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Thermochemistry of phosphate products. Part I: Standard enthalpy of formation of tristrontium phosphate and strontium chlorapatite

I. Khattech, M. Jemal*

Department of Chemistry, University of Tunis, Faculty of Sciences, Tunis 1060, Tunisia

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Abstract

Tristrontium phosphate $Sr_3(PO_4)_2$ (triSr) and strontium chlorapatite $Sr_3(PO_4)_6Cl_2$ (ClapSr) have been prepared and characterized by X-ray diffraction, IR spectroscopy and chemical analysis. Using an isoperibol calorimeter the heat of solution of these products in a 9% weight nitric acid solution were determined. They are (-110.1 ± 1.5) and (-283.6 ± 2.4) kJ mol^{-1} for triSr and ClapSr, respectively. Combining these results with others found by dissolving the products and entities involved in thermochemical cycles, allows to determine the standard heat of formation of these Sr-phosphates. These quantities are: $\Delta_f H^\circ$(triSr, 298 K) $= -4110$ kJ mol^{-1} and $\Delta_f H^\circ$(ClapSr, 298 K) $= -13233$ kJ mol^{-1}. The results are discussed on the basis of the differences in bond enthalpies. © 1997 Elsevier Science B.V.

Keywords: Enthalpy of formation; Heat of solution; Strontium chlorapatite; Tristrontium phosphate

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1. Introduction

Apatites form a well-known family of phosphates that crystallize in the hexagonal system $P6_3/m$. As with calcium salts, they form the major part of the sedimentary phosphate ores and of the mineral of calcified tissues. In bones and dentine, traces of strontium (0.01 to 0.08%) are often found [1–3] but its exact role in the mineralization process of calcified tissues has not yet been totally elucidated [1,4].

On the other hand, little or no thermodynamic data are available for strontium phosphates. The present work is the continuation of a previous one on other Sr-apatites [5]. It deals with synthesis and thermochemical of tristrontium phosphate $Sr_3(PO_4)_2$ and strontium chlorapatite $Sr_3(PO_4)_6Cl_2$.

2. Samples synthesis and characterization

2.1. *Tristrontium (triSr)*

TriSr was prepared by double decomposition reaction according to the method recommended by Heughebaert for tricalcium phosphate but slightly modified [6]. This method consists in dropping a solution of strontium nitrate (0.36 M) into a solution of diammonium phosphate (0.01 M). The pH is maintained near 9.5 by addition of ammonia concentrated solution (28% weight). The precipitate is washed and heated overnight at 70°C, then ignited at 900°C to give the

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*Corresponding author. Tel.: 216 1 885008; fax.: 216 1 500 666.

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Table 1
Crystallographic parameters and Sr/P ratio of strontium phosphates compared to values from literature

	a/(nm)	c/(nm)	Sr/P
triSr	0.5387 ± 0.0001	1.9777 ± 0.0003	1.504
Ref. [7]	0.5378	1.976	—
Ref. [8]	0.5387	1.9780	—
ClapSr	0.9877 ± 0.0003	0.7194 ± 0.0003	1.666
Ref. [9]	0.9859	0.7206	—

triSr. This synthesis can be summarized by the following reaction scheme:

$$3Sr(NO_3)_2 + 2(NH_4)_2HPO_4 + 2NH_3 \rightarrow Sr_3(PO_4)_2 + 6NH_4NO_3$$

2.2. *Phosphostrontium chlorapatite (ClapSr)*

ClapSr was synthesized by solid state reaction between the tristrontium phosphate previously prepared and strontium chloride. The solid mixture is finely ground and heated for a night at 600, 900 then 1100°C in a pure nitrogen atmosphere. Finally the product is cooled slowly.

The purity of each of these products was checked by X-ray diffraction, IR spectroscopy and chemical analysis. Table 1 gives Sr/P ratio and the lattice parameters of the strontium phosphate studied.

The reagents are products used for analysis (99% purity). They are commercialized by Merck and Fluka.

3. Calorimetric study

The calorimetric device is an isoperibol one. It was described previously in detail [10,11]. The sensor is a thermistor (200 Ω at 25°C) which forms one of the fourth arms of a Wheatstone bridge. The solid to be dissolved (or the liquid to be diluted) is put in a very thin globe manufactured at the end of pyrex tube (ext. diameter 5 mm). The reaction to be followed is started by breaking the globe. The device is also provided with an axial stirrer and an ohmic resistance connected to the usual units for calibration by Joule effect (DC supply, volt- and ampere meters, timer). Experimental begins by recording the base line drawn at a quasi-equilibrium state during which the base line does not move significantly from the horizontal one. Thermal effect resulting from Joule effect or from dissolution/dilution reaction, induces a shift 'D' after which the line becomes practically parallel to the previous line. Three to four calibration experiences were performed prior to each dissolution/dilution reaction. The device was tested by the well-known calibration reaction, namely, dissolution of trihydroxymethylaminomethane (or TRIS) in HCl solution (0.1 mol per kg solution).

Each pack of results were processed by the least squares method as recommended by Sands and Pattengill [12,13]. This method has enabled us to choose the simple proportional form for the dependence of the enthalpy measured over the mass (*m*) of TRIS, $\Delta_{sol}H^\circ = A.m$ in which the proportionality constant A can be calculated as:

$$A = \frac{\sum \omega_i \Delta H_i \cdot m_i}{\sum \omega_i \cdot m_i^2}$$

where ω_i is the statistical weight of observation '*i*'. It is expressed as: $\omega_i = 1/\sigma_i^2$, where σ_i^2 is the variance and σ_i is proportional to the error. The proportionality coefficient is the Student factor 't'. As experiments have been carried out in the same conditions, the 't' factor is the same. So one can replace in the 'A' expression σ by the error. The latter was determined as the difference between the two extreme calibration coefficients for every dissolution/dilution process.

The sensitivity of the device did not allow detection of the heat variation incident to progressively increasing the concentration of the dissolved product in the final solution.

The calculated enthalpy of dissolution of TRIS in HCl solution is (-29.6 ± 0.2) kJ mol^{-1}. This value is in good agreement with those found by other authors [14,15].

4. Results and discussion

4.1. *Enthalpy of dissolution*

Measurements of the enthalpy of dissolution of the Sr-phosphate in 9% weight nitric acid (HNO_3; $35.35H_2O$) were carried out in the same volume of acid (350 ml) by successively dissolving variable

Table 2
Enthalpies of solution at 298 K of Sr-phosphates in HNO_3, 35.35 H_2O

Expt. No.	m/g	$\varepsilon/(\mathrm{J\,mm^{-1}})$ kJ mol^{-1}	D/mm	$-\Delta_{sol}H/\mathrm{J}$ kJ mol^{-1}	error/J
1	0.09137	0.30377	70.0	21.264	0.797
3	0.15858	0.30539	124.0	37.868	1.486
4	0.14027	0.30146	111.5	33.613	1.107
5	0.12425	0.29224	96.5	28.201	0.487
6	0.10262	0.28595	81.5	23.305	0.262
7	0.08495	0.31215	59.5	18.573	0.157
$\langle\Delta_{sol}H(Sr_3(PO_4)_2\rangle = (-223.3 \pm 3.5)\,\mathrm{J\,g^{-1}}$					
1	0.15558	0.31075	92.5	28.744	0.395
2	0.15051	0.30621	89.5	27.406	0.250
4	0.11569	0.29852	71.0	21.195	0.341
5	0.07352	0.30769	45.0	13.846	0.175
6	0.14988	0.31012	91.0	28.221	0.290
7	0.24844	0.30581	151.5	46.330	0.519
8	0.12512	0.30643	79.0	24.208	0.355
9	0.11921	0.30135	74.5	22.451	0.128
$\langle\Delta_{sol}H(Sr_{10}(PO_4)_6Cl_2\rangle = (-186.9 \pm 1.6)\,\mathrm{J\,g^{-1}}$					

ε is the mean calibration constant.
D is the shift recorded between the base lines.

amounts of the solids at 298 K. The results are reported in Table 2

4.2. Standard enthalpies of formation

Standard enthalpies of the formation of these compounds are determined by exploring for each of them a succession of reactions of which the final balance leads to the formation reaction of the particular product. Thus one can propose the following series of reaction:

For triSr

$$\{3Sr(NO_3)_2 + 2H_3PO_4\}_{(sln)} \rightarrow Sr_3(PO_4)_{2(s)} + 6\{HNO_3\}_{(sln)} \quad \text{(I)}$$

$$6(HNO_3;35.35H_2O)_{(l)} \rightarrow 3H_{2(g)} + 3N_{2(g)} + 9O_{2(g)} + 212.1H_2O_{(l)} \quad \text{(II)}$$

$$3H_{2(g)} + 2P_{(s)} + 4O_{2(g)} + 1.512H_2O_{(l)} \rightarrow 2(H_3PO_4;0.756H_2O)_{(l)} \quad \text{(III)}$$

$$2(H_3PO_4;0.756H_2O)_{(l)} + \{sln\} \rightarrow \{2H_3PO_4 + 1.512H_2O\}_{(sln)} \quad \text{(IV)}$$

$$3Sr_{(s)} + 3N_{2(g)} + 9O_{2(g)} \rightarrow 3Sr(NO_3)_{2(s)} \quad \text{(V)}$$

$$3Sr(NO_3)_{2(s)} + \{sln\} \rightarrow \{3Sr(NO_3)_2\}_{(sln)} \quad \text{(VI)}$$

$$\{1.512H_2O\}_{(sln)} \rightarrow 1.512H_2O_{(l)} + \{sln\} \quad \text{(VII)}$$

$$3Sr_{(s)} + 2P_{(s)} + 4O_{2(g)} \rightarrow Sr_3(PO_4)_{2(s)}$$

For ClapSr

$$\{10Sr(NO_3)_2 + 6H_3PO_4 + 2HCl\}_{(sln)} \rightarrow Sr_{10}(PO_4)_6Cl_{2(s)} + 20\{HNO_3\}_{(sln)} \quad \text{(VIII)}$$

$$20(HNO_3;35.35H_2O)_{(l)} \rightarrow 3H_{2(g)} + 3N_{2(g)} + 9O_{2(g)} + 707H_2O_{(l)} \quad \text{(IX)}$$

$$9H_{2(g)} + 6P_{(s)} + 12O_{2(g)} + 4.536H_2O_{(l)} \rightarrow 6(H_3PO_4;0.756H_2O)_{(l)} \quad \text{(X)}$$

$$6(H_3PO_4;0.756H_2O)_{(l)} + \{sln\} \rightarrow \{6H_3PO_4 + 4.536H_2O\}_{(sln)} \quad \text{(XI)}$$

$$10Sr_{(s)} + 10N_{2(g)} + 30O_{2(g)} \rightarrow 10Sr(NO_3)_{2(s)} \quad \text{(XII)}$$

$$10Sr(NO_3)_{2(s)} + \{sln\} \rightarrow \{10Sr(NO_3)_2\}_{(sln)} \quad \text{(XIII)}$$

Table 3
Stadard enthalpies of dissolution and enthalpies of formation of well-known compounds and entities at 298 K

	$\Delta_{sol}H^\circ$(298 K)/ kJ mol^{-1}	Ref.	$\Delta_f H^\circ$(298 K)/ kJ mol^{-1}	Ref.
HNO_3, $35.35H_2O$	—	—	−206.8	[18]
H_3PO_4, $0.756H_2O$	−7.87±0.04	[19]	−1271.8	[18]
H_2O	0	[19]	−258.8	[16,17]
$Sr(NO_3)_2$	13.9±0.1	(*)	−978.2	[16,17]
HCl, $53.25H_2O$	−0.35±0.01	(*)	−165.4	[18]

[*] Present work

$$\{111.036H_2O\}_{(sln)} \rightarrow 111.036H_2O_{(l)} + \{sln\} \qquad (XIV)$$

$$H_{2(g)} + Cl_{2(g)} + 106.5H_2O_{(l)} \rightarrow 2(HCl; 53.25H_2O)_{(l)} \qquad (XV)$$

$$2(HCl; 53.25H_2O)_{(l)} + \{sln\} \rightarrow \{2HCl; 106.5H_2O\}_{(sln)} \qquad (XVI)$$

$$10Sr_{(s)} + 6P_{(s)} + 12O_{2(g)} + Cl_{2(g)} \rightarrow Sr_{10}(PO_4)_6Cl_{2(s)}$$

In addition to the dissolution reactions already mentioned (steps I and VIII), these schemes involve several other steps, which include processes of dissolution or dilution in nitric acid solution (steps IV, VI, VII, XI, XIII, XIV and XVI). Their corresponding enthalpies were measured in the same apparatus by the same experimental procedure. Other steps involve the formation reactions of well-known products or entities, the corresponding enthalpies were taken from the literature (Table 3).

Table 4 gathers the standard enthalpies of formation of triSr and ClapSr calculated according to the previous detail, together with the standard quantities for HapSr and FapSr determined in the previous work [5] and those for Ca-apatites extracted from reference [21].

One can conclude that the enthalpy of the formation of tristrontium phosphate −4110 kJ mol^{-1} is in agreement with the value published by Parker et al. 4122.9 kJ mol^{-1} [20]. For the strontium apatites, one can notice that replacement of fluoride by the hydroxide ion then by chloride induces an increase in the enthalpy of formation. The same conclusion can be deduced for calcium apatites. Moreover replacement for F^- by OH^- induces enthalpy variations of the same order of magnitude: 243 and 233 kJ mol^{-1} for Ca and Sr products, respectively. It seems that the difference between the bond enthalpies ($E_{M\text{-}OH} - E_{M\text{-}F}$) is practically the same whatever is the metal (Ca or Sr) in the single cation products. The same conclusion has been previously formulated in the double cation solid solution, since the enthalpy of mixing of Ca and Sr apatites is almost the same for F and OH products whatever is

Table 4
Standard enthalpies of dissolution and enthalpies of formation of strontium phosphates at 298 K

		$\Delta_{sol}H^\circ$(298 K)/ kJ mol^{-1}	$\Delta_f H^\circ$(298 K)/ kJ mol^{-1}	Ref.
$Sr_3(PO_4)_2$		−101.1 ± 1.5	−4110	[a]
$Sr_{10}(PO_4)_6Cl_2$	(ClapSr)	−283.6 ± 2.4	−13233	[a]
$Sr_{10}(PO_4)_6(OH)_2$	(HapSr)	−385.4 ± 3.4	−13371	[5]
$Sr_{10}(PO_4)_6F_2$	(FapSr)	−223.7 ± 2.7	−13604	[5]
$Ca_{10}(PO_4)_6Cl_2$	(ClapCa)	−313.4 ± 0.5	−13139 [b]	[21]
$Ca_{10}(PO_4)_6(OH)_2$	(HapCa)	−364.2 ± 1.7	−13305	[21]
$Ca_{10}(PO_4)_6F_2$	(FapCa)	−194.3 ± 1.4	−13548	[21]

[a] Present work.
[b] Corrected value.

the metal composition [22,23]. On the other hand replacement of OH^- by Cl^- is significantly dependent on the metal: 166 and 138 kJ mol^{-1} for Ca and Sr limit products, respectively (Table 4). The difference between bond enthalpy ($E_{M\text{-}Cl} - E_{M\text{-}OH}$) is smaller for Sr than for Ca products. It has been shown that heat of mixing of the single cation solid products is smaller for Cl than for OH^- apatites [22,24].

These conclusions are also in accordance with crystallographic experimentation performed on single cation apatites, according to which replacement of OH^- by Cl^- induces in Ca-apatites a more important increase of some atomic distances around the screw axis than it does in Sr-apatites [25].

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