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Enthalpies of formation and lattice enthalpies of alkaline metal acetates

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Abstract

The standard ($p° = 0.1$ MPa) molar enthalpies of formation in the crystalline state of the alkaline metal acetates CH_3COOM (M = Li, Na, K, Rb, Cs), at $T = 298.15$ K, were determined by reaction-solution calorimetry as: $\Delta_f H_m°(CH_3COOLi, cr) = -(741.40 \pm 0.95)$ kJ mol^{-1}, $\Delta_f H_m°(CH_3COONa, cr) = -(711.01 \pm 0.51)$ kJ mol^{-1}, $\Delta_f H_m°(CH_3COOK, cr) = -(722.36 \pm 0.49)$ kJ mol^{-1}, $\Delta_f H_m°(CH_3COORb, cr) = -(722.31 \pm 1.09)$ kJ mol^{-1}, $\Delta_f H_m°(CH_3COOCs, cr) = -(726.10 \pm 1.07)$ kJ mol^{-1}. These results, taken together with the enthalpies of formation of the haloacetates XCH_2COOM (M = Li, Na; X = Cl, Br, I) and chloropropionates $ClCH(CH_3)COOM$ (M = Li, Na) re-evaluated from literature data were used to derive a consistent set of lattice energies, and discuss some general trends of the structure–energetics relationship for the CH_3COOM, XCH_2COOM, and $ClCH(CH_3)COOM$ compounds, based on the Kapustinskii approximation. It was found that the lattice energies of the haloacetates are essentially independent of the halogen and ca. 17–25 kJ mol^{-1} smaller than those of the corresponding acetates. In addition, no significant difference between the lattice enthalpy values of the haloacetates and chloropropionates was observed. Finally, linear correlations of very similar slope were obtained by plotting the M—O bond distances derived from the Kapustinskii equation against the published experimental M—O bond distances for alkaline metal acetates and alkoxides. The analysis of these relations suggests that the metal–oxygen bond distances for the lithium, potassium, and rubidium acetates, whose molecular structures in the solid state have not been determined, can be estimated as 214, 288, and 304 pm, respectively.

1. Introduction

The alkaline metal acetates (CH_3COOM, M = Li, Na, K, Rb, Cs) have a wide range of synthetic, industrial, and medical applications [1,2]. Potassium acetate, for example, is used as a diuretic and in the purification of penicillin; lithium acetate is employed as a component of catalysts for the production of polyesters or as an additive to improve their physical properties.

A number of X-ray diffraction [3–6] and thermophysical studies [7–12] have tried to elucidate the structures and phase transitions occurring in these salts at different temperatures. Although some conflicting results exist [3–12], the emerging picture suggests that the structures adopted in the solid state at $p = 0.1$ MPa and $T = 298$ K strongly depend on the metal. Thus CH_3COOLi is triclinic, with $V_{cell}/Z = 0.0876$ nm^3 [3], where V_{cell} is the unit cell volume and Z the number of asymmetric units it contains. For CH_3COONa two orthorhombic modifications are known, with $V_{cell}/Z = 0.0901$ (form I) and 0.0887 nm^3 (form II), respectively [4]. Form II seems to be the thermodynamically stable one [4,9]. The potassium and rubidium acetates are monoclinic with $V_{cell}/Z = 0.1055$ and 0.1108 nm^3, respectively [5,6]. Finally, CH_3COOCs adopts a hexagonal structure [5,6] with $V_{cell}/Z = 0.1467$ nm^3 [6]. Single crystal X-ray diffraction results available for the sodium [4,13] and caesium [6,13] derivatives indicate that on average the metal–oxygen short contacts [14] are $d_{Na—O} = 246$ (form I) and 245 pm (form II), and $d_{Cs—O} = 322$ pm.

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In addition to their industrial importance, these compounds are frequently used in discussions involving the ionic bond model in solids [15–21]. It is therefore surprising that no systematic investigation of their enthalpies of formation in the crystalline state, from which the corresponding lattice enthalpies can be derived, has been made up till now. These data were obtained in this work from reaction–solution calorimetry experiments and used to analyse the structure–energetics relationship in the alkaline metal acetates based on the Kapustinskii approximation.

2. Experimental

2.1. General

All operations involving the acetates were carried out inside a glove box, under an oxygen and water-free (<1 ppm) nitrogen atmosphere, or using standard Schlenk techniques. Differential scanning calorimetry (DSC) experiments were made using a temperature-modulated TA Instruments Inc., 2920 MTDSC apparatus, operated as a conventional DSC. The samples with masses in the range 1.5–4.5 mg, were sealed in aluminium pans and weighed with a precision of 10^{-7} g in a Mettler UMT2 ultra-micro balance. Helium (Air Liquide N55), at a flow rate of $0.5\,cm^3\,s^{-1}$ was used as the purging gas. The temperature and heat flow scales of the instrument were calibrated as previously described [22]. The heating rate was $10\,K\,min^{-1}$.

2.2. Materials

The commercial lithium (Aldrich 99.99%), sodium (Aldrich 99.995%), potassium (Aldrich 99.98%), rubidium (Aldrich 99.8%), and caesium (Aldrich 99.995%) acetates were used without further purification. DSC analysis showed that the rubidium and caesium samples were amorphous to a considerable extent, but that crystallization could readily be achieved on cooling after fusion. The CH_3COORb and CH_3COOCs samples used in the calorimetric experiments were therefore fused inside a Schlenk tube under an N_2 atmosphere, and cooled at a rate of ca. $10\,K\,min^{-1}$ prior to use. The onset, T_{on}, and the maximum, T_{max}, temperatures of the fusion peaks determined by DSC (the indicated uncertainties represent the mean deviation of two independent measurements), and the published temperatures of fusion, T_{fus}, were: $T_{on} = (556.6 \pm 0.2)$ K, $T_{max} = (557.8 \pm 0.1)$ K, $T_{fus} = (557 \pm 2)$ K [7], $T_{fus} = (558 \pm 1)$ K [8] (CH_3COOLi); $T_{on} = (602.5 \pm 0.2)$ K, $T_{max} = (604.1 \pm 0.2)$ K, $T_{fus} = (601.3 \pm 0.2)$ K [7] (CH_3COONa); $T_{on} = (578.4 \pm 0.1)$ K, $T_{max} = (579.7 \pm 0.1)$ K, $T_{fus} = (578.7 \pm 0.3)$ K [7], $T_{fus} = 582$ K [10] (CH_3COOK); $T_{on} = (513.6 \pm 0.1)$ K, $T_{max} = (515.5 \pm 0.2)$ K, $T_{fus} = 514$ K [7] (CH_3COORb); $T_{on} = (464.7 \pm 0.2)$ K, $T_{max} = (467.8 \pm 0.2)$ K, $T_{fus} = 463$ K [7] (CH_3COOCs). The corresponding enthalpies of fusion were: $\Delta_{cr}^l H_m^\circ(CH_3COOLi) = (12.6 \pm 0.1)$, $11.9\,kJ\,mol^{-1}$ [7], $(11.90 \pm 0.22)\,kJ\,mol^{-1}$ [8];

$\Delta_{cr}^l H_m^\circ(CH_3COONa) = (17.4 \pm 0.2), (18.4 \pm 0.4)\,kJ\,mol^{-1}$ [7], $17.9\,kJ\,mol^{-1}$ [7]; $\Delta_{cr}^l H_m^\circ(CH_3COOK) = (12.0 \pm 0.2)$, $(15.2 \pm 0.3)\,kJ\,mol^{-1}$ [7], $(7.65 \pm 0.07)\,kJ\,mol^{-1}$ [10]; $\Delta_{cr}^l H_m^\circ(CH_3COORb) = (8.9 \pm 0.3), 11.0\,kJ\,mol^{-1}$ [7]; $\Delta_{cr}^l H_m^\circ(CH_3COOCs) = (11.0 \pm 0.7), 12.0\,kJ\,mol^{-1}$ [7].

LiCl (Aldrich, 99.999%), NaCl (J.M. Gomes dos Santos, 99.8%) KCl (Aldrich, 99.99%), RbCl (Aldrich, 99.99+%), and CsCl (Aldrich 99.9%) used in the enthalpy of solution measurements were dried in an oven at $T = 373$ K and kept in a desiccator over P_2O_5 prior to use. The enthalpy of solution of acetic acid in the calorimetric solutions was measured using a sample from Aldrich (99.99+%), which was distilled in vacuum and kept under a nitrogen atmosphere prior to use.

2.3. Reaction–solution calorimetry

The reaction–solution calorimeter and the general operating procedure used in the experiments have been described elsewhere [23]. The calorimeter consisted of a transparent Dewar vessel closed by a lid, which supported a stirrer, a quartz crystal thermometer probe, a resistor 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 weighed to $\pm 10^{-5}$ g on a Mettler AT201 balance and transferred to a glove box. It was then filled with the sample and adapted to a glass tap through a silicone tube (Fig. 1). After removal of this set-up from the glove box the tap was connected to a vacuum/N_2 line. The tap was opened to the line, so that the sample could be maintained under a flow of N_2 at atmospheric pressure, and the ampoule was sealed with a torch. The two resulting pieces (closed ampoule + part of the neck) were weighed and the mass of sample was obtained by subtracting the mass of the empty ampoule.

The reaction or solution process under study was started by breaking the glass ampoule in $125\,cm^3$ of the calorimetric liquid. This was preceded by an electrical calibration, in which a potential difference of 3–4 V was applied to a 48 Ω resistance during 200 s. The calorimetric liquid consisted of a $HCl:553.41H_2O$ solution ($0.1\,mol\,dm^{-3}$ Merck, titrisol), or diluted solutions prepared from it containing the appropriate amounts of acetic acid or MCl salts. On average, the approximate masses of sample used in the calorimetric mea-
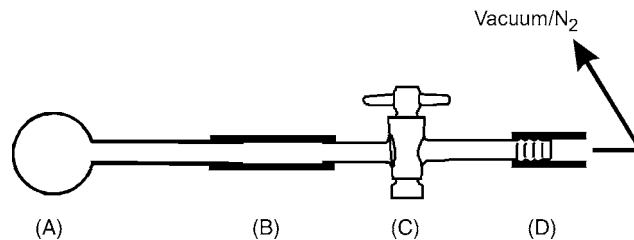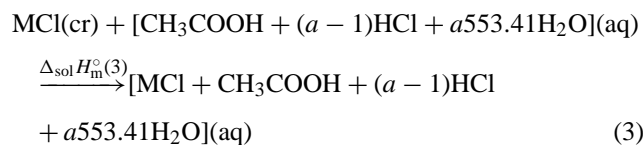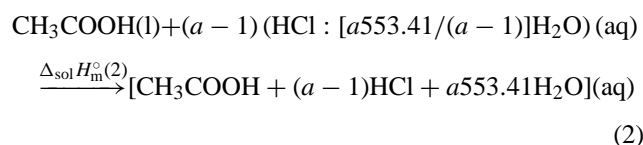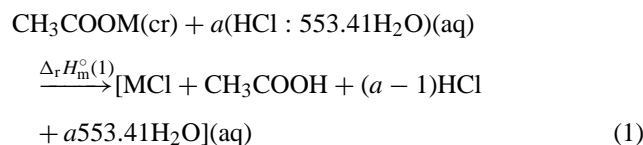

Fig. 1. System for sealing the glass ampoules used in the calorimetric experiments. (A) Glass ampoule; (B) silicone tube; (C) glass tap; (D) connection to the vacuum/N_2 line.

surements of the processes (1)–(3) (see Section 3) were: for reaction (1): m(CH$_3$COOM) = 121 mg (M = Li); 154 mg (M = Na); 254 mg (M = K); 220 mg (M = Rb); 321 mg (M = Cs). For the dissolution process (2): m(CH$_3$COOH) = 115 mg. For the dissolution process (3): m(MCl) = 141 mg (M = Li); 262 mg (M = Na); 312 mg (M = K); 193 mg (M = Rb); 322 mg (M = Cs).
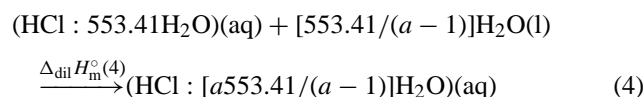
3. Results and discussion

The auxiliary enthalpy of formation data used in the calculations are given in Table 1 [24–31]. All computed molar quantities are based on the 2001 standard atomic masses [32].
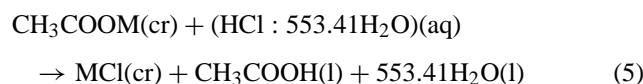
The standard molar enthalpies of formation of the metal acetates CH$_3$COOM (M = Li, Na, K, Rb, Cs) were determined from reaction–solution calorimetric studies of the processes shown in Eqs. (1)–(3):

$$CH_3COOM(cr) + a(HCl : 553.41H_2O)(aq)$$

$$\xrightarrow{\Delta_r H_m^\circ(1)} [MCl + CH_3COOH + (a-1)HCl$$

$$+ a553.41H_2O](aq) \tag{1}$$

$$CH_3COOH(l) + (a-1)(HCl : [a553.41/(a-1)]H_2O)(aq)$$

$$\xrightarrow{\Delta_{sol} H_m^\circ(2)} [CH_3COOH + (a-1)HCl + a553.41H_2O](aq) \tag{2}$$

$$MCl(cr) + [CH_3COOH + (a-1)HCl + a553.41H_2O](aq)$$

$$\xrightarrow{\Delta_{sol} H_m^\circ(3)} [MCl + CH_3COOH + (a-1)HCl$$

$$+ a553.41H_2O](aq) \tag{3}$$

The corresponding results are shown in Table 2, where the uncertainties quoted represent twice the standard deviation of the mean of at least five independent determinations. These values in conjunction with the enthalpy of the dilution process (Table 2):

$$(HCl : 553.41H_2O)(aq) + [553.41/(a-1)]H_2O(l)$$

$$\xrightarrow{\Delta_{dil} H_m^\circ(4)} (HCl : [a553.41/(a-1)]H_2O)(aq) \tag{4}$$

calculated from published data [24], were used to derive the enthalpy of the standard state reaction:

$$CH_3COOM(cr) + (HCl : 553.41H_2O)(aq)$$

$$\rightarrow MCl(cr) + CH_3COOH(l) + 553.41H_2O(l) \tag{5}$$

as:

$$\Delta_r H_m^\circ(5) = \Delta_r H_m^\circ(1) - \Delta_{sol} H_m^\circ(2)$$

$$- \Delta_{sol} H_m^\circ(3) - (a-1)\Delta_{dil} H_m^\circ(4) \tag{6}$$

The standard molar enthalpies of formation of the acetates were finally derived from the corresponding $\Delta_r H_m^\circ(5)$ values

Table 1
Auxiliary thermochemical data[a]

	$\Delta_f H_m^\circ/$kJ mol^{-1}
H$^+$, g	(1536.202 ± 0.080)
Li$^+$, g	(685.783 ± 0.080)
LiCl, cr	−(408.61 ± 0.80)
Na$^+$, g	(609.358 ± 0.080)
NaCl, cr	−(411.153 ± 0.080)
K$^+$, g	(514.26 ± 0.80)
KCl, cr	−(436.747 ± 0.080)
Rb$^+$, g	(490.101 ± 0.080)
RbCl, cr	−(435.35 ± 0.80)
Cs$^+$, g	(457.964 ± 0.080)
CsCl, cr	−(443.04 ± 0.80)
CH$_3$COOH, l	−(484.3 ± 0.2)[b]
CH$_3$COOH, g	−(432.8 ± 2.5)[b]
CH$_3$COO$^-$, g	−(510.8 ± 7.5)[c]
ClCH$_2$COOH, cr	−(512.22 ± 0.49)[d]
ClCH$_2$COOH, g	−(430.03 ± 1.04)[d]
ClCH$_2$COO$^-$, g	−(560.4 ± 8.5)[c]
BrCH$_2$COOH, cr	−(466.98 ± 1.08)[d]
BrCH$_2$COOH, g	−(383.48 ± 3.14)[d]
BrCH$_2$COO$^-$, g	−(517.2 ± 9.0)[c]
ICH$_2$COOH, cr	−(419.78 ± 1.53)[d]
ICH$_2$COOH, g	−(333.31 ± 1.84)[d]
ICH$_2$COO$^-$, g	−(469.1 ± 8.6)[c]
ClCH(CH$_3$)COOH, l	−(534.6 ± 1.1)[e]
ClCH(CH$_3$)COOH, g	−(469.7 ± 1.2)[e]
ClCH(CH$_3$)COO$^-$, g	−(594.2 ± 8.5)[c]
ClCH$_2$COOLi, cr	−(766.4 ± 1.0)[f]
BrCH$_2$COOLi, cr	−(724.0 ± 1.4)[f]
ICH$_2$COOLi, cr	−(675.7 ± 1.8)[f]
ClCH$_2$COONa, cr	−(743.4 ± 0.6)[f]
BrCH$_2$COONa, cr	−(700.3 ± 1.1)[f]
ICH$_2$COONa, cr	−(646.3 ± 1.6)[f]
ClCH(CH$_3$)COOLi, cr	−(800.9 ± 1.4)[g]
ClCH(CH$_3$)COONa, cr	−(772.1 ± 1.1)[g]
HCl:553.41H$_2$O, aq	−(166.598 ± 0.080)

[a] Data from Ref. [24] unless otherwise stated; the enthalpies of formation of the ions are based on the thermal electron convention.

[b] Ref. [25].

[c] The value of $\Delta_f H_m^\circ$(CH$_3$COO$^-$, g) = −(510.8 ± 7.5) kJ mol^{-1} was obtained as a weighed mean of the results derived from the gas phase acidity data, $\Delta_{acid} H_m^\circ$(CH$_3$COOH) = (1458.1 ± 8.4) and $\Delta_{acid} H_m^\circ$(CH$_3$COOH) = (1458.5 ± 12.1) kJ mol^{-1} given in Refs. [26,27], respectively, by using $\Delta_f H_m^\circ$(CH$_3$COOH, g) and $\Delta_f H_m^\circ$(H$^+$, g) in Table 1. The values of $\Delta_f H_m^\circ$(ClCH$_2$COO$^-$, g) = −(560.4 ± 8.5), $\Delta_f H_m^\circ$(BrCH$_2$COO$^-$, g) = −(517.2 ± 9.0), $\Delta_f H_m^\circ$(ICH$_2$COO$^-$, g) = −(469.1 ± 8.6), and $\Delta_f H_m^\circ$[ClCH(CH$_3$)COO$^-$, g] = −(594.2 ± 8.5) kJ mol^{-1} were derived from the gas phase acidity data, $\Delta_{acid} H_m^\circ$(ClCH$_2$COOH) = (1405.8 ± 8.4), $\Delta_{acid} H_m^\circ$(BrCH$_2$COOH) = (1402.5 ± 8.4), $\Delta_{acid} H_m^\circ$(ICH$_2$COOH) = (1400.4 ± 8.4), and $\Delta_{acid} H_m^\circ$[ClCH(CH$_3$)COOH] = (1411.7 ± 8.4) kJ mol^{-1}, published in Ref. [26], and the enthalpies of formation of H$^+$(g), ClCH$_2$COOH(g), BrCH$_2$COOH(g), ICH$_2$COOH(g), and ClCH(CH$_3$)COOH(g) given in Table 1.

[d] Recalculated from the data in Ref. [28].

[e] Ref. [29].

[f] The values of the enthalpies of formation of the haloacetates previously reported in Ref. [30] were revised in the present work by using the enthalpies of formation of ClCH$_2$COOH(cr), BrCH$_2$COOH(cr), and ICH$_2$COOH(cr) are given in Table 1.

[g] Ref. [31].

Table 2
Results of the reaction–solution calorimetric experiments on CH$_3$COOM alkaline metal acetates, at $T = 298.15$ K (data in kJ mol^{-1})

Compound	M = Li	M = Na	M = K	M = Rb	M = Cs
a	6.57294	6.06697	5.27843	7.71466	7.49214
$\Delta_r H_m^\circ(1)$	$-(22.45 \pm 0.24)$	$-(15.97 \pm 0.34)$	$-(16.76 \pm 0.22)$	$-(16.77 \pm 0.16)$	$-(19.30 \pm 0.53)$
$\Delta_{sol} H_m^\circ(2)$	$-(2.12 \pm 0.28)$	$-(2.12 \pm 0.28)$	$-(2.12 \pm 0.28)$	$-(2.12 \pm 0.28)$	$-(2.12 \pm 0.28)$
$\Delta_{sol} H_m^\circ(3)$	$-(35.20 \pm 0.29)$	(4.23 ± 0.11)	(17.67 ± 0.24)	(16.33 ± 0.63)	(17.69 ± 0.31)
$\Delta_{dil} H_m^\circ(4)^a$	-0.041	-0.045	-0.052	-0.035	-0.036
$\Delta_r H_m^\circ(5)$	(15.09 ± 0.47)	$-(17.85 \pm 0.45)$	$-(32.09 \pm 0.43)$	$-(30.74 \pm 0.71)$	$-(34.64 \pm 0.67)$
$\Delta_f H_m^\circ(CH_3COOM, cr)$	$-(741.40 \pm 0.95)$	$-(711.01 \pm 0.51)$	$-(722.36 \pm 0.49)$	$-(722.31 \pm 1.09)$	$-(726.10 \pm 1.07)$

[a] Data from Ref. [24].

and the auxiliary data in Table 1 as:

$\Delta_f H_m^\circ(CH_3COOM, cr)$

$$= -\Delta_r H_m^\circ(5) + \Delta_f H_m^\circ(MCl, cr)$$

$$+ \Delta_f H_m^\circ(CH_3COOH, l)$$

$$- \Delta_f H_m^\circ(HCl : 553.41H_2O, aq) \qquad (7)$$

The obtained values are indicated in Table 2. The $\Delta_f H_m^\circ(cr)$ results shown in Table 2 for CH$_3$COONa and CH$_3$COOK differ from $\Delta_f H_m^\circ(CH_3COONa, cr) = -708.81$ and $\Delta_f H_m^\circ(CH_3COOK, cr) = -723.0$ kJ mol^{-1}, previously reported in the NBS Tables [24], by 2.20 and 0.64 kJ mol^{-1}, respectively. The value of CH$_3$COORb in Table 2 is in excellent agreement with that published by Johnson and Warr [$-(722.6 \pm 1.0)$ kJ mol^{-1}] [33].

If ionic structures are assumed for the CH$_3$COOM compounds in the solid state, the corresponding lattice energies at $T = 298$ K are given by the internal energy changes associated with the following process at that temperature [15–18]:

$$CH_3COOM(cr) = M^+(g) + CH_3COO^-(g) \qquad (8)$$

and can be calculated from:

$\Delta_{lat} U_{298}^\circ(CH_3COOM)$

$$= \Delta_f H_m^\circ(CH_3COO^-, g) + \Delta_f H_m^\circ(M^+, g)$$

$$- \Delta_f H_m^\circ(CH_3COOM, cr) - 2RT \qquad (9)$$

where R is the gas constant and T the absolute temperature. The $\Delta_{lat} U_{298}^\circ(CH_3COOM)$ values computed from Eq. (9) using the auxiliary data in Table 1 are listed in Table 3 under the heading Experimental. For sodium and potassium the obtained results are in agreement within the experimental error with $\Delta_{lat} U_{298}^\circ(CH_3COONa) = 807$ kJ mol^{-1} and $\Delta_{lat} U_{298}^\circ(CH_3COOK) = 726$ kJ mol^{-1} reported in the compilation by Jenkins and Roobottom [34]. For lithium, however, the value in Table 3 is 68.4 kJ mol^{-1} greater than $\Delta_{lat} U_{298}^\circ(CH_3COOLi) = 843$ kJ mol^{-1} quoted in that compilation [34]. Considerable differences are generally found between the $\Delta_{lat} U_{298}^\circ(CH_3COOM)$ results in Table 3 and those predicted by Kim et al. [35] based on a correlation of experimental lattice enthalpies and gas phase heterolitic bond dissociation enthalpies calculated by density functional theory: 848 kJ mol^{-1} (M = Li), 752 kJ mol^{-1} (M = Na),

683 kJ mol^{-1} (M = K). Also included in Table 3 are the lattice energies of the haloacetates XCH$_2$COOM (M = Li and Na; X = Cl, Br, I) and chloropropionates ClCH(CH$_3$)COOM (M = Li and Na), which were derived from the auxiliary data in Table 1. The obtained results for the haloacetates are essentially independent of the halogen and 17–25 kJ mol^{-1} smaller than the corresponding values for the acetates. It is also interesting to note that no significant differences are observed between $\Delta_{lat} U_{298}^\circ$ for the haloacetates and chloropropionates.

A comparison of the lattice energies of the acetates, haloacetates, and chloropropionates with those of the corresponding hydroxides, (1021.0 ± 0.5) kJ mol^{-1} (LiOH) [36], (885.2 ± 0.5) kJ mol^{-1} (NaOH) [36], (789.3 ± 0.5) kJ mol^{-1} (KOH) [36], (758.5 ± 0.5) kJ mol^{-1} (RbOH) [36], and (725.4 ± 0.5) kJ mol^{-1} (CsOH) [36], is shown in Fig. 2.

The lattice energy values obtained in this work may be analysed by using the Kapustinskii approximation represented by Eq. (10) [16,17]:

$\Delta_{lat} U_0^\circ[XCH(R)COOM]$

$$= 1.079 \times 10^5 (\nu Z_+ Z_-/(r_+ + r_-)) \qquad (10)$$

In this expression, $\Delta_{lat} U_0^\circ[XCH(R)COOM]$ is the lattice energy of the XCH(R)COOM salt (M = Li, Na, K, Rb, Cs; X = Cl, Br, I; R = H, CH$_3$) at 0 K in kJ mol^{-1}, ν is the number of ions in the molecule (in this case, $\nu = 2$), Z_+ and

Table 3
Lattice energies of alkaline metal acetates and propionates (data in kJ mol^{-1})^a

Compound	Experimental	Eq. (10)	Δ
CH$_3$COOLi	911.4 ± 7.2	914	2.6
ClCH$_2$COOLi	886.8 ± 8.6	877	9.8
BrCH$_2$COOLi	887.6 ± 9.1	877	10.6
ICH$_2$COOLi	887.6 ± 8.8	874	13.6
ClCH(CH$_3$)COOLi	887.5 ± 8.6	874	13.5
CH$_3$COONa	804.6 ± 7.1	824	19.4
ClCH$_2$COONa	787.4 ± 8.5	793	5.6
BrCH$_2$COONa	787.5 ± 9.1	793	5.5
ICH$_2$COONa	781.8 ± 8.7	790	8.2
ClCH(CH$_3$)COONa	782.3 ± 8.6	790	7.7
CH$_3$COOK	720.9 ± 7.2	724	3.1
CH$_3$COORb	696.7 ± 7.2	692	4.7
CH$_3$COOCs	668.3 ± 7.2	660	8.3

[a] The term $\Delta = |\Delta_{lat} U_{298}^\circ(exp) - \Delta_{lat} U_0^\circ(Eq. 10)|$ represents the absolute value of the difference between the values of the experimental lattice enthalpies and those obtained from Eq. (10).
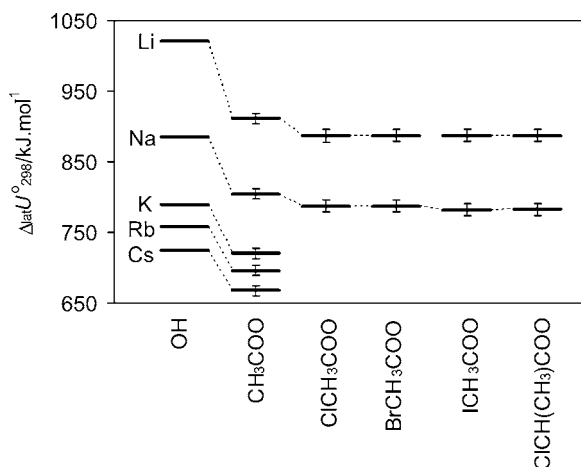
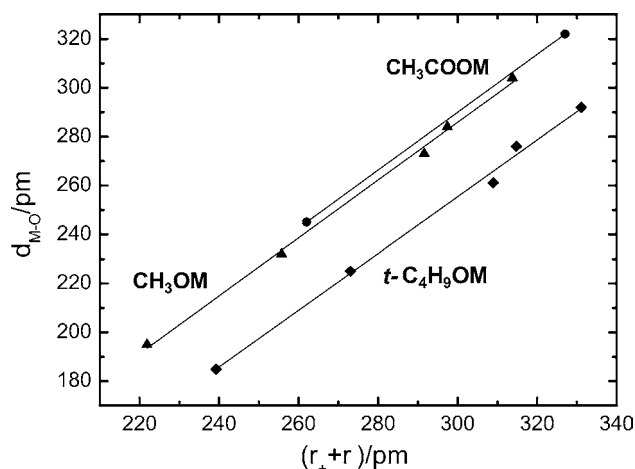Fig. 2. Lattice energies of alkaline metal hydroxides, acetates, and chloropropionates.

Fig. 3. Plots of the experimental interatomic distances d_{M-O} in alkaline metal acetates, methoxides and *t*-butoxides against the corresponding $r_+ + r_-$ [see Eqs. (12)–(14), respectively].

Z_- are the charges of the cation and the anion, respectively, and r_+ and r_- the corresponding thermochemical radii in pm. Note that $\Delta_{lat}U_0^\circ[XCH(R)COOM]$ is related with $\Delta_{lat}U_{298}^\circ[XCH(R)COOM]$ in Table 3 through Eq. (11):

$$\Delta_{lat}U_{298}^\circ[XCH(R)COOM]$$
$$= \Delta_{lat}U_0^\circ[XCH(R)COOM] + (H_{298}^\circ - H_0^\circ)_{M^+}$$
$$+ (H_{298}^\circ - H_0^\circ)_{XCH(R)COO^-}$$
$$- (H_{298}^\circ - H_0^\circ)_{XCH(R)COOM} - 2RT \qquad (11)$$

where R is the gas constant and $T = 298.15\,\text{K}$. The information needed to compute the correction term $X = (H_{298}^\circ - H_0^\circ)_{M^+} + (H_{298}^\circ - H_0^\circ)_{XCH(R)COO^-} - (H_{298}^\circ - H_0^\circ)_{XCH(R)COOM} - 2RT$ is only partially available for the compounds studied in this work [8–10,24]. A value of X smaller than the uncertainty that affects the experimental values of the lattice enthalpy in Table 3 is, however, expected. For example, in the case of the Li, Na, and K hydroxides, $X = 2.43$, -0.64, and $-2.30\,\text{kJ mol}^{-1}$, respectively [24]. Hence, in the following discussion it will be considered that $\Delta_{lat}U_{298}^\circ[XCH(R)COOM] = \Delta_{lat}U_0^\circ[XCH(R)COOM]$.

From Eq. (10) and the experimental $\Delta_{lat}U_{298}^\circ$ [XCH(R)COOM] data in Table 3 it was possible to derive the M−OOC(R)CHX interatomic distances, $(r_+ + r_-)$. The obtained results in conjunction with the ionic radii of the cations given by Shannon [37], $r_+(\text{Li}^+) = 90\,\text{pm}$, $r_+(\text{Na}^+) = 116\,\text{pm}$, $r_+(\text{K}^+) = 152\,\text{pm}$, $r_+(\text{Rb}^+) = 166\,\text{pm}$, and $r_+(\text{Cs}^+) = 181\,\text{pm}$ lead to the following average values for the radii of the anions: $r_-(\text{CH}_3\text{COO}^-) = 146\,\text{pm}$, $r_-(\text{ClCH}_2\text{COO}^-) = 156\,\text{pm}$, $r_-(\text{BrCH}_2\text{COO}^-) = 156\,\text{pm}$, $r_-(\text{ICH}_2\text{COO}^-) = 157\,\text{pm}$, and $r_-[\text{ClCH}(\text{CH}_3)\text{COO}^-] = 157\,\text{pm}$. As shown in Table 3 using this set of r_+ and r_- values and Eq. (10) it is possible to reproduce the experimental $\Delta_{lat}U_0^\circ[XCH(R)COOM]$ data with an average deviation of $8.7\,\text{kJ mol}^{-1}$ and a maximum relative deviation of 2.4%.

When the $r_+ + r_-$ distances calculated from Eq. (10) for the sodium and caesium acetates ($r_+ + r_- = 262\,\text{pm}$ for

CH$_3$COONa and 327 pm for CH$_3$COOCs, respectively) are plotted against the corresponding distances $d_{Na-O} = 245$ and $d_{Cs-O} = 322\,\text{pm}$ quoted above, the following linear relation is obtained:

$$d_{M-OOCCH_3} = 1.185 \times (r_+ + r_-) - 65.369 \qquad (12)$$

If the same correlation is applied to data for alkaline metal methoxides and *t*-butoxides the two following equations result [36]:

$$d_{M-OCH_3} = (1.182 \pm 0.033) \times (r_+ + r_-)$$
$$- (68.87 \pm 9.11) \qquad (13)$$

$$d_{M-O^tC_4H_9} = (1.1604 \pm 0.0993) \times (r_+ + r_-)$$
$$- (92.70 \pm 30.55) \qquad (14)$$

Eqs. (12)–(14) have very similar slopes (Fig. 3). This suggests that by using Eq. (12) and $r_+ + r_- = 236\,\text{pm}$ (Li), 298 pm (K), and 312 pm (Rb) derived from Eq. (10) the following average bond distances may be predicted for the lithium, potassium, and rubidium acetates, whose molecular structures in the solid state have not been determined: $d_{Li-O} = 214\,\text{pm}$, $d_{K-O} = 288\,\text{pm}$ and $d_{Rb-O} = 304\,\text{pm}$.

Acknowledgments

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