Talanta, Vol. 41, No. 1, pp. 15–19, 1994
Printed in Great Britain. All rights reserved

0039-9140/94 \$6.00 + 0.00
Copyright © 1993 Pergamon Press Ltd

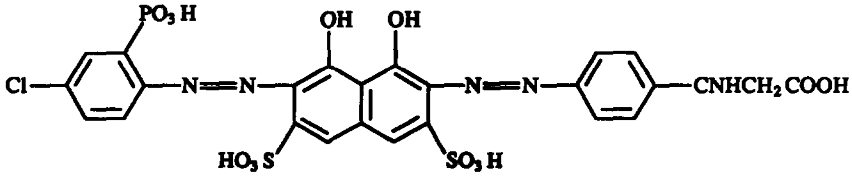
REACTION AND KINETICS IN SYSTEM OF RARE EARTHS WITH *p*-HIPPUROCHLOROPHOSPHONAZO

JINGGUO HOU, JINGWAN KANG and JINZHANG GAO*
Institute of Chemistry, Northwest Normal University, Lanzhou 730070, China

(*Received* 25 *November* 1992. *Revised* 19 *May* 1993. *Accepted* 2 *July* 1993)

Summary—The β-type reactions, in which rare earth ions react with chlorophosphonazo reagents, are extremely sensitive and have been applied widely to determination of rare earths. The reactions and kinetic behavior of the β-type homo- and iso-nuclear chelates of rare earth with *p*-hippurochlorophosphonazo (CPA-pHA) have been investigated by a spectrophotometric method. Some kinetic parameters, such as the reaction rate constants, the half lives and the activation energies, were measured. The competing reactions between lanthanoid ions forming and non-forming β-type chelates were also studied. The effects and trends of different organic solvents on the β-type chelates have been discussed. A reaction mechanism of β-type chelates has been proposed.

Among the reactions of chlorophosphonazo reagents with lanthanoid ions, it is very worth while to study the β-type chromogenic reactions because of their special selectivity and high molar extinction coefficients in analysis. Much attention has been paid to the β-type chelates by analytical workers.[1,2,3] We have studied systems of Ln^{3+}–CPA–III (chlorophosphonazo-III) and Ln^{3+}–*p*-ICP (*p*-iodochlorophosphonazo).[4,5] The β-type and α-type chelates of some lanthanoid ions with the azo-type colouring reagents can be formed at different conditions. A synergistic chromogenic phenomenon can be observed if some ions (*i.e.* heavy rare earth ions) forming β-type chelate and other ions (*i.e.* light rare earth ions) non-forming β-type coexist in the system. The molar absorptivity of this iso-nuclear β-type chelates may be higher than that of homo-nuclear β-type chelates. This can be applied to determine the trace amounts of light rare earths in the presence of heavy rare earths.[5] However, there is a lack of information about the kinetics and mechanism of β-type chelates. In this paper, we describe the combining ratio, kinetic behavior, and propose a systematic approach to the mechanism forming β-type chelates of rare earth ions with CPA–pHA. See Scheme 1 for structure.



EXPERIMENTAL

Apparatus

All the absorption spectra were measured by a UV-300 automatic recording spectrophotometer (Shimadzu, Japan) with a constant temperature system. The pH value was determined by means of a pHs-2 meter (Shanghai, China).

Reagents

Standard solutions of lanthanoid chloride were prepared from their corresponding oxides of spectrum purity. The *p*-hippurochlorophosphonazo was purchased from Wuhan University, which was used without further purification. Buffer solution of pH 3.4 was made from sodium acetate and hydrochloric acid.

Procedure

The coloured solution was obtained by adding 1.0×10^{-4} mol/l CPA-pHA working solution of 1.0 ml into the solution, which was adjusted to pH 3.4 by NaAc–HCl buffer solution, containing rare earth ions. As soon as the solutions of CPA-pHA and rare earth ions

---

*Author to whom correspondence should be addressed.

were mixed, the absorption spectra and the reaction time can be obtained by a recorder. The maximum absorption can be observed at about 727 nm after the reaction had been going for 3 h.

RESULTS AND DISCUSSION

Absorption spectra

The chromogenic reactions of the solution of lanthanoid and yttrium ions have been investigated at pH 3.4. Only Eu, Gd, Tb, Ho, Er, Tm, Yb, Lu, and Y are able to form homo-nuclear β-type chelates with CPA-pHA. The maximum absorption peaks of chelates shift from 724 to 728 nm and their intensity increase with the increasing of atomic number (see Fig. 1).

A synergistic chromogenic phenomenon can be found due to forming a new β-type iso-nuclear chelate when another lanthanoid ion of an equimolar concentration and one of Eu to Lu are added together into the solution. In general, the molar absorptivities of iso-nuclear β-type chelates are higher than those of homo-nuclear β-type chelates. However, molar absorptivities of a few iso-nuclear chelates, such as the chelates consisting of La^{3+} and Ce^{3+} with Tb^{3+} or Dy^{3+} are to decrease due to the presence of La^{3+} or Ce^{3+}. The reason is that a more stable α-type chelates of La^{3+} or Ce^{3+} with CPA-pHA restrain the formation of iso-nuclear β-type chelates. The typical absorption spectra of iso-nuclear β-type chelates of Yb^{3+} with Ln^{3+} are shown in Fig. 2 (where Ln = La, Ce, ..., Tm, Lu and Y).

Optimum forming conditions and composition of β-type chelates

The pH value of solution plays an important role in the formation of the β-type chelates. The maximum absorption of the β-type chelate is observed in NaAc-HCl buffer solution of pH 3.4. The transformation from α-type to β-type chelates has been traced and the reactions are finished within 3 h. The molar ratio method has been employed to determine the composition ratio of β-type chelates and found to have a composition ratio of 1:1 for homo-nuclear chelates and 1:2:3 (Ln:Ln′:CPA-pHA) for iso-nuclear chelates, respectively. Furthermore, the actual combining ratio of homo-nuclear β-type chelates has been ensured to be 3:3 by a graphical method of the dilution effect model.[6,7,8] The structure of iso-nuclear chelates may be similar with that of homo-nuclear chelates.

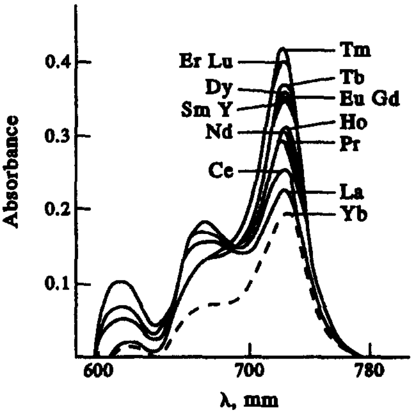


Fig. 2. The absorption spectra of iso-nuclear β-type chelates $[Ln^{3+}$–(CPA-pHA)–$Ln^{3+}]$, pH = 3.40, NaAc–HCl, $[Ln^{3+}] = [C_R] = 6.0 \times 10^{-6}$ mol/l.

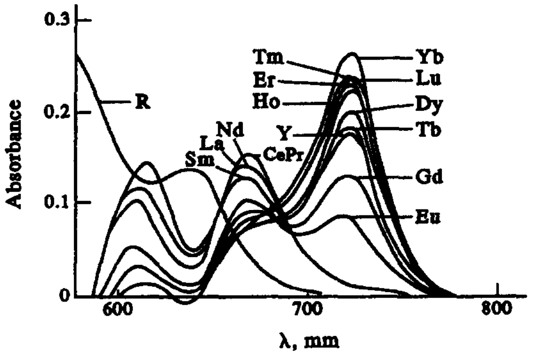


Fig. 1. The absorption spectra of homo-nuclear β-type chelates Ln^{3+}–(CPA-pHA). pH 3.40 NaAc–HCl, $[Ln^{3+}] = [C_R] = 6.0 \times 10^{-6}$ mol/l.

Kinetics of β-type chelates

Figure 3 shows an absorption spectrum of Y(III) with CPA-pHA which the α-type changes into the β-type chelate in NaAc-HCl buffer solution at 298 ± 0.2 K. Figure 4 indicates that chelate is a first-order reaction. The rate constants and the half lives at 298 ± 0.2 K and

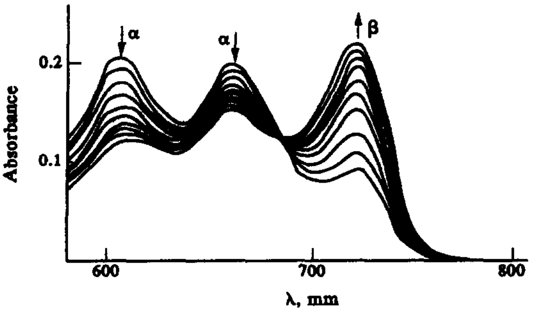


Fig. 3. The equal-time absorption spectra of the Y^{3+}–(CAP-pHA) chelate $[Y^{3+}] = [C_R] = 8.0 \times 10^{-6}$ mol/l, pH = 3.40, NaAc–HCl, $T = 298 \pm 0.2$ K.

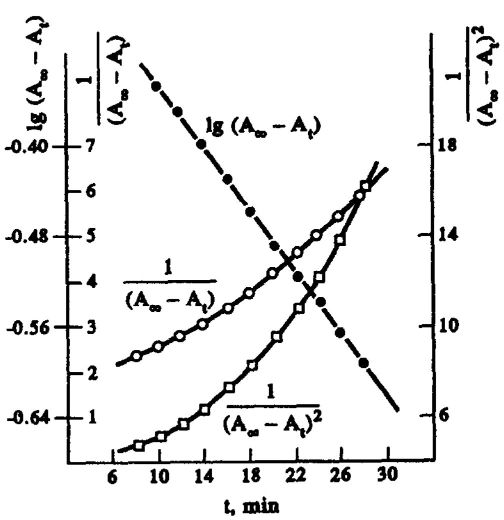


Fig. 4. The reaction order of Yb^{3+}–(CPA-pHA) system $[Y^{3+}] = [C_R] = 8.0 \times 10^{-6}$ mol/l, pH = 3.40, NaAc–HCl, $T = 298 \pm 0.2$ K.

the activation energies of reactions of rare earth ions with CPA-pHA are listed in Table 1.

The data in Table 1 show that the reaction rates increase and the activation energies decrease with the increasing atomic number of rare earth. The reaction from the α-type to the β-type chelates are also influenced obviously by the temperature. When the temperature was raised, the reaction rates were accelerated but absorbances were lowered greatly. For example, the reaction of Eu(III) and Gd(III) with CPA-pHA, which transformed from the α-type to the β-type chelates, had not been observed if the temperature reached 308 K. Therefore, the reaction of the β-type may be a polymer process of heat release.

The influence of organic solvents on the process from α-type to β-type chelates has also been investigated. It is found the organic solvents lower the transformation rates and the absorbances of the process from the α-type to the β-type chelates. The non-proton organic solvents have a more significant effect than the others. According to the Scatchard theory model,[9] the relationship between the rate constant of the β-type reaction and the static dielectric constant of organic solvent has been studied. The kinetic equation of the Scatchard theory is expressed as follows:

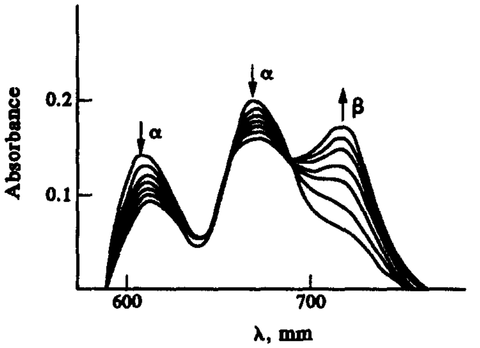


Fig. 5. The equal-time absorption spectra of iso-nuclear β-type chelate $[Yb^{3+}] = [Nd^{3+}] = 4.0 \times 10^{-6}$ mol/l, pH 3.40, NaAc–HCl, $[C_R] = 8.0 \times 10^{-6}$ mol/l, $T = 298 \pm 0.2$ K.

$$\ln k_1 = \ln k_0 + \frac{Z_A Z_B \epsilon^2}{RKT} (1/D_0 - 1/D) \quad (1)$$

where ϵ is electronic charge, D is static dielectric constant, D_0 is standard state static dielectric constant, K is Boltzmann constant. If $\ln k_1$ plots against $1/D$, a linear relationship can be obtained and expressed as follows for proton solvents (methanol, ethanol, 1-propanol, 1,2-ethandiol) and non-proton solvents (acetone, methyl-sulfoxide, acetonitrile and DMF), respectively:

$$\log k_1 = -4.1999 \quad (1/D) + 39.0921; \quad (R = 0.9749) \quad (2)$$

$$\log k_2 = -5.3648 \quad (1/D) + 84.9559; \quad (R = 0.9912). \quad (3)$$

The results point out that the influence of organic solvents on the β-type reaction is concerned with change of static electricity of media and solventized effect of the products or the reactants. Otherwise, the organic solvents may affect the β-type reaction by means of changing capability of proton dissociation and movement in the solution.[2]

Kinetics of synergistic chromogenic phenomena

The rate constants of the iso-nuclear β-type reactions, where the Yb(III)–(CPA-pHA)–Ln(III) systems are used as a typical instance, have been measured. The spectra (see Fig. 5) show that the iso-nuclear β-type chelates

Table 1. The k, $t_{1/2}$ and E_a of homo-nuclear β-type reaction

	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
k (sec^{-1}) × 10^3	0.143	0.132	0.201	0.894	0.952	2.87	2.78	4.79	3.40	1.24
$t_{1/2}$ (min)	81	87.5	49	13	12	4	4.3	2.4	3.4	9.3
E_a (kJ/mol)	—	—	137.19	54.16	53.11	38.03	37.18	37.37	37.07	37.62

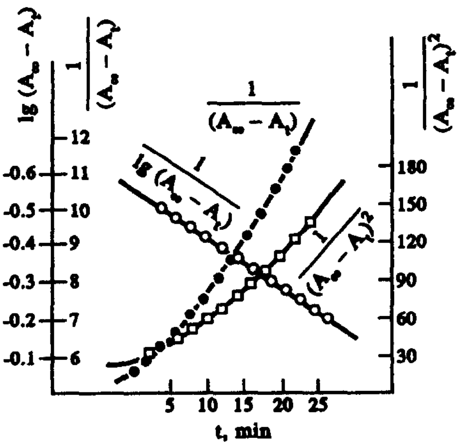


Fig. 6. The reaction order of the iso-nuclear system, pH = 3.40, NaAc–HCl, $T = 298 \pm 0.2$ K, $[Nd^{3+}] = [Yb^{3+}] = 4.0 \times 10^{-6}$ mol/l $[C_R] = 8.0 \times 10^{-6}$ mol/l.

produce from the α-type, too. The results of Fig. 6 seem to be a first-order reaction. The data in Table 2 indicate that the reaction rates increase gradually with the increasing of atomic number of the light rare earth ions participating to form the iso-nuclear β-type chelates. That is to say, the possibility of the light rare earth ions taking part in the formation of the iso-nuclear β-type chelates enhances gradually to Yb(III).

The competing reaction between light rare earth ions and the β-type of heavy rare earth ions

In order to understand the reaction mechanism of the iso-nuclear β-type chelates, the following method was adopted. First, a stable homo-nuclear β-type chelate of Yb(III) with CPA-pHA was prepared in 3 h. Secondly, adaptive amounts of the light rare earth ion were added into the above solution and mixed rapidly. Then, the spectrum of this system was recorded at equal-time intervals. This experiment shows that the change of absorption spectrum of the homo-nuclear β-type chelate of Yb(III)–(CPA-pHA) is hardly observed if the concentration of added light rare earth ion is less 10 times than that of Yb(III) ion. In contrast, the decrease of the homo-nuclear β-type chelate absorption peaks and the raising of the α-type chelate absorption peaks can be observed when the concentration of added light rare earth ion is 10 times or more than that of Yb(III) ion (see Fig. 7). This fact indicates that no synergistic chromogenic phenomena appear as soon as the homo-nuclear β-type chelates have been formed before the light rare earth ions are added into the systems. In other words, the light rare earth ions can participate in the reaction of the iso-nuclear β-type but must be added into the solution simultaneously with Yb(III) ion. This also points out the inversibility of the β-type reactions.

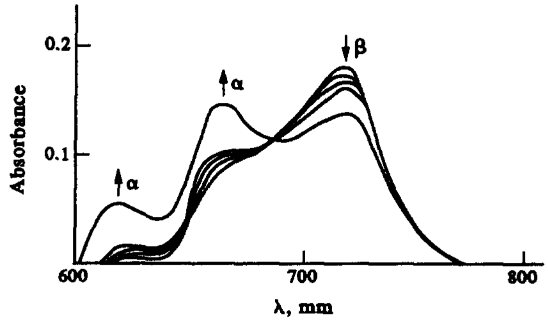


Fig. 7. The absorption spectra of the competing reaction of Ce^{3+} with Yb^{3+}–(CPA-pHA) system pH 3.40, NaAc–HCl, $T = 298 \pm 0.2$ K $[Ce^{3+}] = 20[Yb^{3+}]$, $[Yb^{3+}] = 8.0 \times 10^{-6}$ mol/l, $[C_R] = 8.0 \times 10^{-6}$ mol/l.

Table 3 lists the rare constants of competing reactions when the light rare earth ions are added into the system of homo-nuclear β-type of the Yb(III)–(CPA-pHA). Here the concentration of the light rare earth ions are 20 times that of Yb(III) ion.

It can be found from Table 3 that the rate constants decrease gradually. This may imply that the competing capability with the homo-nuclear β-type reaction from La to Sm is to decrease. Between the large amounts of light rare earth ion and the homo-nuclear β-type chelate of Yb(III)–(CPA-pHA), the following competing equilibrium might be suggested:

$$\underset{(\beta\text{-type})}{Yb_3(\text{CPA-pHA})_3} \underset{Ln^{3+}}{\overset{\text{excess}}{\rightleftharpoons}} \underset{(\alpha\text{-type})}{2Yb(\text{CPA-pHA})} + \underset{(\alpha\text{-type})}{Ln(\text{CPA-pHA})} + Yb^{3+}$$

where Ln = La, Ce, Pr, Nd and Sm.

Table 2. The reaction rate constants of Yb(III)–(CPA-pHA)–Ln(III) systems $T = 298 \pm 0.2$ K, pH 3.40, NaAc–HCl

	Yb–La	Yb–Ce	Yb–Pr	Yb–Nd	Yb–Sm	Yb–Eu	Yb–Gd
k (sec^{-1}) × 10^3	0.615	0.793	1.10	1.83	2.34	2.87	2.35
$t_{1/2}$ (min)	18.78	14.56	10.5	6.31	4.94	4.02	4.91

Table 3. The rate constants of competing reactions. $T = 298 \pm 0.2$ K, pH = 3.40, NaAc–HCl

	La	Ce	Pr	Nd	Sm
k (sec^{-1}) × 10^4	1.95	1.80	1.57	1.32	1.03

CONCLUSIONS

According to the above results, the following conclusions may be drawn.

(1) The homo- and iso-nuclear β-type chelates are polymers of formation from the α-type chelates. The β-type chelates become more and more stable from La to Lu, and on the contrary, the α-type chelates are more stable from Lu to La.

(2) The synergistic chromogenic phenomena can be observed only if light and heavy earth ions coexist in the system. The reason for these phenomena and results may be attributed to the activation energy of reaction from α-type to β-type chelates. The β-type reactions between the α-type chelates of heavy rare earth ion and light rare earth ion are allowed by the activation energy but the β-type reactions between the α-type chelates of light rare earth ion itself are forbidden. The data of activation energies depend on the stereochemical structures of chromogenic reagents and the ion radii of lanthanoid ions.

(3) A detailed and actual understanding about the β-type homo- or iso-nuclear chelates of lanthanoid ions with chlorophosphonazo reagents may find a new and sensitive spectrophotometric analytical method to determine light rare earths in the presence of heavy rare earths.

REFERENCES

1. T. Taketatsu and N. Kono, *Chem. Lett.*, 1974, **7**, 989.
2. Ximao Yu, Ruxu Cai, Shi Zhong Tian and Yune Zeng, *Gao Deng Xue Xiao Hua Xue Xue Bao*, 1985, **9**, 776.
3. Pingqi Dai, Ximao Yu and Yune Zeng, *Fen Xi Hua Xue*, 1987, **6**, 613.
4. Jinzhang Gao, Xiangming Zhu and Guangbi Bai, *Anal. Lett.*, 1985, **8**, A12.
5. Jinzhang Gao, Ruyao Chen, Jingguo Hou and Guangbi Bai, *The Analyst*, 1987, **112**, 1177.
6. B.W. Budesinsky, *Z. Phys. Chem.*, 1971, **76**, 311.
7. D. V. Gonzolez-Garcia, A. Arrebola-Ramirez and M. Roman-Ceba, *Talanta*, 1979, **26**, 215.
8. Huiming Shi and Xiwen He, *Fen Xi Hua Xue*, 1979, **7**, 228.
9. G. Scatchard, *Chem. Rev.*, 1932, **10**, 229.