M sodium-gluconate.

TABLE 1

pH	$\Delta[NaOH] \times 10^3$	$-\Delta[TGl] \times 10^3$	$[Y(NO_3)_3] \times 10^3$	a/b	n	$[C^{2+}] \times 10^3$	$[Y^{3+}] \times 10^3$	$[HG] \times 10^3$	$K \times 10^6$	$K_1 \times 10^6$	$K_2 \times 10^8$
2.8	0.794	0.05	4.96	0.1797	0.342	0.979	3.981	4.283	7.23		
3.3	0.963	0.06	4.883	0.355	0.557	1.526	3.357	2.954	7.71		
3.8	0.745	0.046	4.808	0.635	0.796	2.121	2.687	1.421	8.81		
5.2	0.798	0.05	4.691	0.978	1.159					1.19	
5.4	1.235	0.078	4.664	0.986	1.267					1.43	
5.6	1.747	0.11	4.63	0.991	1.392					1.62	
7.0	5.754	0.36	4.425	0.999	2.382						6.18
7.6	6.21	0.388	4.398	1.0	2.501						2.52
8.0	6.366	0.398	4.39	1.0	2.541						1.18

TABLE 2

pH	[TGI] $\times 10^8$	[Y(NO ₃) ₃] $\times 10^3$	[HGI] $\times 10^4$	[C ⁺] $\times 10^4$	[C ²⁺] $\times 10^8$	K ₃ $\times 10^8$
4.92	10.938	3.906	2.945	3.065	3.599	1.03
4.94	11.539	3.846	3.082	3.197	3.526	1.04
4.96	12.121	3.788	3.194	3.304	3.458	1.05

Below the 1 : 1 metal-ligand ratio, the ions C²⁺, C⁺ and Y³⁺ are present. It can also be shown that

$$[HGI] = \frac{[TGI] - [H^+]}{\left(1 + \frac{k}{[H^+]}\right) + \left(1 + \frac{[H^+]}{K_1}\right)} \quad (9)$$

$$[C^+] = [H^+] + [HGI]$$

$$[C^{2+}] = \frac{[H^+]}{K_1} [C^+]$$

The equilibrium constant, K₃ of the reaction (5) calculated as before is found to be 3.52×10^{-4} (table-3).

It can be shown that $\frac{K_3 \times k}{K_1} = K$.

The mean value of K₃ $\times k/K_1$ is 6.9×10^{-2} which agrees well with the value of K recorded in table-1.

In the experiment-3, (Fig. 3), the metal-ligand ratio is nearly 1 : 5 and the formation of the complex is therefore assumed to be complete. It is found in the experiment-1 that complexes C²⁺ and C⁺ exist in the pH range, 4.6–6.0. Similarly the complexes C⁺ and C are formed between pH 6.0 and 8.4. The existence of these complexes are expected in the similar pH ranges in the experiment-3. It can be shown as in the manganese-tartrate complex⁷ that

$$[C^+] = [H^+] + [NaOH] + \frac{[TGI] - [Y(NO_3)_3]}{\left(1 + \frac{k}{[H^+]}\right)} \quad (10)$$

TABLE 3

pH	[TGI] $\times 10^8$	[Y(NO ₃) ₃] $\times 10^3$	[HGI] $\times 10^4$	[C ⁺] $\times 10^4$	[C ²⁺] $\times 10^8$	[Gl ⁻] $\times 10^3$	[Y ³⁺] $\times 10^3$	K ₃ $\times 10^4$	K $\times 10^3$
4.82	4.044	4.596	1.251	1.402	1.506	2.272	2.95	3.17	6.18
4.81	4.296	4.570	1.337	1.492	1.640	2.373	2.781	3.50	6.83
4.80	4.546	4.546	1.423	1.582	1.778	2.469	2.61	3.89	7.59

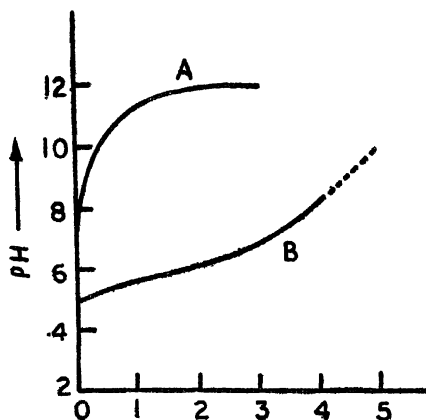


FIG. 3

0.1 M NaOH added ml.

Fig. 3. pH titration of 50.0 ml of solution containing 5.0×10^{-3} g. mole of potassium nitrate and 1.25×10^{-2} g. mole of sodium gluconate (curve A) and that of the same volume of another solution containing the same quantities of the above constituents with 2.5×10^{-4} g. mole of yttrium nitrate (curve B. Experiment 3) against 0.1 M sodium hydroxide.

[C²⁺] is calculated by subtracting [C⁺] from [Y(NO₃)₃]. The equilibrium constant, K₁ of the reaction (3) is found to be 2.44×10^{-6} (Table-4) which is similar to the values recorded in table-1.

TABLE 4

pH	[NaOH] $\times 10^3$	[TGI] $\times 10^3$	[Y(NO ₃) ₃] $\times 10^3$	[C ⁺] $\times 10^8$	[C ²⁺] $\times 10^8$	K ₁ $\times 10^6$
5.5	1.768	2.456	4.912	1.994	2.918	2.16
5.7	2.534	2.437	4.873	2.676	2.197	2.43
5.9	3.288	2.418	4.836	3.377	1.559	2.73

Similarly above pH 6.0 it can be shown as before that

$$[C] = [H^+] + [NaOH] - [Y(NO_3)_3] + \frac{[TGI] - [Y(NO_3)_3]}{1 + \frac{k}{[H^+]}} \quad (11)$$

TABLE 5

pH	[NaOH] $10^3 \times$	[TGI] $\times 10^3$	[Y(NO ₃) ₃] $\times 10^3$	[C] $\times 10^8$	[C ⁺] $\times 10^8$	K ₂ $\times 10^8$
7.0	6.015	2.35	4.70	1.322	3.378	3.92
7.4	6.542	2.337	4.673	1.872	2.801	2.66
8.0	7.063	2.324	4.647	2.417	2.230	1.09

$[C^+]$ is obtained by subtracting $[C]$ from $[Y(NO_3)_3]$. The equilibrium constant, K_a of the reaction (4) is found to be 2.56×10^{-6} (Table-5) which is similar to those of K_a recorded in table-1.

Acknowledgement

The authors are grateful to the U.G.C., New Delhi and B.S.I.R. Orissa for financial assistance.

References

1. N. A. KOSTROMINA, *Russ. J. Inorg. Chem.*, 1960, 5, 46.
2. N. A. KOSTROMINA, *Russ. J. Inorg. Chem.*, 1963, 8, 988.
3. R. K. PATNAIK and S. PANI, *J. Indian Chem. Soc.*, 1957, 34, 673.
4. R. K. PATNAIK and S. PANI, *J. Indian Chem. Soc.*, 1961, 38, 364.
5. K. K. TRIPATHY and R. K. PATNAIK, *Acta Chim (Budapest)*, 1973, 79, 279.
6. K. K. TRIPATHY and R. K. PATNAIK, *J. Inorg. Nuclear Chem.*, 1973, 35, 1050.
7. K. K. TRIPATHY and R. K. PATNAIK, *Indian J. Chem.*, 1967, 5, 511.
8. C. PANDA and R. K. PATNAIK, *Indian J. Chem.*, 1976, 14A, 446.
9. R. K. CANNAN and A. KIBRICK, *J. Amer Chem. Soc.*, 1938, 60, 2314.