J Therm Anal Calorim (2010) 100:441–446
DOI 10.1007/s10973-009-0657-4

Standard enthalpies of formation of Li, Na, K, and Cs thiolates

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Portuguese Special Chapter
Received: 6 October 2008 / Accepted: 11 March 2009 / Published online: 14 January 2010

Abstract The standard enthalpies of formation of alkaline metals thiolates in the crystalline state were determined by reaction-solution calorimetry. The obtained results at 298.15 K were as follows: $\Delta_f H_m^o(\mathrm{MSR, cr})/\mathrm{kJ\ mol^{-1}} = -259.0 \pm 1.6$ ($LiSC_2H_5$), -199.9 ± 1.8 ($NaSC_2H_5$), -254.9 ± 2.4 ($NaSC_4H_9$), -240.6 ± 1.9 (KSC_2H_5), -235.8 ± 2.0 ($CsSC_2H_5$). These results where compared with the literature values for the corresponding alkoxides and together with values for $\Delta_f H_m^o(\mathrm{MSH, cr})$ were used to derive a consistent set of lattice energies for MSR compounds based on the Kapustinskii equation. This allows the estimation of the enthalpy of formation for some non-measured thiolates.

Keywords Alkaline metal thiolates · Lattice energy · Thermochemical radii · Thermochemistry · Enthalpy of formation

Introduction

Alkaline metals compounds have a major importance in synthetic chemistry [1]. Their alkoxide, thiolate, and cyclopentadienyl salts are among the most used ones when the intention is to introduce a functional group in the coordination sphere of a metal. [2–10] Alkoxides are also industrially relevant as additives to improve the temperature and pressure resistance of mineral lubricant oils and to minimise the corrosive properties of detergents [8, 11]. Despite their abundant use, structural and energetic studies of alkaline metal compounds still sparse. For alkoxides and cyclopentadienyl derivatives X-ray diffraction information exists for some compounds [12–23] and the enthalpies of formation have been measured for several among them [24–29]. Alkaline metal thiolate salts have, to our knowledge, X-ray structures or formation enthalpies not known to date. However, several structural characterizations exist for alkaline-earth thiolates [30–33].

In this article, the enthalpies of formation of Li, Na, K, and Cs thiolates were determined for the first time by reaction-solution calorimetry. These results, together with a previously developed estimation method, allowed predicting the enthalpies of formation of the Rb derivatives.

Experimental section

General

All syntheses were carried out under an oxygen and water free (<2 ppm) nitrogen atmosphere, inside a glove-box or using standard Schlenk techniques. THF was pre-dried over 4 Å molecular sieves and distilled under sodium. Pentane was distilled over P_2O_5 and kept in a glove-box over 4 Å molecular sieves. Ethanethiol (Aldrich, 97%) and butanethiol (Aldrich, 99+%) were distilled under nitrogen atmosphere in a fume cupboard and kept inside a glovebox. Lithium, sodium and potassium (Aldrich, 99.9%) was used as small pieces to which the oxidised surface was removed inside a glove-box. Caesium (Aldrich, 99.95+%) were kept

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inside a glove-box and used as supplied. All solvents were degassed twice by freeze-taw cycles before use.

Infrared spectra (IR) were obtained with a Perkin-Elmer 577 spectrophotometer calibrated with polystyrene film, with samples mounted as Nujol mulls between KBr plates. Elemental analysis (C, H, and S) was performed on an automatic analyzer CE-Instruments EA-110 CHNS-O.

Thiolates

Lithium, sodium, and potassium thiolates used in the calorimetric experiments were prepared by adding chunks of the metal to a solution containing the appropriate thiol in 20 mL of THF. The mixture was stirred by ca. 1 h. The excess metal was removed and the solution taken to dryness. The resulting solid was washed twice with pentane and dried in high vacuum (10^{-4}–10^{-5} torr). A similar procedure was followed in the synthesis of the caesium thiolate. In this case, the metal was used in the form of small chips and added to an excess of the thiol in THF solution. The IR spectra made to all the final products showed that the obtained thiolates were thiol and hydroxide free. Elemental analysis calcd. (%) for $LiSC_2H_5$ (68.06): C 35.29, H 7.40, S 47.10; found: C 35.12, H 7.49, S 46.81; for $NaSC_2H_5$ (84.11): C 28.56, H 5.99, S 38.12; found: C 28.12, H 6.32, S 38.03; for KSC_2H_5 (100.22): C 23.97, H 5.03, S 31.99; found: C 24.14, H 4.91, S 31.85; for $CsSC_2H_5$ (194.03): C 12.38, H 2.60; found: C 11.98, H 2.71; for $NaSC_4H_9$ (112.16): C 42.83, H 8.09, S 28.58; found: C 41.94, H 8.02, S 28.76.

Reaction-solution calorimetry

The enthalpies of reaction and solution needed to determine the enthalpies of formation of the alkaline metal thiolates studied in this work were measured by using a calorimeter specially built for experiments with oxygen and water sensitive compounds. Details of the apparatus and of the experimental procedure were previously reported [25]. In brief, the calorimeter consisted of a transparent Dewar vessel closed by a lid, which supports a stirrer, a quartz crystal thermometer probe, a resistance for electrical calibration, and an ampoule breaking system. The assembled vessel was immersed in a thermostatic water bath whose temperature was controlled at 298 ± 10^{-3} K by a Tronac PTC-40 unit. In a typical experiment, a thin-walled glass ampoule was loaded with 20–100 mg of the thiolate sample inside a glove-box, sealed in vacuum, and weighed to ±10^{-5} g. The reaction was started by breaking the glass ampoule in 140 ml of distilled and deionised water. This was preceded by an electrical calibration, in which a potential difference of ca. 2.0 V was applied to a 48 Ω resistance during ca. 180 s. The temperature changes inside the reaction vessel were recorded to 10^{-4} K at fixed intervals of 10 s by a Hewlett-Packard quartz thermometer (HP 2804A).

Table 1 Auxiliary thermochemical data at 298.15 K (data in kJ mol^{-1})

Compound	$\Delta_f H^o_m$	Ref.	$\Delta_{ea} H^o_m(SR)$	Ref.
LiSH, cr	−251.5 ± 0.8	34		
NaSH, cr	−237.23 ± 0.08	34		
KSH, cr	−265.10 ± 0.08	34		
RbSH, cr	−266.9 ± 0.8	34		
CsSH, cr	−274.5 ± 0.8	34		
C_2H_5SH, l	−73.6 ± 0.6	35		
n-C_4H_9SH, l	−124.7 ± 1.2	35		
LiOH, cr	−484.93 ± 0.08	34		
NaOH, cr	−425.609 ± 0.008	34		
KOH, cr	−424.76 ± 0.08	34		
RbOH, cr	−418.19 ± 0.08	34		
CsOH, cr	−417.23 ± 0.08	34		
H_2O, l	−285.830 ± 0.040	36		
SH, g	142.67 ± 0.08	34	228.31 ± 0.09	38
SC_2H_5, g	116.7 ± 6.3	37	194.64 ± 0.38	38
S-n-C_4H_9, g	74.7 ± 6.4	37	202.1 ± 1.9	38

Results and discussion

The auxiliary enthalpy of formation and electroaffinity data used in the calculations are given in Table 1 [34–36].[1,2] The 2005 IUPAC recommended standard atomic masses were used in the calculation of all molar quantities [39].

The enthalpies of formation of the metal thiolates MSR ($M = Li$, Na, K, Cs; $R = C_2H_5$; $M = Na$, $R = n$-C_4H_9) investigated in this work, were obtained from calorimetric measurements of the enthalpies of reaction 1 and of the dissolution processes indicated in Scheme 1.

It can be concluded from Scheme 1 that:

$$\begin{aligned}\Delta_f H^o_m(\mathrm{MSR, cr}) = &-\Delta_r H^o_m(1) + \Delta_{sln} H^o_m(1)\\ &+ \Delta_{sln} H^o_m(2) + \Delta_f H^o_m(\mathrm{MOH, cr})\\ &+ \Delta_f H^o_m(\mathrm{RSH, l}) - \Delta_f H^0_m(\mathrm{H_2O, l}) \qquad (1)\end{aligned}$$

Here $\Delta_r H^o_m(1)$ represents the enthalpy change for the reaction of MSR with distilled and deionised water under

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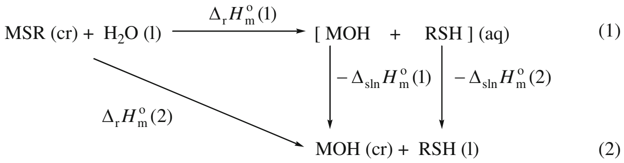
[1] Formation enthalpies of SC_2H_5 and S-n-C_4H_9 were calculated using data from Ref. [34] for the enthalpies of formation of the gaseous thiols and the hydrogen, and assuming a 380.7 ± 6.3 kJ mol^{-1} value for the S–H bond according to Ref. [37].

[2] $\Delta_{ea} H^o_m(SR) = E_{ea}(SR) + 6.197$ kJ mol^{-1}, where E_{ea} is the electron affinity of the SR species given in Ref. [37]. The addition of the 6.197 kJ mol^{-1} factor to $E_{ea}(SR)$ (thermal ion convention) makes the $\Delta_{ea} H^o_m(SR)$ values consistent with the $\Delta_i H^o_m(M)$values taken from Ref. [34].



Scheme 1 Calorimetric processes under study

the actual experimental conditions, $\Delta_{\mathrm{sln}}H^{\mathrm{o}}_{\mathrm{m}}(1)$ is the enthalpy of dissolution of stoichiometric amounts of MOH in H_2O, and $\Delta_{\mathrm{sln}}H^{\mathrm{o}}_{\mathrm{m}}(2)$ is the enthalpy of solution of RSH in diluted aqueous MOH.

The concentrations of the MOH (M = Li, Na, K, Cs) compounds present in the final calorimetric solutions were always very small, with the typical molar ratios $n_{\mathrm{MOH}} : n_{\mathrm{H_2O}}$ being 1:6,000 or less. The solutions were, therefore, assumed to be infinitely diluted and $\Delta_{\mathrm{sln}}H^{\mathrm{o}}_{\mathrm{m}}(1)$ was calculated as -23.5 ± 0.8 kJ mol^{-1} (LiOH), -44.5 ± 0.8 kJ mol^{-1} (NaOH), -57.6 ± 0.8 kJ mol^{-1} (KOH), and -71.0 ± 1.1 kJ mol^{-1} (CsOH), based on $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{MOH, cr})$ and $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{MOH} \cdot \infty\mathrm{H_2O},\ \mathrm{aq})$ data reported in the literature [34, 36]. The $\Delta_{\mathrm{sln}}H^{\mathrm{o}}_{\mathrm{m}}(2)$dissolution were measured for C_2H_5SH and n-C_4H_9SH in a diluted solution of NaOH (similar concentration as in the average final conditions of studied reactions were used), obtaining 1.95 ± 0.65 and 3.7 ± 1.2 kJ mol^{-1} for C_2H_5SH and n-C_4H_9SH, respectively. To our knowledge, the only values that can be compared with our ones are the obtained by Plyasunova et al [40]. Those authors define group contributions for the calculation of the corresponding enthalpies of vaporization and hydration $\Delta_{\mathrm{vap}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{RSH,\ l})$ and $\Delta_{\mathrm{h}}H^{\infty}_{\mathrm{m}}(\mathrm{RSH} \cdot \infty\mathrm{H_2O})$, respectively) for a variety of compounds. Using those values $\Delta_{\mathrm{sln}}H^{\mathrm{o}}_{\mathrm{m}}(2) = -1.4 \pm 1.0$ kJ mol^{-1} (ethanethiol) and –0.41 ± 4.6 kJ mol^{-1} (1-butanethiol), could be calculated. The differences to the ones now measured probably rely on the change of the ionic strength of the solution (NaOH in our case and water in the literature one). Since the ionic strength does not change with the nature of the hydroxide used, the values of $\Delta_{\mathrm{sln}}H^{\mathrm{o}}_{\mathrm{m}}(2)$ measured in sodium hydroxide solution were used for all the alkaline metal thiolates studied.

The results of the experimental measurements of $\Delta_{\mathrm{r}}H^{\mathrm{o}}_{\mathrm{m}}(1)$ (Table 2), $\Delta_{\mathrm{sln}}H^{\mathrm{o}}_{\mathrm{m}}(1)$, and $\Delta_{\mathrm{sln}}H^{\mathrm{o}}_{\mathrm{m}}(2)$ in conjunction with the auxiliary data in Table 1 enabled the calculation of $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{MSR, cr})$ through Eq. 1 (Table 2). All experimental results reported in this work are the mean of five independent measurements and the uncertainties quoted represent twice the standard deviation of the mean.

Table 2 Reaction enthalpies, and standard enthalpies of formation of alkaline metals alkoxides at 298.15 K (Data in kJ mol^{-1})

MOR	$-\Delta_{\mathrm{r}}H^{\mathrm{o}}_{\mathrm{m}}(1)$[a]	$-\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{MOR, cr})$		Δ[d]
		Experimental[b]	Estimated[c]	
LiSH		251.5 ± 0.8[e]	263.7 ± 9.8	12.2
$LiSC_2H_5$	35.2 ± 1.0	259.0 ± 1.6	226.5 ± 11.6	−32.5
LiS-n-C_4H_9			273.2 ± 11.8	
NaSH		237.23 ± 0.08[e]	238.3 ± 9.8	1.1
$NaSC_2H_5$	56.0 ± 1.4	199.9 ± 1.8	207.6 ± 11.6	7.6
NaS-n-C_4H_9	50.4 ± 1.5	254.9 ± 2.4	254.9 ± 11.8	0.0
KSH		265.10 ± 0.08[e]	277.4 ± 9.8	12.2
KSC_2H_5	27.6 ± 1.4	240.6 ± 1.9	251.4 ± 11.6	10.8
KS-n-C_4H_9			299.2 ± 11.8	
RbSH		266.9 ± 0.8[e]	260.7 ± 9.8	−6.2
$RbSC_2H_5$			235.4 ± 11.6	
RbS-n-C_4H_9			283.3 ± 11.8	
CsSH		274.5 ± 0.8[e]	261.5 ± 9.8	−13.0
$CsSC_2H_5$	38.4 ± 1.3	235.8 ± 2.0	237.4 ± 11.6	2.0
CsS-n-C_4H_9			285.8 ± 11.8	

[a] This work, reaction with water (see text)

[b] This work, unless otherwise stated

[c] Estimated using Kapustinskii equation

[d] $\Delta = \Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (experimental) – $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (estimated)

[e] See Ref. [34]

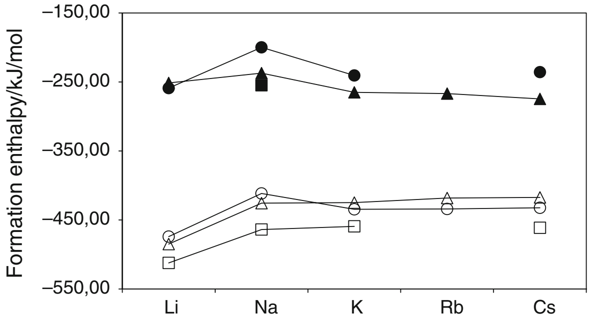
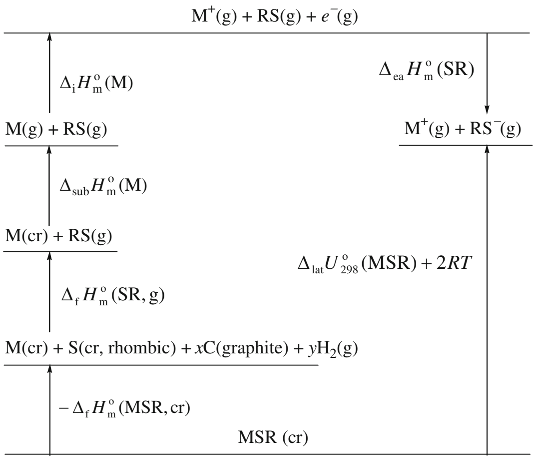


Fig. 1 Experimental enthalpies of formation for MSR (see text) and MOR [27]. MSH (*filled triangles*), MSC_2H_5 (*filled circles*), MS-n-C_4H_9 (*filled squares*), MOH (*open triangles*), MOC_2H_5 (*open circles*) and MO-n-C_4H_9 (*open squares*)

Since those are the first alkaline metal thiolates which enthalpy of formation was measured, the obtained values could not be compared with any literature data. However, they can be compared with the values for the corresponding alkoxides (Fig. 1) [27]. Despite a difference in the absolute values a general common pattern could be found. The curves follow each other, suggesting that both families of compounds have similar type of bonding to the metals. For both families the sodium derivative with SC_2H_5 or OC_2H_5 shows to be the less stable of each family.

If an ionic structure is assumed for each MSR compound in the solid state, the corresponding lattice energy, $\Delta_{\mathrm{lat}}U^{\mathrm{o}}(\mathrm{MSR})$, can be defined as the *internal energy* change associated with the following process:



Scheme 2 Born–Haber cycle for tiolates

$$\mathrm{MSR(cr)} \rightarrow \mathrm{M^+(g)} + \mathrm{RS^-(g)} \quad (\mathrm{M} = \text{alkaline metal};\ \mathrm{R} = \text{alkyl}) \tag{2}$$

The value of $\Delta_{lat}U^o(MSR)$ at 298.15 K, $\Delta_{lat}U^o_{298}(MSR)$, can be computed from Eq. 3 which directly results from the Born–Haber cycle in Scheme 2.

$$\begin{aligned}\Delta_{lat}U^o_{298}(MSR) = & -\Delta_f H^o_m(MSR,cr) + \Delta_f H^o_m(SR,g) \\ & + \Delta_{sub}H^o_m(M) + \Delta_i H^o_m(M) \\ & - \Delta_{ea}H^o_m(SR) - 2RT\end{aligned} \tag{3}$$

In this equation, R is the gas constant, T is the absolute temperature, $\Delta_{sub}H^o_m(M)$ and $\Delta_i H^o_m(M)$ represents the enthalpy of sublimation and the enthalpy of ionisation of the metal, respectively, and $\Delta_{ea}H^o_m$ is the enthalpic electron affinity of the SR radical [38]. The obtained $\Delta_{lat}U^o_{298}(MSR)$ values are compared in Table 3 with the lattice enthalpies previously reported for several alkaline metal alkoxides [27]. These results were derived by using $\Delta_{sub}H^o_m(M) =$ 159.37 ± 0.08 kJ mol^{-1} (Li), 107.32 ± 0.08 kJ mol^{-1} (Na), 60.59 ± 0.08 kJ mol^{-1} (K), 76.065 ± 0.008 kJ mol^{-1} (Cs) [34] $\Delta_i H^o_m(M) =$ 526.41 ± 0.08 kJ mol^{-1} (Li), 502.04 ± 0.08 kJ mol^{-1} (Na), 425.02 ± 0.08 kJ mol^{-1} (K), 381.90 ± 0.08 kJ mol^{-1} (Cs); [34] and the auxiliary data in Table 1. A general tendency for a decrease of the lattice energy with the increase of the alkyl chain length observed for the alkoxides was also observed for the thiolates with heavier metals (K and Cs). For sodium thiolates does not exist a clear tendency and for Li compounds the change seems to be in the opposite direction when compared with the alkoxides.

Table 3 Lattice energies of the alkaline metal thiolates and alkoxides (in kJ mol^{-1}) and thermochemical radii (in pm) of the metal cations and of the thiolate and alkoxides anions

M	OR/SR	r_-	$\Delta_{lat}U^o_{298}$(MOR/MSR)	
			Estimated[a]	Experimental[b]
Li, $r_+ = 85.6$	OH	123.5	1031.7	1021.0 ± 0.5
	OC_2H_5	136.4	972.0	966.8 ± 5.1
	O-n-C_4H_9	141.3	950.9	952.5 ± 15.1
	SH	165.6	858.9	846.7 ± 0.8
	SC_2H_5	174.6	829.4	861.9 ± 6.5
	S-n-C_4H_9	175.4	826.7	
Na, $r_+ = 119.4$	OH	123.5	888.2	885.2 ± 0.5
	OC_2H_5	136.4	843.6	827.8 ± 5.0
	O-n-C_4H_9	141.3	827.7	827.6 ± 15.9
	SH	165.6	757.0	756.0 ± 0.2
	SC_2H_5	174.6	734.0	726.4 ± 6.6
	S-n-C_4H_9	175.4	731.9	731.9 ± 7.1
K, $r_+ = 155.3$	OH	123.5	774.0	789.3 ± 0.5
	OC_2H_5	136.4	739.9	755.6 ± 5.3
	O-n-C_4H_9	141.3	727.6	727.9 ± 15.2
	SH	165.6	672.4	660.1 ± 0.8
	SC_2H_5	174.6	654.1	643.3 ± 6.6
	S-n-C_4H_9	175.4	652.4	
Rb, $r_+ = 161.2$	OH	123.5	758.0	758.5 ± 0.5
	OC_2H_5	136.4	725.3	731.0 ± 5.4
	O-n-C_4H_9	141.3	713.5	
	SH	165.6	660.2	666.4 ± 0.8
	SC_2H_5	174.6	642.6	
	S-n-C_4H_9	175.4	641.0	
Cs, $r_+ = 177.5$	OH	123.5	716.9	725.4 ± 0.5
	OC_2H_5	136.4	687.5	697.1 ± 5.5
	O-n-C_4H_9	141.3	676.9	673.6 ± 15.5
	SH	165.6	628.9	641.9 ± 0.8
	SC_2H_5	174.6	612.9	610.8 ± 6.6
	S-n-C_4H_9	175.4	611.4	

[a] Estimated from Eq. 4 by using the r_+ and r_- values listed in this table

[b] Experimental values calculated from Eq. 5 (MSR) or taken from Ref. [27] (MOR)

The obtained lattice energy values may be analysed using the Kapustinskii approximation represented by Eq. 4,[3] which was proposed to predict how the lattice energy varies with the size of the constituent ions regardless of structural alterations in the solid state.

$$\Delta_{lat}U^o_0(MSR) = 1.079 \times 10^5 \frac{v \cdot Z_+ Z_-}{r_+ + r_-} \tag{4}$$

In this expression, $\Delta_{lat}U^o_0(MOR)$ is the lattice energy at 0 K in kJ mol^{-1}, v is the number of ions in the molecule (in this case, $v = 2$), Z_+ and Z_- are the charges of the cation and the anion, respectively, and r_+ and r_- the corresponding radii in pm. Note that $\Delta_{lat}U^o_0(MSR)$ is related with$\Delta_{lat}U^o_{298}(MSR)$ in Table 3 through Eq. 5.

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[3] For a detailed discussion of Kapustinskii equation see Ref. [41].

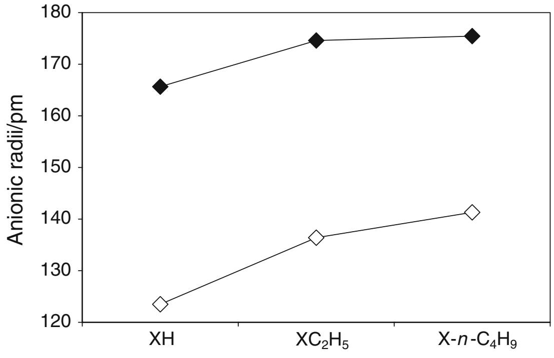

Fig. 2 Thermochemical ionic radii for thiolates (this work) and alkoxides [27]. Radii for SR^- (*filled diamonds*) and for OR^- (*open diamonds*)

$$\begin{aligned}\Delta_{\mathrm{lat}}U^{\mathrm{o}}_{298}(\mathrm{MSR}) &= \Delta_{\mathrm{lat}}U^{\mathrm{o}}_{0}(\mathrm{MSR}) + (H^{\mathrm{o}}_{298} - H^{\mathrm{o}}_{0})_{\mathrm{M}^+} \\ &\quad + (H^{\mathrm{o}}_{298} - H^{\mathrm{o}}_{0})_{\mathrm{SR}^-} - (H^{\mathrm{o}}_{298} - H^{\mathrm{o}}_{0})_{\mathrm{MSR}} \\ &\quad - 2RT \qquad (5)\end{aligned}$$

where R is the gas constant and $T = 298.15$ K. The information needed to compute the correction term $X = (H^{\mathrm{o}}_{298} - H^{\mathrm{o}}_{0})_{\mathrm{M}^+} + (H^{\mathrm{o}}_{298} - H^{\mathrm{o}}_{0})_{\mathrm{SR}^-} - (H^{\mathrm{o}}_{298} - H^{\mathrm{o}}_{0})_{\mathrm{MSR}} - 2RT$ is not available for the thiolates studied in this work. A fairly small value of X (comparable to the uncertainty that affects most experimental values of the lattice enthalpy in Table 3) is, however, expected. No values are available for MSH also, but as an example, in the case of the Li, Na, and K hydroxides, $X = 2.43$, -0.64, and -2.30 kJ mol^{-1}, respectively [34]. Hence, in the following discussion it will be assumed that, to a good approximation, $\Delta_{\mathrm{lat}}U^{\mathrm{o}}_{298}(\mathrm{MSR}) = \Delta_{\mathrm{lat}}U^{\mathrm{o}}_{0}(\mathrm{MSR})$

From Eq. 4 and the experimental $\Delta_{\mathrm{lat}}U^{\mathrm{o}}_{298}(\mathrm{MSR})$ data in Table 3, it was possible to derive the M–SR interatomic distances ($r_+ + r_-$). To obtain the r_- values for the thiolate anions the previously optimized r_+ for the alkaline metal cations, $r_+(\mathrm{Li}^+) = 90$ pm, $r_+(\mathrm{Na}^+) = 116$ pm, $r_+(\mathrm{K}^+) = 152$ pm, $r_+(\mathrm{Rb}^+) = 166$ pm, and $r_+(\mathrm{Cs}^+) = 181$ pm [27] were used. For SH^- and $C_2H_5S^-$, the mean of the r_- values obtained for the different metals were considered, leading to $r_-(\mathrm{SH}) = 165.6 \pm 5.2$ pm, $r_-(\mathrm{SC_2H_5}) = 174.6 \pm 6.8$ pm, and $r_-(\mathrm{S}\text{-}n\text{-}\mathrm{C_4H_9}) = 175.4$ pm. In Fig. 2 these values are compared with the corresponding $r_-(\mathrm{OR})$ values taken from literature [27]. Again, a similar pattern seems to exist but with smaller differences in the case of the thiol compounds.

Also presented in Table 3 are the lattice enthalpies of the alkaline metal thiolates estimated from Eq. 4 by using the previously calculated r_+ and r_- data. The r_+ and r_- calculated by the above procedure are called “thermochemical radii”. Little physical significance should be attributed to them. This was clearly shown, for several alkoxides reported in literature, for which the experimental interatomic distances exist, where their values are considerable different, despite the fact that a correlation could be established between both distances [27]. Their main importance is the capacity to reproduce the lattice energies through Eq. 4.

It is concluded that Eq. 4 reproduces the experimental $\Delta_{\mathrm{lat}}U^{\mathrm{o}}_{298}(\mathrm{MSR})$ data with an average absolute deviation of 9.8 kJ mol^{-1} and a maximum relative deviation of 3.9%. The obtained $\Delta_{\mathrm{lat}}U^{\mathrm{o}}_{298}(\mathrm{MSR})$ values were subsequently used to estimate the enthalpies of formation of various unmeasured metal thiolate compounds ($RbSC_2H_5$, MS-n-C_4H_9; M = Li, K, Rb, Cs) by using Eq. 3. As mentioned above, these results are also listed in Table 2. It should be stressed that despite the fact the error associated with these estimated values to be considerably larger than the one in the case of the experimentally determined enthalpies, the enthalpy of formation value should be a reasonable approximation for the cases were experimental values are not available. Moreover, this study shows that a simple model, like the Kapustinskii one here described, can accommodate a large variety of compounds, such as alkoxides, phenoxides, thiolates, or MCp (Cp = cyclopentadienyl) for alkaline and alkaline-earth metals. The extension of such a model to higher valence state metals is under study.

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